CHAPTER-(5)

RESULTS AND DISCUSSION

QUATERNARY LIQUID-LIQUID PHASE EQUILIBRIUM DATA

CHAPTER-5

RESULTS AND DISCUSSION FOR QUATERNARY LIQUID-LIQUID PHASE EQUILIBRIUM DATA

5.0.0 ABSTRACT:-

Based on experimental results reported in Chapter-4 under the heading

Part I: Quaternary Liquid Liquid Phase Equilibrium Data.

this Chapter-5 contains derived results and the relevant discussion pertaining to following aspects:-

- (i) Mutual solubility data (Binodal curves)
- (ii) Tie line data and Plait Points
- (iii) Extraction capacity and Selectivity of mixed solvents
- (iv) Distribution coefficients
- (v) Modified Hand's plots
- (vi) Hand's constants 'k' & 'n'
- (vii) Generalized correlation for predicting the values of Hand's constant: [k]

(viii) Correlating as well as predicting quaternary liquid liquid phase

equilibrium data by NRTL method

5.1.0 Graphical presentation of quaternary liquid liquid mutual solubility data:-

Mutual solubility data in this investigation reported in Tables -1 to 30 in Chapter 4:- Experimental, have been plotted as curves in different Figures- M-1 to M-30 and relevant details are as under:-

Mutual solubility data for systems involving B/T/X-H/H'/O- Dmf+W has been plotted in Figures M-1 to M-15 and mutual solubility data for systems involving B/T/X-H/H'/O- Dmso+W has been plotted in Figures- M-16 to M-30.

Derived Tables-1.1 and 2.1 contains an additional information about mutual solubility data in terms of different ratios for 45 systems for mixed solvent – Dmf+W and additional 45 systems for mixed solvent – Dmso+W. The data about ratios of non solute / solute and solubility data of non solute in solvent under different sets of conditions wherein temperatures has been varied from 20 $^{\circ}$ C,30 $^{\circ}$ C to 40 $^{\circ}$ C, anti solvent concentration has been varied from 0%W, 10%W to 20%W; solute component has been changed from the Benzene to Toluene to Xylene and non solute has been changed from Hexane to Heptane to Octane.

Effect of different parameters like Temperature, anti solvent Concentration and Molecular weightof aromatics & Molecular weight of aliphatics on Mutual solubility Data have been discussed in subsequent pages.

Conclusions drawn under each Heading in subsequent pages are expected to be very useful while * Discussing Tie line Data for these two mixed solvents: (Dmf+W) & (Dmso+W)".

5.1.1 Discussion for mutual solubility data for systems involving mixed solvents : (Dmf+W) & (Dmso+W).

Discussion for effect of prime parameters – anti solvent concentration & temperature and secondary parameters molecular weight of aromatics & aliphatics on mutual solubility data has been divided under ten categories as under:

- (i) Systems consisting of B-H- Dmf-W at three different temperatures and three different antisolvent concentration values
- (ii) Systems consisting of T-H- Dmf-W at three different temperatures and three different antisolvent concentration values.
- (iii) Systems consisting of X-H- Dmf-W at three different temperatures and three different antisolvent concentration values.
- (iv) Systems consisting of B-Hep- Dmf-W at three different temperatures and three different antisolvent concentration values.
- (v) Systems consisting of B-Oct- Dmf-W at three different temperatures and three different antisolvent concentration values.

(vi) Systems consisting of B-H- Dmso-W at three different temperatures and three different antisolvent concentration values.

- (vii) Systems consisting of T-H- Dmso-W at three different temperatures and three different antisolvent concentration values.
- (viii) Systems consisting of X-H- Dmso-W at three different temperatures and three different antisolvent concentration values.
- (ix) Systems consisting of B-Hep- Dmso-W at three different temperatures and three different antisolvent concentration values.
- (x) Systems consisting of B-Oct- Dmso-W at three different temperatures and three different antisolvent concentration values.

The basis for discussion has been mainly kept on "How selectivity of newer solvents (Dmf+W) &(Dmso+W) can be altered ?"

5.1.2 Curves for mutual solubility data for systems involving B-H- Dmf+W and relevant conclusions:

Mutual solubility data curves plotted in Figures M-1,M-2 and M-3 for systems B-H- Dmf+W at three different Temperatures 20 0 C ,30 0 C and 40 0 C and additional information reported in Table-1.1, reveals the following :-

(i) Mutual solubility data depicted in Figures M-1,M-2 and M-3 indicate that for concentration of anti solvent being 0%W, all Binodal curves are of closed type. However when antisolvent concentration increases from 0%W to 10%W and subsequently to 20%W, all the Binodal curves become open type wherein plait point lies at infinity.

(ii) At fixed value of temperature as anti solvent concentration increases from 0%W to 10%W and up to 20% W, solubility of aromatics as well as aliphatics in solvent rich phase (extract phase) decreases. However, rate of decrease of solubility of aliphatics in solvent rich phase is relatively very high in comparison to solubility of aromatics in solvent rich phase. As a result, selectivity values are expected to be very high when antisolvent concentration of water is of the order of 20% by weight in mixed solvent -- Dmf+W.

Thus for example ,from Figure M2 at 30 0 C for fixed value of solvent composition of 60%, the values of composition of Hexane in solvent rich phase for 0%W, 10%W and 20%W are 28%, 17% and 1.5% respectively. Thus the values of ratio of H/B in solvent phase subsequently decrease from 2.33 to 0.74 and up to 0.4



system B-H-100/90/80%Dmf-0/10/20% W at 20 °C







Solubility Solubility Solubility Solubility Solubility 18.05 22.86 25.79 16.61 4.28 4.44 2.35 9.32 4.95 8.03 4.54 5.37 3.86 .88 3.21 40 °C 15.29 14.24 04.10 08.53 04.25 02.30 04.87 Hep ы О 01.85 07.44 04.34 5.10 03.72 20.5 18.61 03.11 Η H Ξ 95.90 96.89 95.75 97.70 85.75 91.47 81.39 92.56 95.66 94.90 96.28 98.34 98.15 84.71 79.5 ∞ Ś 2 S S Additional Information about Mutual Solubility Data for Systems-B/T/X-H/H'/O- Dmf+W H Solubility solubilit solubilit Solubilit solubilit 17.93 14.82 14.87 7.49 21.85 2.84 6.88 1.33 4.14 4.32 4.35 2.73 1.03 3.02 1.05 Basis: B=0% * 12.940 17.934 87.09 12.909 01.316 06.440 04.144 01.015 06.970 04.168 02.930 01.040 Oct 30 ⁰C 02.757 Hep 02.66 03.97 Ξ н 15.2 98.99 93.56 95.86 82.07 97.07 87.05 95.83 98.68 97.16 93.03 97.24 98.96 84.80 96.03 Ś S S S S Solubility Solubility Solubility Solubilit Solubilit 01.36 01.10 14.92 01.72 13.99 04.87 17.65 02.18 14.82 02.46 03.23 00.44 04.17 4.54 0.75 20 ⁰C Hep 15.00 oct O H 12.98 01.69 12.28 04.00 01.35 04.64 02.40 01.08 03.13 02.13 00.44 12.91 0.75 H 4.34 H System B-Hep-Dmf-W System B-Oct-Dmf-W 98.9 System X-H-Dmf-W System B-H-Dmf-W System T-H-Dmf-W S 85 98.31 87.73 98.65 96.00 99.25 95.36 87.0 95.66 97.87 96.9 99.56 97.6 87.1 S S S S 0.212 0.025 0.013 0.006 0.053 0.026 (Hep/B) 0.032 0.053 2.077 (Oct/B) (H/T) 2.077 (H/X)0.006 (H/B) 0.33 0.6 1.11 20 ⁰C 1.25 Hep 0.25 ы О 0.5 0.25 15 27 27 2 Η H 5 2 H 39.75 38.75 39.75 39.5 19 20 39 33 38 38 39 13 B 25 30 3 × р Д E. Basis:Solvent in Extract=60% (Oct/B) Hep/B 0.039 0:013 (X/H (HAB) 0.02 0.04 HTT) 1.35 0.48 1.22 0.54 0.82 0.14 0.01 0.74 0.04 2.33 ŝ 30 ⁰C 0.5 Hep 30 oct 0.75 1.5 0.5 5.1 1.5 4 18 52 28 5 H ·Η Η 38.5 38.5 39.5 39.5 39.5 38.5 m [2 26 73 B 35 18 17 51 × 33 2 [-- р (Hep/B) 0.0526 (Oct/B)0.2903 1.3529 (H/X)0.018 0.90 (H/B) 0.04 3.44 0.48 0.05 0.48 0.04 (HAT) 2.33 0.08 0.05 40 ⁰C Hep c O 0.75 1.5 1.5 19 13 53 H 5 13 9 Ξ 30 28 H 2 2 31 3 39.25 38.5 38.5 38 27 37 27 38 31 2 12 38 р р δ ф 21 10%10% 10% 20% 10% 20% 10% 20% 20% 20% % %0 %0 % %0 ≽ ≽ ≥ ≥ ≥

Table-1.1

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Ref Tab 1-15

respectively. Thus %PE values (Benzene in extract phase) for 0%W, 10%W and 20% W are excepted to be 33% B,58%B and 96%B respectively.

The corresponding values of solubility of Hexane in mixed solvent for 0%Benzene in mixed solvent as the basis at 30 ⁰ C, for solvents having three antisolvent concentrations of 0%W, 10%W and 20%W are 17.93%, 4.13% and 2.73% respectively.

(iii) As antisolvent concentration increases, the solubility of Hexane in mixed solvent decreases drastically. It is also expected that selectivity of mixed solvent containing 20% W is also expected to be highest .Similar conclusions can be drawn for other two Temperatures namely 20 °C and 40°C.

(iv) Under otherwise identical conditions when one compares ratio of H/B for three temperatures namely 20°C, 30°C and 40°C, it is observed that as temperature increases, the ratio of H/B also increases. Thus over all result in expected to be decrease in selectivity values of mixed solvent as temperature increases.

Thus for example, from Table 1.1 it is observed that for a fixed value of anti solvent concentration of the order of 0% w, as temperature is increased from 20°C, 30°C to 40°C, the values of H/B ratio increases from 1.1, 2.33 to 3 respectively. When temperature is increased from 20°C to 30°C and up to 40°C, similar observations can be made for other antisolvent concentrations namely 10%W and 20%W.

5.1.3 Curves for mutual solubility data for systems involving T-H- Dmf+W and relevant conclusions:

Mutual solubility data curves plotted in Figure M-4, M -5 and M -6 for system T -H- Dmf+W at three different temperatures 20 0 C 30 C and 40 0 C and additional information reported in Table 1.1, reveals the following :-

(i)Similar trend is observed for different systems involving components: T-H-Dmf-W i.e. with an increase in temperature, selectivity of mixed solvent decreases under otherwise identical conditions. Also with an increase in anti solvent concentration, the values of selectivity are expected to increase.



system T-H-100/90/80%Dmf-0/10/20% W at 20 °C



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(ii)Thus, for example at 40°C when anti solvent concentration is increased from 0% W to 10%W and up to 20%W, the ratio of H/T decreases from 2.33 to 0.081 and up to 0.05 respectively.

Further, at fixed value of anti solvent concentration 20%W as temperature is increased from 20°C to 30°C and up to 40°C, the ratio of H/T increase from 0.025 to 0.04 and up to 0.05 respectively.

(iii)As solute component- Benzene gets replaced by component – Toluene under otherwise identical conditions, the ratio of non-solute/solute decreases. Hence when solute Benzene in replaced by Toluene, it is expected that selectivity of mixed solvent increases. Thus for example, from Table 1.1 at temperature 30°C and anti solvent concentration 0% W, the values of ratio for systems- B-H- Dmf+W and T-H- Dmf+W are 2.33and 1.35 respectively. The corresponding values of solubility of Hexane are also decreased from 17.93% to 14.82% respectively at 30 °C and 0% W anti solvent concentration.

(iv)However there are some exceptions to above sighted trends forfollowing systems(i) Temperature 20 °C. and anti solvent concentration 0% W, (ii)also temperature 30 °C and anti solvent concentration 10 % W.

5.1.4 Curves for mutual solubility data for systems involving X-H- Dmf+W and relevant conclusions:

Mutual solubility data curves plotted in Figures M-7, M -8 and M -9 for systems -X -H- Dmf+W at three different temperatures 20° C $\cdot 30^{\circ}$ C and 40° C and additional information reported in Table 1.1, reveals the following :-

(i) Conclusions already drawn in preceding paragraphs namely "As temperature increases and anti solvent concentration decreases, selectivity values are expected to decrease under otherwise identical conditions" is valid for all nine systems under consideration involving solute-Xylene.

(ii)Thus for example, at 30°C when anti solvent concentration is increased from 0% W to 10%W and up to 20%W, the ratio of H/X decreases from 1.22 to 0.035 and up to 0.02 respectively.



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system X-H-100/90/80%Dmf-0/10/20% W at 20 °C







Further at fixed value of anti solvent concentration of 0%W, as temperature is increased from 20°C to 30°C and up to 40°C, the ratio of H/X increases from 1.00 to 1.22 and up to 1.35 respectively.

(iii) As solute component Benzene/Toluene gets replaced by component – Xylene under otherwise identical conditions, the ratio of non-solute/solute decreases. Thus for example ,at 30 °C temperature and anti solvent concentration 0% of W when Benzene is replaced by Toluene and subsequently by Xylene , the ratio of Hexane/ Solute decreases from 2.33, 1.35 to 1.12 respectively. Thus selectivity of mixed solvent is expeted to increase with an increase in molecular weight of aromatics.

Similarly for example at 40°C when anti solvent concentration is increased from 0% W to 10%W and up to 20%W, the ratio of H/X decreases from 3, 2.33 to 1.35 respectively.

5.1.5 Curves for mutual solubility data for systems-B-Hep-Dmf+W and for systems-B-Oct-Dmf+W and relevant conclusions:

Mutual solubility data curves plotted in Figures M-10, M -11 and M -12 for Systems- B -Hep- Dmf+W and in Fig M-13, M -14 and M -15 for systems- B -Oct-Dmf+W at three different temperatures 20 0 C,30 0 C and 40 0 C and additional information reported in Table 1.1, reveals the following :-

(i) Conclusions already drawn in preceding paragraphs namely "As temperature increases and anti solvent concentration decreases, selectivity values are expected to decrease under otherwise identical conditions" is valid for all 18 different systems under consideration consisting of non solutes- Heptane and Octane.

Thus for example, for system consisting of non solute- Heptane (B-H'-Dmf+W) for fixed value of temperature of 30 °C as anti solvent concentration increases from 0% to 10% W and up to 20%W, the ratio of Heptane/Benzene decreases from 3 to 0.54 and up to 0.013 respectively.

Similarly for example, for system consisting of non solute Octane , for fixed value of temperature 30 °C as anti solvent concentration increases from 0% to 10% W



Fig.-M .10 Mutual Solublity data of antisolvent effect as parameters for system B-H'-100/90/80%Dmf-0/10/20% W at 20 °C



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Fig.-M .14 Mutual Solublity data of antisolvent effect as parameters for system B-Oct-100/90/80%Dmf-0/10/20% W at 30 °C



and up to 20%W, the ratio of Octane/Benzene deceases from 0.8 to 0.14 and up to 0.01 respectively.

Thus as anti solvent concentration increases, selectivity values for liquid-liquid extraction of aromatics increase and highest value is obtained for system involving nonsolute Octane and having water concentration of 20% by weight.

(ii) It is interesting to observe that as non solute Hexane is replaced by Heptane the value of ratio of non solute /solute increases. Hence as a result when Hexane is replaced by Heptane, the value of selectivity decreases. However, when Heptane is further replaced by Octane, selectivity values again increase.

Thus for example ,at temperature of 20 °C and anti solvent concentration of water of 0% W, when Hexane is replaced by Heptane and subsequently by Octane, the ratios of non solute/ solute are 1.1, 2.01 and 0.6 respectively.

Further at temperature 40 °C and 0%W when Hexane is replaced by Heptane and subsequently by Octane, the ratios of non solute/solute are 3, 3.44 and 0.9 respectively.

Thus selectivity values are expected to be highest for system consisting of non solute Octane and lowest for non solute consisting of Heptane. The reason for such abnormal behavior is not clear.

5.1.6 Curves for mutual solubility data for systems involving B-H- Dmso+W and relevant conclusions:

Mutual solubility data curves plotted in Figures M-16,M-17 and M-18 for systems B-H- Dmso+W at three different temperatures 20 0 C ,30 0 C and 40 0 C and additional information reported in Table 2.1, reveals the following :-

(i)Mutual solubility data depicted in Figures M-16, M-17 and M-18 indicate that for concentration of anti solvent being 0%W, all Binodal curves are of closed type. However when antisolvent concentration increases from 0% to 10% and subsequently to 20%W all the Binodal curves become open type wherein plait point lies at infinity.







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Solubility Solubility Solubility Solubility Solubility 04.94 02.43 01.52 1.19 8.39 1.46 3.60 0.97 2.07 1.87 2.72 1.02 1.24 0.25 0.19 40 ⁰ C 04,86 02.37 01.50 03.48 01.18 00.96 02.03 01.84 02.65 Hep 07.74 01.44 01.23 00.25 00.19 01.01 oct O Щ H H 98.16 96.52 79.97 92.26 97.14 98.50 99.04 97.35 98.56 97.64 98.82 98.99 S 98.77 99.75 99.81 Ś S S Ω Additional Information about Mutual Solubility Data for Systems-B/T/X-H/H'/O- Dmso+W Solubility Solubility Hep Solubility Solubility Solubility 04.09 01.52 01.22 1.26 1.63 1.23 2.05 1.08 2.04 1.02 7.21 0.61 0.71 0.24 0.06 Basis: B=0% 30 ⁰C 01.50 03.93 01.21 06.7 oct O 00.00 01.6 01.2 02.0 00.7 Η 01.2 01.0 00.2 00.6 Ξ 01.1 Η 2 98.400 S 93.273 98.880 98.79 99.29 96.07 98.50 97.99 98.75 98.93 98.00 98.99 99.39 99.76 99.95 S S 0 0 Solubility Solubility S Hep Solubility Solubility Oct Solubility 00.62 01.79 00.96 01.80 01.83 00.80 00.40 01.24 00.13 0.48 4.00 0.24 0.75 00.06 1.91 0.97 20 ⁰C 01.76 00.62 00.79 01:23 00.95 00.13 99.60 00.40 1.88 0.96 0.48 3.85 0.24 0.75 00.06 H Ξ H B-Hep-Dmso-W B-Oct-Dmso-W System X-H-Dmso-W System B-H-Dmso-W T-H-Dmso-W 99.05 98.20 99.38 S 99.52 98.24 98.12 96.15 99.25 99.88 99.04 98.77 77.66 99.21 99.95 S S 0.013 Hep/B 0.176 0.039 (H/X) 0.039 0.013 0.053 0.013 Oct/B) 0.026 0.013 0.25 0.013 (H/B) 0.333. 0.081 (HVT) 0.18 0.111 System System] System 20 °C Hep 0.75 0.75 0.25 0.25 oct O 0.25 0.25 0:5 0.25 1.5 H Η Η 2 4 19.25 19.25 19.75 19.75 19.75 19.75 9.75 18.5 19.5 17 19 18 15 16 X g g В 1 (Hep/B) (Oct/B) 0.21 0.053 0.026 0.026 0.026 0.026 (X/H) 0.176 0.053 0.176 0.176 Basis:Solvent in Extract=80% 0.026 (H/B) (HVT) 0.333 0.333 0.053 0.25 30 °C Hep s O 3.5 0.5 0.5 0.5 0.5 Η 4 S 16.5 19.5 19.5 19.5 19.5 19.5 19 19 19 5 17 16 В 17 15 р × ф Hep/B (Oct/B) 0.039 0.039 0.039 0.039 0.039 (X/H 0.176 0.053 (H/B) (THT) 0.08 0.25 0.33 0.11 0.11 0.3 0.4 0.2 0 Hep (0.75 0.75 oct O 0.75 0.75 40 ⁰C 4.5 3.4 0.75 1.5 H H 2 H 5 3 16.600 19.25 19.25 19.25 19.25 19.25 18.5 15.5 14.5 19 18 18 ф 16 15 17 m × 10% 20% 10%20% 10% 20% 10% 20% 10%20% %0 M_0% %0 % %0 N ≽ \geq ≽

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(ii)At fixed value of temperature as anti solvent concentration increases from 0%W to 10%W and up to 20% W, solubility of aromatics as well as aliphatics in solvent rich phase (extract phase) decreases. However, rate of decrease of solubility of aliphatics in solvent rich phase is relatively very high in comparison to solubility of aromatics in solvent rich phase. As a result, selectivity values are expected to be very high when antisolvent concentration of water is of the order of 20% by weight in mixed solvent – Dmso+W.

Thus for example ,from Figure M-18 for fixed value of solvent composition of 80%, the values of composition of Hexane in solvent rich phase for 0%W, 10%W and 20%W are 4.0%, 2.0 % and 0.75% respectively. Thus the values of ratio of H/B in solvent phase subsequently decrease from 0.25 to 0.11 and up to 0.038 respectively. Thus %PE values (Benzene in extract phase) for 0%W, 10%W and 20% W are excepted to be 80%B,90%B and 96.2%B respectively.

The corresponding values of solubility of Hexane in mixed solvent for 0% Benzene in mixed solvent as the basis at 40° , for solvents having three antisolvent concentrations of 0%W,10%W and 20%W are 2.94%, 2.42% and 1.52% respectively.

(iii) As antisolvent concentration increases, the solubility of Hexane in mixed solvent decreases drastically. It is also expected that selectivity of mixed solvent containing 20% W is also expected to be highest. Similar conclusions can be drawn for other two temperatures namely 20 °C and 40°C.

(iv) Under otherwise identical conditions when one compares ratio of H/B for three temperatures namely 20°C, 30°C and 40°C, it is observed that as temperature increases, the ratio of H/B also increases. Thus over all result in expected to be decrease in selectivity values of mixed solvent as temperature increases.

Thus for example, from Table 2.1 it is observed that for a fixed value of anti solvent concentration of the order of 20% w, as temperature is increased from 20°C, 30°C to 40°C, the values of H/B ratio increases from 0.011, 0.026 to 0.038 respectively. When temperature is increased from 20°C to 30°C and up to 40°C, similar observations can be made for other antisolvent concentrations namely 10%W and 20%W.

5.1.7 Curves for mutual solubility data for systems involving T-H- Dmso+W and relevant conclusions:-

Mutual solubility data curves plotted in Figures M-19 , M -20 and M -21 for system T -H- Dmso+W at three different temperatures 20 0 C 3 O 0 C and 40 0 C and additional information reported in Table 2.1 , reveals the following :-

(i)Similar trend is observed for different systems involving components : T-H-Dmso-w i.e. with an increase in temperature, selectivity of mixed solvent decreases under otherwise identical conditions. Also with an increase in anti solvent concentration, the values of selectivity are expected to decrease.

(ii)Thus, for example at 30°C when anti solvent concentration is increased from 0% W to 10%W and up to 20%W, the ratio of H/T decreases from 0.333 to 0.25 and up to 0.026 respectively.

Further, at fixed value of anti solvent concentration 20%W as temperature is increased from 20°C to 30°C and up to 40°C, the ratio of H/T increase from 0.011 to .026 and up to 0.038 respectively.

(iii)As solute component- Benzene gets replaced by component – Toluene under otherwise identical conditions, the ratio of non-solute/solute increases. This is expected to be abnormal behavior when one compares this observation with that of system involving mixed solvent Dmf+W wherein this ratio was decreasing. Thus for example, at temperature of the order of 30°C and anti solvent concentration of the order of 0% W ,in system when Benzene is replaced by Toluene for a fixed value of solvent 80 %,the ratio of non solute /solute increases from 0.176 to 0.333 under otherwise identical conditions.

Solubility of Hexane in solvent under conditions of solute Benzene being zero also increase from 4.09% to 7.21% under otherwise identical conditions of temperature T=30 °C and anti solvent concentration = 0%W.

Thus selectivity of mixed solvent (Dmso+W) when Benzene is replaced by Toluene is expected to decrease with an increase in molecular weight. This observation involves contradiction when one compares it with systems involving mixed solvent (Dmf+W). The reason for such an abnormal behavior is not clear.



Fig.-M .19 Mutual Solublity data of antisolvent effect as parameters for system T-H-100/90/80%Dmso-0/10/20% W at 20 °C



system T-H-100/90/80%Dmso-0/10/20% W at 30 °C

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5.1.8 Curves for mutual solubility data for systems involving X-H- Dmso+W and relevant conclusions:-

Mutual solubility data curves plotted in Figures M-22, M -23 and M -24 for systems X -H- Dmso+W at three different temperatures 20 0 C '30 0 C and 40 0 C and additional information reported in Table 2.1, reveals the following :-

(i)Conclusions already drawn in preceding paragraphs namely "As temperature increases and anti solvent concentration decreases, selectivity values are expected to decrease under otherwise identical conditions" is valid for all nine systems under consideration involving solute-Xylene.

(ii)Thus for example, at 30°C when anti solvent concentration is increased from 0% W to 10%W and up to 20%W, the ratio of H/X decreases from 0.176 to 0.053 and up to 0.026 respectively.

Further at fixed value of anti solvent concentration of 10%W as temperature is increased from 20°C to 30°C and up to 40°C, the ratio of H/X increases from 0.038 to 0.053 and up to 0.111 respectively.

(iii)From Table 2.1 it can be concluded that for systems involving mixed solvent Dmso+W as Benzene is further replaced by Toluene and Toluene is replaced by Xylene, the ratio of non-solute/solute follows a maxima for solute- Toluene. Hence for systems involving solute- Toluene, selectivity is expected to be lowest (with reference to % PE) and for systems involving Xylene, the selectivity is expected to be highest.

Thus for example ,for a fixed value of solvent concentration 80% W, anti solvent concentration= 20% and temperature of the order of 30 $^{\circ C}$, the value of ratio of H/aromatics, when Benzene is replaced by Toluene and Toluene further replaced by Xylene are 0.21, 0.333 and 0.176 respectively.

Since ratio is lowest for Xylene, selectivity values for systems involving Xylene are expected to be highest. Further same ratio is highest for solute Toluene, the selectivity values for systems involving Toluene are expected to be lowest.

As has been already discussed, the reason for this behavior is not clear.



system X-H-100/90/80%Dmso-0/10/20% W at 20 °C

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5.1.9 Curves for mutual solubility data for systems B-Hep-Dmso+W and for systems B-Oct-Dmso+W and relevant conclusions:-

Mutual solubility data curves plotted in Figures M-25, M -26 and M -27 for system B -Hep- Dmso+W and in Fig M-28, M -29 and M -30 for systems- B -Oct-Dmso+W at three different temperatures 20 0 C,30 0 C and 40 0 C and additional information reported in Table 2.1, reveals the following :-

(i) Conclusions already drawn in preceding paragraphs namely "As temperature increases and anti solvent concentration decreases, selectivity values are expected to decrease under otherwise identical conditions" is valid for all 18 different systems under consideration consisting of non solutes- Heptane and Octane.

Thus for example, for system consisting of non solute Octane (B-O-Dmso+W), for fixed value of temperature of 30 °C as anti solvent concentration increases from 0%W to 10% W and up to 20%W, the ratio of Octane /Benzene decreases from 0.176 to 0.053 and up to 0.026 respectively.

Similarly for example, for system consisting of non solute Heptane, for fixed value of anti solvent concentration of 0%W as temperature is increased from 20 °C to 30 °C and up to 40 °C, the ratio of Heptane /Benzene increases from 0.258 to 0.333 and up to 0.41 respectively.

Thus as anti solvent concentration increases, selectivity values for liquid-liquid extraction of aromatics increase and highest value is obtained for system involving non-solute Octane and having water concentration of 20% by weight.

(ii) It is interesting to observe that as non solute Hexane is replaced by Heptane the value of ratio of non solute /solute increases. Hence as a result when Hexane is replaced by Heptane the value of selectivity decrease. However, when Heptane is replaced by Octane selectivity values again increase.

Thus for example ,at temperature of 20 °C and anti solvent concentration of water of 0% W, when Hexane is replaced by Heptane and subsequently by Octane , the ratio of non solute/ solute are 0.21, 0.333 and 0.176 respectively.



system B-Hep-100/90/80%Dmso-0/10/20% W at 20 °C

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Further at temperature 40 °C and 0%W when Hexane is replaced by Heptane and subsequently by Octane, the ratios of non solute/solute are 0,25, 0.41 and 0.2 respectively.

Thus selectivity values are expected to be highest for system consisting of non solute Octane and lowest for non solute consisting of Heptane. The reason for such abnormal behavior is not clear.

5.2.0 Discussion for Quaternary Liquid-Liquid Phase Equilibrium Tie line data:-

Mutual solubility data reported in Tables 1to 30 and Tie line data for different quaternary systems reported in Tables 31 to 60 in Chapter -4 : Experimental has been presented in graphical form in terms of Binodal curves and corresponding straight lines for different Tie lines in Figurs- T-1 to T-30.

Tie line data for different systems consisting of B/T/X-H/H'/O-Dmf+W have been depicted in Figurs- T-1 to T-15

Further Tie line data for different systems consisting of B/T/X-H/H'/O-Dmso+W have been depicted in Figurs- T-16 to T-30.

Critical analysis of different Tie line data diagrams indicates that when anti solvent concentration of water in a mixed solvent is zero, Binodal curves are generally of closed type. As anti solvent concentration increases to 10 % and up to 20 %, generally Binodal curves for both mixed solvents are of open type.

Later on for subsequent discussion on extraction capacity and selectivity, distribution coefficient values and Hand's constant's values, the quaternary liquidliquid phase equilibrium data –(Mutual solubility data and Tie line data) obtained in this investigation could be utilized conveniently for interpretation purpose.

For interpretation purpose, basically four parameters have been considered as under;-

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(i) Effect of temperature

Table. - 1

Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots

for the Quaternary System :Beneze(B)- Hexane (H)-Dmf(D) + Water(w) at 20°C

Sr. Sr.Nc	%Dmf+Water	X _{BE}	X _{HE}	X _{DE+WE}	X _{BR}	X _{HR}	XDR+WR	D1	\mathbf{D}_2	S ₁	S2	H ₁	\mathbf{H}_2
-	•				•			•	•				
y	100+0	5.000	15.000	80.000	2.500	92.500	5.000	0.050	0.025	0.250	0.026	-1.204	-1.568
7	•	10.000	17.000	73.000	5.000	87.000	5.000	0.100	0.050	0.370	0.054	-0.863	-1.241
'n		12,000	21.000	67.000	10.000	85.000	5.000	0.120	0.100	0.364	0.105	-0.747	-0.929
4		17.000	24.000	54.000	12.700	81.000	6.300	0.170	0.127	0.415	0.136	-0.502	-0.805
ŝ		22.500	27.000	50.500	17.000	73.000	10.000	0.225	0.170	0.455	0.189	-0.351	-0.633
9	90+10	28.500	12.000	54.500	70.000	29.000	1.000	0.285	0.700	0.704	0.707	-0.282	0.383
2		7.800	11.500	81.500	24.500	73.000	2.500	0.078	0.245	0.404	0.251	-1.019	-0.474
~		24.000	11.000	65.000	62.500	35.500	2.000	0.240	0.625	0.686	0.638	-0.433	0.246
6		17.500	12.000	70.500	44.000	53.750	2.250	0.175	0.440	0.593	0.450	-0.605	-0.087
. 10		20.750	11.500	67.750	53.250	44.750	2.000	0.208	0.533	0.643	0.543	-0.514	0.076
11	80+20%	2.700	1.200	96.100	20.000	75.000	5.000	0.027	0.200	0.692	0.211	-1.551	-0.574
12		6.700	1.500	91.800	43.500	54.000	2.500	0.067	0.435	0.817	0.446	-1.137	-0.094
13		11.500	1.500	87.000	60.000	39.000	1.000	0.115	0.600	0.885	0.606	-0.879	0.187
14		29.000	1.500	69.500	85.000	14.000	1.000	0.290	0.850	0.951	0.859	-0.380	0.783
15		20.250	1.500	78.250	72.500	26.500	1.000	0.203	0.725	0.931	0.732	-0.587	0.437
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-1.790-1.311-1.311-1.322-1.722-1.932-1.932-1.932-0.416-0.4160.4070.4070.4070.662-0.7990.527-0.1610.527-0.1610.527-0.1610.527-0.1610.527-0.1610.527-0.1610.527-0.1610.536-0.1610.536-0.161-0.161-0.161-0.161-0.161-0.161-0.161-0.161-0.161-0.161-0.161-0.1200-0.1200-0.12000-0.12000-0.120 \mathbf{H}_2 H, 0.061 0.277 0.488 0.719 0.137 0.137 0.016 0.047 0.091 0.019 0.012 0.179 0.408 0.446).714 Data processing Table of parameters for Distribution, Selectivity diagrams and Hand's plots Ś for the Quaternary System : Benzene(B)- Hexane (H)-Dmf(D) + Water(w) at 30°C 5 $\mathbf{\tilde{D}}_{2}$ ģ X_{DR+WR} 7.000 9.800 12.000 19.200 13.500 33.980 33.980 33.980 4.500 4.500 3.000 1.500 2.300 5.000 4.500 3.500 0.500 53,500 28,500 42,500 Table. - 2 X_{HR} 1.000 4.000 26.500 46.700 69.700 13.500 75.300 17.000 39.000 43.000 71.000 57.000 1.500 4.200 8.000 1.500 X_{BR} X_{DE+WE} 90.600 43.700 95.750 90.500 79.000 84.870 76.500 75.000 73.500 85.000 67.000 91.250 59.900 76.500 70.500 65.000 18.500 21.500 25.000 19.800 23.000 23.000 10.000 14.000 16.100 6.700 11.100 1.250 1.000 0.750 0.500 0.500 X_{HE} 4.200 2.200 6.000 5.000 19.000 24.000 24.000 45.200 3.000 3.000 8.750 8.750 8.750 5.000 8.000 10.000 14.620 X_{BE} %Dmf+Water 80+20% 100+0 90+10 Sr. Sr.Nc 1515

-0.118 0.298 0.721 0.486 -0.326 -1.226 -0.778 -0.969 0.035 -0.731 0.311 \mathbf{H}_2 -0:389 -1.727 -0.492 -0.626 -0.153 0.161 0.020 -1.255 -1.168 -0.381 -0.691 0.727 H, 0.056 0.143 0.157 0.097 0.432 0.665 0.840 0.754 0.320 0.211 0.520 0.672 0.784 ທີ 0.243 0.260 0.254 0.696 0.680 0.717 0.887 0.462 0.614 0.713 0.239 0.797 0.744 5 0.640 0.815 0.728 0.125 0.130 0.088 0.415 0.308 0.052 0.205 0.510 0.655 0.775 ñ 0.018 0.062 0.140 0.160 0.123 0.160 0.255 0.355 0.550 0.453 0.051 0.105 ñ X_{DR+WR} 12.500 9.150 3.000 4.000 3.800 3.000 3.500 7.300 3.940 2.500 1.200 47.000 87.500 75.000 70.000 15.500 23.750 65.300 82.000 76.500 54.500 32.200 32.000 21.300 X_{HR} 30.800 41.500 64.000 81.500 20.500 72.750 5.200 12.500 13.000 65.500 77.500 8.800 X_{BR} XDE+WE 96.100 91.300 87.900 56.000 43.500 38.500 78.500 38.000 51.750 62.500 50.500 43.250 33.500 43.500 45.500 36.000 12.000 14.000 11.500 7.000 7.000 2.100 X_{HE} 2.500 3.100 25.500 35.500 16.000 16.000 12.250 55.000 45.250 10.500 5.100 1.800 6.200 9.000 X_{BE} %Dmf+Water 80+20% 100+0 90+10 Sr. Sr.No.

Table. - 3

Data processing Table of parameters for Distribution , Selectivity diagrams and Hand's plots

for the Quaternary System : Benzene(B)- Hexane (H)-Dmf(D) + Water(w) at 40°C

Table. - 4

Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots

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for the Quaternary System : Toluene (T) Hexane (H)-Dmf(D) + Water(w) at 20°C

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Sr. Sr.No.	%Dm1+Water	X _{TE}	X _{HE}	XDE+WE	X _{TR}	XHR	X _{DR+WR}	DI	D2	S	S ²	Н	H ₂
	100+0	9.750	13.250	77.000	8.900	84.200	6.900	0.098	0.089	0.424	0.096	-0.897	-0.976
7		16.000	19.500	64.500	17.000	74.500	8.500	0.160	0.170	0.451	0.186	-0.605	-0.642
ŝ		20.500	35.000	44.500	20.500	69.500	10.000	0.205	0.205	0.369	0.228	-0.337	-0.530
4		18.000	27.000	55.000	18.000	72.500	9.500	0.180	0.180	0.400	0.199	-0.485	-0.605
ŝ	х. х	12.870	18.000	64.130	12.950	79.050	8.000	0.129	0.130	0.417	0.141	-0.697	-0.786
9	20+80	2.000	1.000	97.000	27.000	68.500	4.500	0.020	0.270	0.667	0.283	-1.686	-0.404
7		4.000	1.000	95.000	43.500	50.000	4.000	0.040	0.435	0.800	0.465	-1.376	-0.060
∞	•	8.500	1.200	90.300	65.000	32.000	3.000	0.085	0.650	0.876	0.670	-1.026	0.308
6	•	10.000	1.000	89.000	79.500	18.000	2.500	0.100	0.795	0.909	0.815	-0.949	0.645
10		6.250	1.000	92.750	54.250	42.250	3.500	0.063	0.543	0.862	0.562	-1.171	0.109

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	•	for 1	he Quatei	rnary Sy	stem : Tol	uene (T) Hexan	e (H)-Dn	1(D)+ (Water(w)) at 30 °C		 	
·		: ; ;	и 41 44 4	: 	4 4 4 4 4						. « - -	, ,		,
- =	Sr. Sr.No.	%Dmf+Water	X _{TE}	X _{HE}	X _{DE+WE}	X _{TR}	X _{HR}	X _{DR+WR}	'n	D2	S,	S_2	H ₁	F
			į				-						÷	
		100+0	3.500	17.000	79.500	2.000	88.000	10.000	0.035	0.020	0.171	0.022	-1.356	-1.6
	6		8.250	17.500	74.250	5.000	85.000	10.000	0.083	0.050	0.320	0.056	-0.954	-
	ŝ		13.000	18.000	69.000	10.000	78.000	12.000	0.130	0.100	0.419	0.114	-0.725	°,
	4		15.000	22.000	63.000	13.200	74.000	12.800	0.150	0.132	0.405	0.151	-0.623	Ģ
	ŝ		19.000	28.000	53.000	18.000	61.500	19.500	0.190	0.180	0.404	0.226	-0.446	0-
	9	90+10	7.800	4.800	87.400	18.200	74.800	7.000	0.078	0.182	0.619	0.196	-1.049	-0.6
	۲.	•	12.600	6.000	81.400	27.000	65.500	7.500	0.126	0.270	0.677	0.292	-0.810	-0.3
÷	~		15.000	6.000	79.500	37.500	54.500	8.100	0.150	0.375	0.714	0.408	-0.724	0
	6		25.000	3.500	71.500	53.000	37.000	10.000	0.250	0.530	0.877	0.589	-0.456	0.1
	10		37.000	3.000	60.000	70.000	24.000	6.000	0.370	0.700	0.925	0.745	-0.210	0.4
	[]	80+20%	7.500	1.600	90.400	45.000	50.500	4.500	0.075	0.450	0.824	0.471	-1.081	Ģ
" <u>.</u>	12	•	10.000	1.800	88.200	49.000	46.500	4.500	0.100	0.490	0.847	0.513	-0.945	0.0
	13		11.000	1.600	87.400	61.000	35.500	3.500	0.110	0.610	0.873	0.632	-0.900	0.7
	14		15.000	1.200	83.800	74.000	23.000	3.000	0.150	0.740	0.926	0.763	-0.747	0.5
	15		3.000	1.400	95.600	67.500	29.500	3.000	0.030	0.675	0.682	0.696	-1.503	0
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-1.306 -1.039 -0.216 0.316 -0.492 -0.040 -0.195 0.925 -0.983 0.508 0.248 0.154 0.462 0.821 H, -0.706 -0.806 -0.973 -0.770 -0.883 -0.517 -1.498 -1.052 -0.468 -1.270 0.710 -1.091 -0.772 0.035 H, 0.084 0.869 0.378 0.674 0.244 0.477 0.763 0.389 0.106 0.743 0.071 0.094 0.588 Data processing Table of parameters for Distribution, Selectivity diagrams and Hand's plots Ś for the Quaternary System :Toluene (T) Hexane (H)-Dmf(D) + Water(w) at 40 °C 0.308 0.278 0.231 0.714 0.889 0.254 0.314 0.800 0.886 0.688 0.865 0.588 0.308 0.943 0.962 ທົ 0.085 0.070 0.040 0.060 0.240 0.860 0.310 0.607 0.465 0.740 0.370 0.620 0.077 0.695 0.520 Ď, 0.225 0.030 0.120 0.100 0.060 0.075 0.110 0.310 0.510 0.110 0.080 0.250 0.050 0.160 0.140 ā X_{DR+WR} 16.500 1973年1979年(1979年)(1989年)(1989年) 1999年(1999年)(1999年) 20.000 15.000 18.300 10.000 10.000 11.500 6.500 1.000 1.500 1.500 3.000 5.000 3.000 71.500 76.500 81.000 79.000 74.000 13.000 51.000 29.300 74.500 51.000 23.000 24.000 58.000 X_{IIR} 35.000 36.500 Table. - 6 74.000 52.000 69.500 86.000 31.000 50.700 24.000 46.500 37.000 7.000 6.000 52.000 8.500 7.700 X_{IR} X_{DE+WE} 61.000 64.000 74.000 84.000 74.000 94.400 93.000 82.000 70.500 65.000 47.000 90.200 73.500 65.000 82.500 .. 2 . 27.000 26.000 20.000 22.000 24.000 1.500 3.500 2.100 2.000 4.000 2.000 5.000 3.500 2.000 XHE 14.000 31.000 51.000 11.000 3.000 3.000 8.000 5.000 5.000 12.000 6.000 11.000 7.500 X_{TE} Sr. Sr. No. %Dmf+Water 30+20% 100+0 90+10 14 15 Ľ 13

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		Data proc	essing Ta	uble of pa	rameters	for Dist	ribution	,Selectiv	rity diag	rams an	d Hand's	; plots		
•			n Her Her Her Her Her Her Her Her Her Her									3	•	. 1
		for 1	he Quate	rnary Sy	stem : Xy	lene(X)-	. Hexane	(H)-Dm	f(D) + V	Vater(W) at 20°C			
,				, 1 - ⁷ . - 1			4 4 4 4 4		· · · · · · · · · · · · · · · · · · ·				• • •	
	Sr. Sr.No.	%Dmf+Water	X _{XE}	X _{HE}	X _{DE+WE}	X _{XR}	X _{HR}	X _{DR+WR}	Dı	D2	S1	S2	H	H ₂
• .					,		•					•		
		100+0	2.900	13.000	84.100	1.990	96.150	1.500	0.029	0.020	0.182	0.020	-1.462	-1.684
	~ ~		9.700	15.800	74.500	8.900	87.800	3.300	0.097	0.089	0.380	0.092	-0.885	-0.994
			14.400	19.700	65.900	16.250	79.800	3.950	0.144	0.163	0.422	0.169	-0.661	-0.691
	4 v		6.300 17 050	17 750	79.300	5.440	92.150 82.800	2.400	0.063	0.054	0.304	0.056	-1.100	-1.229
		90+10	1.240	3.450	94.180	8.220	86.500	5.280	0.121	0.108	0.404	0.115	-0.765	-0.888
•	1	;	5.500	3.600	90.900	36.500	59.150	4.350	0.055	0.365	0.604	0.382	-1.218	-0.210
	∞ `c		12.500	3.250	84.250	66.000	30.950	3.050	0.125	0.660	0.794	0.681	-0.829	0.329
	× 2	:	0/ 5.5	4.000 5.000	92.050	22.360	72.540	5.100	0.034	0.224	0.457	0.236	-1.439	-0.511
	. 11	80+20	1.500	0.650	97.950	35.900	61.000 61.000	4.000 3 100	0.900	0.513	0.947	0.534	0.020	0.059
	12		5.000	0.500	94.500	70.500	28.000	1.500	0.050	0.705	0.909 0.909	0.716	-1.012	0.401
2	13		3.250	0.500	96.250	53.200	44.000	2.800	0.033	0.532	0.867	0.547	-1.472	0.082
16	14		4.120	0.500	95.380	61.850	35.950	2.200	0.041	0.619	0.892	0.632	-1.365	0.236
3	C7		2.380	0.500	97.120	44.400	526.000	3.000	0.024	0.444	0.826	0.078	-1.611	-1.074

Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots

Table. - 8

for the Quaternary System : Xylene(X)- Hexane (H)-Dmf(D) + Water(W) at 30°C

Sr. Sr.No.	%Dmf+Water	X _{XE}	X _{HE}	X _{DE+WE}	X _{XR}	X _{HR}	X _{DR+WR}	ď	D2	S1	S2	H,	,H,
							, ., , , ,	, ,, ,			۱. ۲.	t .	•
1	100+0	9.700	17.050	73.250	4.800	91.000	4.200	0.097	0.048	0 363	0.050	-0.878	1 778
7		12.700	19.400	67.900	10,100	85,400	4 500	0 177	0 101	0.306	0.106	0/0.0-	0/7.1-
ŝ		16.800	22.050	60.650	15.700	78.500	5.300	0.168	0.157	0.432	0.167	-0.558	0090-
4	•	14.300	20.700	65.000	12.300	84.000	6.000	0.143	0.123	0.409	0.128	-0.658	-0.07
5	; ,	15.300	21.500	63.200	14.000	78.000	8.000	0.153	0.140	0.416	0.152	-0.616	-0.746
7	90+10	5.000	6.250	88.750	21.000	73.200	5.800	0.050	0.210	0 444	0 273	-1 249	CV2 U-
∞		8.500	5.800	85.700	35.000	59.500	5.500	0.085	0.350	0.594	0.370	-1 004	710.01
6		16.500	4.800	78.700	57.000	38.000	5.000	0.165	0.570	0.775	0.600	-0.678	0.176
10		19.200	3.300	77.500	62.000	33.500	4.900	0.192	0.620	0.853	0.649	-0.606	0.267
-		12.500	4.000	83.500	46.000	48.000	6.000	0.125	0.460	0.758	0.489	-0.825	-0.018
13	80+20	1.200	2.600	96.200	21.500	70.700	7.800	0.012	0.215	0.316	0.233	-1 904	-0.517
14		2.900	2.000	95.100	37.500	56.500	6.000	0.029	0.375	0.592	0.399	-1.516	-0.178
15	•	4.700	2.000	93.300	53.500	41.300	5.200	0.047	. 0.535	0.701	0.564	-1.298	0.112
16		5.400	1.900	92.700	63.000	32.900	4.100	0.054	0.630	0.740	0.657	-1.235	0.282
17		13.000	1.800	85.200	79.500	17.800	2.700	0.130	0.795	0.878	0.817	-0.816	0.650

Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots

for the Quaternary System : Xylene(X)- Hexane (H)-Dmf(D) + Water(W) at 40°C

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- 2 1 4 5 6 8	90+10	18.000 5.000 12.000 13.500 16.500	5.000 8.600 7.250 7.000 6.300	77.000	002 C7					·			
・こう <i>よ</i> ら ての	> • •	5.000 12.000 13.500 16.500	7.000 6.300	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		32,000	V 500	0.100	367 0	000	27.6		
1 m 4 m r o		5.000 12.000 13.500 16.500	8.600 7.250 7.000 6.300			000.70	000-+	001.0	CC0.0	0./03	C00.U	100.0-	0.298
т π τ τ τ τ τ τ τ τ τ τ τ τ τ τ τ τ τ τ		12.000 13.500 16.500	7.250 7.000 6.300	86.400	22.500	71.850	5.650	0.050	0.225	0.368	0.238	-1.238	-0.504
4 10 10 0		13.500	7.000 6.300	80.750	41.000	53.700	5.300	0.120	0.410	0.623	0.433	-0.828	-0.117
	- -	16.500	6.300	79.500	52.000	43.300	4.700	0.135	0.520	0.659	0.546	-0.770	0.080
۲ ۵				77.200	54.500	41.000	4.500	0.165	0.545	0.724	0.571	-0.670	0.124
•	80+20	4.100	3.100	92.800	29.100	64.100	6.800	0.041	0.291	0.569	0.312	-1.355	-0.343
0	L	6.200	3.900	90.900	41.700	53.500	4.800	0.062	0.417	0.614	0.438	-1.166	-0.108
6	•	8.200	1.700	90.100	61.500	34.800	3.700	0.082	0.615	0.828	0.639	-1.041	0.247
10		7.200	3.400	88.900	51.600	43.500	5.000	0.072	0.516	0.679	0.543	-1.092	0.074
11		5.150	23.200	91.650	35.400	57.900	6.700	0.052	0.354	0.182	0.379	-1.250	-0.214
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		•				·							

Table. - 9

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		H ₂	-1.61 -1.37 -0.99	-1.07 -0.28 -0.12 -0.12 -0.03 -0.03	
		н	-1.613 -1.423 -1.176 -1.293	-1.233 -0.765 -0.943 -0.427 -0.629 -0.528	
•	s plots	S2	0.024 0.040 0.092 0.065	0.07/ 0.342 0.203 0.430 0.482 0.482 0.532	·
	d Hand's at 20°C	s.	0.111 0.150 0.200 0.444	0.474 0.628 0.569 0.754 0.686 0.722	
· ·	grams an /ater(W)	D,	0.022 0.037 0.078 0.058	0.008 0.338 0.200 0.565 0.475 0.525	×
	vity diag f(D) + W	- É	0.020 0.030 0.050 0.040	0.045 0.135 0.095 0.250 0.175 0.175	
· · · · · · · · · · · · · · · · · · ·	n ,Selecti (H')-Dm	X _{DR+WR}	7.500 7.800 15.200 11.050	1.400 1.450 1.310 1.400 1.350	
ole1 0	fribution B)-Hept	X _H rR	90.300 88.500 77.000 83.200 81.730	64.850 64.850 75.019 51.100 46.150	
Tal	s for Dis Benzene(XBR	2.200 3.700 7.800 5.750 6.770	33.750 20.000 56.500 47.500 52.500	
•	urameter ystem :]	X _{DE+WE}	82.000 79.500 75.000 78.500	78.500 83.300 66.850 74.480 70.900	
	ble of pa ernary S	X _{H'E}	16.000 17.050 20.000 5.000	8.000 7.200 8.150 8.020 8.100	
•	essing Ta the.Quat	X _{BE}	2.000 3.000 5.000 4.000	13.500 9.500 25.000 17.500 21.000	
	Data proc for	%Dmf+Water	100+0	90+10	
		Sr.No	- 0 n 4 v	6 9 10 10	
• • •			•		and the second sec

0.831 -1.255 -0.972 -1.959 -1.499 -0.469 -0.104 0.052 -0.280 -0.034 0.102 -0.489 -0.106 0.328 0.474 H, -1.138 -0.878 -1.558 -1.302 -0.730 -0.533 -0.252 -0.626 -0.384 -1.214 0.637 0.328 -0.725 -0.741 -0.861 Щ 0.096 0.253 0.440 0.530 0.344 0.481 0.559 0.245 (439) 0.128 0.053 0.011 0.680 0.749 0.031 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots ທີ for the Quaternary System : Benzene(B)-Hept(H')-Dmf(D) + Water(W) at 30°C 0.670 0.573 0.633 0.697 0.281 0.107 0.168 0.565 0.582 0.787 0.550 0.818 0.912 0.382 0.224 5 0.080 0.512 0.469 0.548 0.240 0.435 0.115 0.045 0.028 0.425 0.660 0.241 0.715 ñ 0.250 0.148 0.022 0.140 0.305 0.168 0.055 0.115 0.055 0.000.0 0.195 0.180 0.310 0.125 Ā X_{DR+WR} 8.000 10.500 14.500 10,000 4.900 3.000 3.400 3.500 2.500 2.000 2.000 1.000 3.000 4.500 75.000 91.000 71.000 54.000 45.400 63.200 78.000 81.000 86.750 50.650 43.250 74.000 55.500 31.000 X_{H'R} 24.000 Table. -1 1 51.200 33.200 24.100 42.500 46.850 54.750 24.000 43.500 56.000 11.500 4.500 8.000 1.000 2.750 71.500 X_{BR} X_{DE+WE} 75.200 66.500 54.500 77.150 60.500 81.250 66.300 75.500 68.000 79.500 70.750 90.00 83.500 78.000 56.000 1.1.1 20.200 19.000 23.000 18.300 19.000 0.800 14.000 15.000 12.500 4.500 X_{H'E} 4.000 5.000 4.000 3.000 12.500 9.000 9.000 14.000 19.500 30.500 30.500 11.750 14.750 11.750 11.750 11.750 11.750 11.750 11.750 11.750 11.750 11.750 5.500 18.000 11.500 31.000 X_{BE} %Dmf+Water 90+10 100+080+20 Sr.No 13 13 93.

				<u> </u>		·										
		${\rm H}_{3}$	-1.653	-1.457	-1.298	-1.212	-0.643	-0.174	0.160	-0.378	-0.003	-0.176	0.308	0.660	0.063	0.466
		H ₁	-1.426	-1.176	-0.917	-0.715	-0.875	-0.454	-0.148	-0.637	-0.290	-1.072	-0.513	-0.278	-0.730	-0.393
t plots		S ₂	0.022	0.034	0.048	0.076	0.185	0.401	0.591	0.295	0.498	0.400	0.670	0.821	0.536	0.745
l Hand's	at 40°C	SI	0.150	0.200	0.255	0.306	0.495	0.665	0.771	0.610	0.723	0.652	0.920	0.958	0.845	0.966
rams and	ater(W)	. D ₂	0.020	0.030	0.042	0.065	0.170	0.375	0.572	0.273	0.474	0.380	0.650	0.800	0.515	0.725
vity diag	(D) + W	D1	0.030	0.050	0.082	0.130	0.105	0.230	0.370	0.168	0.300	0.075	0.230	0.340	0.153	0.285
,Selectiv	H')-Dm	X _{DR+WR}	8.000	11.000	12.400	14.500	8.240	6.550	3.200	7.700	5.000	5.000	3.000	2.500	4.000	2.700
le1 2 ribution	B)-Hept(X _{H'R}	90.000	86.000	83.400 81.500	79.000	74.760	55.950	39.600	65.050	47.650	57.000	32.000	17.500	44.500	24.800
Tab for Dist	enzene()	X _{BR}	2.000	3.000	4.200 5.000	6.500	17.000	37.500	57.200	27.250	47.350	38.000	65.000	80.000	51.500	72.500
rameters	ystem : B	X _{DE+WE}	80.000	75.000	65.000 65.000	67.500	78.800	65.400	52.000	72.550	58.500	88.500	75.000	64.500	81.950	70.500
ble of pa	ernary S	X _{H'E}	17.000	20.000	24.000 26.000	29.500	10.700	11.600	11.000	10.700	11.500	4.000	2.000	1.500	2.800	1 000
ssing Ta	he Quate	X _{BE}	3.000	000.0	9.000 9.000	13.000	10.500	23.000	37.000	16.750	30.000	7.500	23.000	34.000	15.250	28.500
Data proce	for t	%Dmf+Water	100+0				90+10	•		- - -	•	80+20	• •* •			
		Sr.No	(7 7	ר ר ע	Ś	4	∞	6	9:		13	14	15	16	17
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0.489 -0.364 -0.350 -0.583 -0.683 -0.522 -0.285 -0.088 -0.748 1.371 0.938 0.641 -0.471 0.262 0.494 H, 0.510 -0.820 -1.068 -1.258 -0.930 -0.728 -1.009 -1.358 0.827 0.581 0.404 -1.666 -1.413 -0.784 0.931 H, 0.103 0.186 0.302 0.353 0.309 0.207 0.172 0.342 0.450 0.152 0.253 0.646 0.245 0.231 0.757 0.041 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots <u>ທີ່</u> for the Quaternary System : Benzene(B)-Oct(O)-Dmf(D) + Water(W) at 20°C 0.576 0.718 0.615 0.526 0.676 0.568 0.582 0.754 0.927 0.802 0.856 0.350 0.495 0.943 0.521 0.963 S 0.180 0.236 0.290 0.338 0.290 0.205 0.170 0.240 0.338 0.445 0.150 0.250 0.640 0.040 0.101 0.750 ก์ 0.110 0.180 0.235 0.125 0.100 0.039 0.095 0.075 0.050 0.150 0.089 0.037 0.140 0.021 0.220 Ā X_{DR+WR} 066.0 1.950 3.900 1.100 1.030 L.020 1.030 2.660 3.300 4.120 1.100 1.100 1.110 1.050 0.970 72.800 67.100 64.900 81.890 79.900 65.170 83.950 73.970 35.010 94.050 87.270 78.700 78.400 54.480 XH'R 52.080 24.030 18.000 23.600 29.000 33.800 29.000 17.000 24.000 33.800 [5.000 25.000 64.000 0.070 20.500 44.500 4.000 75.000 X_{BR} X_{DE+WE} 88.850 81.100 73.900 65.100 59.600 87.800 90.500 85.200 30.100 97.380 95.670 85.150 82.600 90.450 77.150 X_{H'E} 10.100 13.700 4.800 6.900 7.250 9.700 4.900 4.700 4.500 4.800 4.900 0.700 0.520 0.620 0.850 0.850 ÷ 10.000 5.000 11.000 8.000 20.100 23.500 12.500 7.500 3.700 14.000 9.500 5.000 8.850 2.100 22.000 3.900 XBE %Dmf+Water 0+001 90+10 80+20 Sr.No 14 ×.

Table.-13

-0.848 -0.555 -0.455 -0.445 -0.445 -0.450 -0.450 0.167 0.167 0.167 0.167 0.167 0.167 0.167 0.427 0.230 Н, -0.623 -0.373 -0.275 -1.112 -0.885 -0.624 -0.545 -0.471 0.400 -1.062 0.986 0.771 0.717 H, 0.262 0.349 0.505 0.218 0.319 0.170 0.595 0.349 0.728 0.124 0.151 0.264 0.527 0.438 0.630 Data processing Table of parameters for Distribution, Selectivity diagrams and Hand's plots Š. for the Quaternary System : Benzene(B)-Oct(O)-Dmf(D) + Water(W) at 30°C 0.508 0.539 0.568 0.573 0.558 0.646 0.702 0.775 0.805 0.732 0.797 0.864 0.765 0.839 S 0.120 0.145 0.208 0.298 0.250 0.167 0.258 0.344 0.497 0.585 0.345 0.521 0.721 0.433 0.623 ŋ 0.127 0.165 0.188 0.212 0.235 0.075 0.128 0.178 0.274 0.320 0.070 0.112 0.200 0.156 160.0 ค XDR+WR 3.750 6.500 1.700 3.450 5.310 1.500 1.520 1.560 1.650 1.100 1.050 0.950 1.050 .050 X_{H'R} 84.550 81.500 74.700 81.800 72.680 64.040 39.800 64.450 46.850 26.950 69.690 63.700 48.650 55.650 36.650 X_{BR} 25.000 20.800 29.800 16.700 25.800 34.400 49.700 52.100 72.100 12.000 58.500 34.500 43.300 52.300 X_{DE+WE} 85.950 66.000 62.700 80.200 74.650 64.630 60.250 90.490 76.850 75.000 69.400 59.000 86.550 88.100 81.400 12.300 14.100 XH'E 15.200 16.100 17.500 5.950 7.000 7.550 7.970 7.750 2.560 2.850 3.150 2.800 3.000 17.800 27.400 21.200 23.500 7.500 12.800 32.010 7.000 11.200 20.000 12.700 18.800 9.100 XBE %Dmf+Water 90+10 100+030+20 Sr.No 13 12 15

Table. -1 4

-0.747 -0.695 -0.459 -0.580 -0.315 -0.093 0.098 -0.860 .1.074 -1.025 -0.888 -0.577 -0.309 -0.217 -0.431 H, -1.256 0.918 -0.650 -0.308 -0.086 -0.851 -0.583 -0.582 -0.360 -0.883 0.074 -1.071 -0.834 -0.780 0.940 Ē 0.326 0.447 0.556 0.209 0.329 0.378 0.270 0.208 0.078 0.086 0.152 0.168 0.258 0.115 0.121 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots 5 for the Quaternary System : Benzene(B)-Oct(O)-Dmf(D) + Water(W) at 40°C 0.708 0.769 0.820 0.549 0.647 0.688 0.895 0.845 0.892 0.769 0.446 0.464 0.521 0.532 0.533 S 0.110 0.200 0.310 0.420 0.520 0.118 0.203 0.319 0.364 0.261 0.083 0.145 0.160 0.240 0.075 ĥ 0.240 0.110 0.170 0.300 0.410 0.510 0.050 0.075 0.140 0.108 0.174 0.192 0.125 0.095 Ā X_{DR+WR} 5.000 3.750 4.000 6.500 2.700 3.100 3.100 3.600 3.500 3.650 4.570 4.720 7.000 4.000 64.000 52.000 41.500 X_{H'R} 88.850 87.950 80.930 79.280 69.000 85.000 76.000 85.500 76.600 65.000 60.000 70.400 11.000 20.000 42.000 52.000 1.800 20.300 6.400 6.100 16.000 24.000 4.500 7.500 8.300 XBR X_{DE+WE} 84.000 76.000 61.000 88.400 85.200 50.000 43.000 90.100 34.300 87.000 76.700 66.600 73.300 55.000 11.810 12.500 16.000 16.860 21.000 5.000 9.000 9.000 6.000 1.700 X_{H'E} 4.100 4.100 2.300 3.000 24.000 11.000 5.000 7.500 12.500 9.500 10.800 17.400 19.200 17.000 30.000 41.000 51,000 14.000 0.000 X_{BE} %Dmf+Water 80+20 0+001 90+10 Sr.No

Table.(-15

-0.004 0.280 0.765 -0.485 -0.027 -0.298 -0.130 -0.063 0.045 -0.255 0.564 0.949 0.513 0.591 H, 0.619 -0.509 -0.459 -0.395 -0.315 -1.505 -0.860 -0.243 -1.996 -1.690 -1.279 -1.158 -0.821 0.491 H 0.335 0.426 0.464 0.526 0.357 0.497 0.656 0.853 0.247 0.485 0.786 0.899 0.235 0.367 0.204 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots Ś for the Quaternary System : Benzene(B)- Hexane (H)-Dmso(D') + Water(W) at 20°C 0.923 0.973 0.956 0.736 0.759 0.774 0.818 0.796 0.750 0.980 0.990 0.996 0.997 0.799 ā 0.230 0.330 0.415 0.450 0.510 0.485 0.610 0.815 0.243 0.360 0.200 0.475 0.770 .890 ĥ 0.310 0.120 0.360 0.215 0.010 0.050 0.181 0.220 0.240 0.270 0.130 0.020 0.230 0:030 0.065 ā X_{D'R+WR} 3.000 1.500 2.500 3.030 2.500 7.000 4.500 3.000 2.000 2.000 1.500 2.000 2.000 2.000 000. 75.000 65.500 56.000 51.970 46.000 63.000 49.000 32.000 14.000 74.200 50.500 21.000 X_{H'R} 52.000 78.000 10.000 47.500 45.000 51.000 35.000 48.500 61.000 81.500 24.300 77.000 23.000 33.000 41.500 89.000 36.000 20.000 X_{BR} X_{D'E+WE} 69.000 67.000 63.000 77.500 97.980 75.360 64.040 71.200 86.000 87.000 98.980 94.980 93.480 96.000 7.950 5.790 .000 XHIE 6.500 7.000 7.000 6.000 000 1.000 000.1 0.020 0.020 0.020 0.020 .000 13.000 12.000 36.000 21.500 18.140 22.000 24.000 27:000 31.000 23.000 1.000 2.000 5.000 3.000 6.500 X_{RE} %Dmso+Water 90+10 80+20 100+0 Sr.No 4

225

Table. -1 6

-0.032 -0.696 -0.352 -0.157 0.116 0.335 -0.335 -0.802 -0.802 0.738 0.212 0.146 -0.354 -0.691 -0.058 0.240 0.322 \mathbf{H}_2 -0.176 0.055 -0.582 -1.362 -1.276 -1.015 -0.887 -0.748 -0.668 -0.950 -2.396 -2.093 -1.762 -0.467 -1.647 -1.051 1.915 H. 0.169 0.364 0.260 0.482 0.583 0.307 0.168 0.308 0.566 0.684 0.136 0.260 0.155 0.411 .466 0.381 0.677 .365 Data processing Table of parameters for Distribution , Selectivity diagrams and Hand's plots 5 for the Quaternary System : Benzene(B)- Hexane (H)-Dmso(D') + Water(W) at 30°C 0.946 0.800 0.921 0.927 0.938 0.785 0.821 0.732 0.796 0.500 0.500 0.926 0.800 0.889 0.944 0.917 Ś 0.150 0.256 0.310 0.165 0.165 0.303 0.405 0.555 0.670 0.360 0.465 0.447 0.504 0.135 0.672 0.371 á 0.368 0.445 0.195 0.040 0.050 0.238 0.088 0.115 0.150 0.175 0.100 0.004 0.008 0.017 0.080 0.157 0.022 0.012 ā X_{D'R+WR} 7.200 1.390 2.790 4.000 3.000 2.500 1.500 1.750 1.400 2.000 2.000 1.000 1.000 1.100 0.300 0.700 X_{H'R} 70.000 60.400 48.100 36.000 81.000 82.000 68.000 58.100 42.500 31.000 63.000 85.500 73.200 53.200 82.000 73.000 32.000 62.500 37.100 3.500 15.000 50.400 6.500 6.500 0.250 10.500 55.500 57,000 6.000 25.700 l6.500 X_{BR} 14.700 31.000 57.200 6.000 X_{D'E+WE} 81.500 90.000 79.500 69.700 55.200 39.200 74.500 92.000 94.500 90.500 88.600 84.000 89.200 99.500 99.100 98.200 97.600 98.700 16.300 6.500 8.000 5.000 0.900 1.000 X_{H'E} 2.000 4.800 4.000 5.000 0.750 1.000 0.800 0.100 0.100 0.100 0.200 0.100 8.000 15.700 23.800 36.800 44.500 19.500 19.500 5.000 8.750 11.500 15.000 17.500 10.000 0.400 0.800 1.700 2.200 XBE %Dmso+Water 90+10 80+20 100+0 Sr.No

Table. -17

-0.727 -0.424 -0.281 -0.191 -0.191 -0.004 -0.129 -0.748 -0.748 0.150 -0.770 -0.770 -0.253 -0.253 -0.011 -1.104 H, -0.745 -0.420 #DIV/0! -1.072 -0.918 -0.666 -0.743 -1.186 -0.484 -1.880 -1.627 -1.038 -2.219 -1.736 Ħ, 0.426 0.152 0.585 0.145 0.359 0.507 0.073 0.274 0.344 0.392 0.349 0.497 0.158 Data processing Table of parameters for Distribution, Selectivity diagrams and Hand's plots ທີ for the Quaternary System : Benzene(B)- Hexane (H)-Dmso(D') + Water(W) at 40°C 0.800 0.773 1.000 0.818 0.882 0.750 0.856 0.929 0.958 0.988 0.923 0.947 0.652 0.840 S 0.330 0.493 0.422 0.150 0.355 0.503 0.072 0.266 0.380 0.345 0.565 0.143 0.150 0.250 $\mathbf{\tilde{D}}_2$ 0.180 0.150 0.060 0.160 0.345 0.105 0.237 0.013 0.023 0.075 0.006 0.018 ď X_{D'R+WR} 5.000 4.000 3.000 1.200 000.1 1.000 1.000 1.500 1.400 1.000 1.300 2.770 49.800 56.800 84.000 40.000 84.300 63.500 49.000 X_{H'R} 91.500 80.000 70.560 63.000 59.000 64.300 73.000 15.000 26.600 33.000 38.000 34.500 19.300 12.200 15.000 56.500 14.300 35.500 50.300 X_{BR} 7.200 X_{D'E+WE} 88.500 89.000 67.000 92.000 72.300 98.700 97.500 87.000 83.500 83.000 89.500 99.300 98.100 X_{H'E} 4.000 4.000 7.500 2.000 4.000 2.000 2.000 4.000 0.100 0.100 0.100 0.050 0.100 25.500 25.500 34.500 10.500 18.000 15.000 6.000 23.700 1.300 2.300 7.500 0.600 8.200 1.800 XBE %Dmso+Water 100+0 90+10 80+20 Sr.No

Table. -18

Table. -1 9

Data processing Table of parameters for Distribution , Selectivity diagrams and Hand's plots

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for the Quaternary System : Toluene (T) Hexane (H)-Dmso(D') + Water(W) at 20°C

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Sr.No	%Dmso+Water	\mathbf{X}_{TE}	X _{H'E}	X _{D'E+WE}	X _{TR}	X _{H'R}	X _{D'R+WR}	ų	· D ₂	ŝ	S.	H	H,
	, , ,		1 . 1 /					, ,,, ,	•	- - -	-3	• . • .	•
	100+0	13,000	5.000	82.000	27.000	70.500	2.500	0.130	0.270	0.722	0.277	-0.800	-0417
7		25.000	5.000	70.000	57.000	38.500	4.500	0.250	0.570	0.833	0.597	-0.447	0170
ŝ		30.500	9.500	60.000	56.000	26.000	17.000	0.305	0.560	0.763	0.683	-0.294	0.333
4		18.000	5.000	77.000	43.000	54.000	3.000	0.180	0.430	0.783	0.443	-0.631	-0.099
S	•	16.500	5.000	78.500	35.100	62.200	2.700	0.165	0.351	0.767	0.361	-0.677	-0.248
9		21.800	5.000	73.200	50.000	46.000	4.000	0.218	0.500	0.813	0.521	-0.526	0.036
7	01+06	7.500	0.500	92.000	60.000	32.100	7.900	0.075	0.600	0.938	0.651	-1.089	0.272
∞ .	, ,	9.500	0.500	90.00	68.000	28.100	3.900	0.095	0.680	0.950	0.708	-0.977	0.384
6		12.000	0.100	87.900	82.000	17.500	0.500	0.120	0.820	0.992	0.824	-0.865	0.671
10		5.000	0.100	94.900	49.000	44.200	6.800	0.050	0.490	0.980	0.526	-1.278	0.045
		3.500	0.100	96.400	37.000	58.100	4.800	0.035	0.370	0.972	0.389	-1.440	-0.196
12	80+20	1.000	0.010	066'86	29.000	70.000	1.000	0.010	0.290	.066*0	0.293	-1.996	-0.383
13		2.000	0.010	066.76	65.000	33.500	1.500	0.020	0.650	0.995	0.660	-1.690	0.288
14		2.200	0.010	061.790	69.500	29.000	1.500	0.022	0.695	0.995	0.706	-1.648	0.380
15		3.500	0.010	96.190	84.000	14.500	1.500	0.035	0.840	766.0	0.853	-1.439	0.763
- 16	•	1.500	0.010	98.490	47.000	51.500	1.500	0.015	0.470	0.993	0.477	-1.817	-0.040

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	Data proc	essing Ta	able of p:	arameters	for Dist	ribution	, Selectiv	rity diag	rams an	d Hand's	s plots	ء • • •	· · ·
•	for the	e Quateri	nary Sys	tem : Tolı	tene (T)	Hexane	(H)-Dm	so(D') +	Water(V) at 30	ç	· · ·	
		•					н	•	•			•	••
Sr.No	%Dmso+Water	X _{TE}	X _{H'E}	X _{D'E+WE}	X _{TR}	X _{H'R}	X _{D'R+WR}	D1	\mathbf{D}_2	S.	S2	H ₁	\mathbf{H}_2
. · •									4 8 8		. · · .		
,	100+0	16.500	4.000	79.500	28.000	70.000	2.000	0.165	0.280	0.805	0.286	-0.683	-0.39
7		10.500	5.000	84.500	12.000	84.500	3.500	0.105	0.120	0.677	0.124	-0.906	-0.84
ŝ		23.400	4.000	74.600	47.000	49.000	4.000	0.234	0.470	0.854	0.490	-0.504	-0.0
4		12.000	5.000	83.000	16.250	82.250	1.500	0.120	0.163	0.706	0.165	-0.840	-0.70
S		14.500	4.000	81.500	24.000	74.000	2.000	0.145	0.240	0.784	0.245	-0.750	-0.48
9	-	18:500	4.000	77.500	32.000	64.000	4.000	0.185	0.320	0.822	0.333	-0.622	-0.30
6	90+10	4.300	1.500	94.200	23.000	74.000	3.000	0.043	0.230	0.741	0.237	-1.341	-0.50
~		5.000	1.500	93.500	43.000	55.000	2.000	0.050	0.430	0.769	0.439	-1.272	-0.10
6		6.750	1.300	91.950	63.000	34.000	3.000	0.068	0.630	0.839	0.649	-1.134	0.26
10	•	15.000	2.000	83.000	89.500	15.000	1.500	0.150	0.895	0.882	0.856	-0.743	0.77
		13.000	2.000	85.000	73.000	24.500	2.500	0.130	0.730	0.867	0.749	-0.815	0.47
12	80+20	0.800	0.320	98.880	23.000	75.000	2.000	0.008	0.230	0.714	0.235	-2.092	-0.51
13	•	1.500	0.300	98.200	44.000	54.000	2.000	0.015	0.440	0.833	0.449	-1.816	-0.0
14		2.000	0.200	97.800	66.000	32.000	2.000	0.020	0.660	0.909	0.673	-1.689	0.31
15		2.500	0.100	97.400	84.000	15.000	1.000	0.025	0.840	0.962	0.848	-1.591	0.74
16		1.100	0.320	98.580	34,000	65.500	0.500	0.011	0.340	0.775	0.342	-1.952	-0.28

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-0.465 -0.262 -0.047 0.069 -0.151 -0.151 0.238 0.238 0.238 0.238 0.238 0.238 0.238 0.238 -0.054 0.281 -0.265 H, -0.515 -0.319 -0.240 -0.473 -0.371 -0.371 -0.364 -0.564 -0.564 -0.855 -0.663 -1.572 -1.179 -1.341 1.424 H, 0.473 0.540 0.314 0.414 0.442 0.255 0.354 0.634 0.863 0.543 0.793 0.241 0.249 0.656 0.352 Data processing Table of parameters for Distribution , Selectivity diagrams and Hand's plots ซี for the Quaternary System : Toluene (T) Hexane (H)-Dmso(D') + Water(W) at 40°C 0.800 0.966 0.980 0.857 0.926 0.872 0.775 0.756 0.776 0.927 0.956 0.786 0.964 **5**. 0.250 0.455 0.510 0.308 0.405 0.405 0.420 0.580 0.820 0.510 0.710 0.235 0.450 0.630 0.343 ñ 0.097 0.140 0.214 0.120 0.176 0.220 0.255 0.300 0.330 0.233 0.275 0.026 0.044 0.062 คี X_{D'R+WR} 10.500 5.000 8.500 5.000 6.000 2.000 1.000 3.800 5.500 2.000 2.210 2.500 4.000 4,000 2.750 X_{H'R} 13.000 43.000 64.000 50.700 43.500 67.200 53.000 33.500 18.500 74.000 51.000 33.000 73.000 57.280 63.000 Table. -21 45.500 51.000 23.500 45.000 63.000 30.800 40.500 42.000 82.000 51.000 71.000 25.000 35.000 58.000 34.250 XIR XD'E+WE 89.500 85.500 78.200 72.000 70.240 62.500 57.390 69.200 64.550 86.000 81.000 97.020 95.400 93.670 96.000 X_{H'E} 8.000 7.500 9.600 7.500 7.940 0.770 0.500 0.440 2.000 1.400 0.380 6.000 0.230 0.380 22.000 25.500 30.000 33.000 23.300 27.500 9.730 14.000 21.360 12.000 17.600 2.600 4.350 X_{TE} 6.200 3.620 %Dmso+Water 100+0 90+10 80+20 Sr.No 5

 Table. -22

 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots

 for the Quaternary System : Xylene(X)- Hexane (H)-Dmso(D') + Water(W) at 20°C

	Sr.No	%Dmso+Water	X _{XE}	X _{H'E}	X _{D'E+WE}	Xxr	Xur	Xn'ever	Ģ	á	Ø	Ś	н	Щ
· 12.		· ;	÷	1 4 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7		(), , , , , , , , , , , , , , , , , , ,			•• • •	4 4	2	7	ī	7
		100+0	0.700	1.900	97.400	42.000	56.000	2.000	0.007	0.420	0.269	0.429	-2.143	-0.125
	6		2.000	1.930	96.070	54.500	43.200	2.300	0.020	0.545	0.509	0.558	-1.682	0.101
-	m ,		4.000	2.000	94.000	71.000	25.900	3.100	0.040	0.710	0.667	0.733	-1.371	0.438
	4		2.400	1.600	96.000	59,000	38.110	2.880	0.024	0.590	0.600	0.608	-1.602	0.190
	ŝ		2.950	2.800	95.160	67.500	28.790	3.700	0.030	0.675	0.513	0.701	-1.509	0.370
	9	•	2.600	1.800	95.600	64.500	32.800	2.700	0.026	0.645	0.591	0.663	-1.565	0.294
	2	90+10	0.180	0.960	98.860	43.000	52.800	4.200	0.002	0.430	0.158	0.449	-2.740	-0.089
	∞.		0.200	0.950	98.850	50.500	36.350	5.150	0.002	0.505	0.174	0.581	-2.694	0.143
	6		0.250	0.940	98.810	60.500	34.300	5.200	0.003	0.605	0.210	0.638	-2.597	0.246
	10		0.300	0.920	98.780	71.000	23.950	5.050	0.003	0.710	0.246	0.748	-2.518	0.472
	11		0.400	0.900	98.700	81.000	14.770	4.230	0.004	0.810	0.308	0.846	-2.392	0.739
	12	80+20	0.100	0.590	99.325	49.000	46.360	2.640	0.001	0.490	0.145	0.514	-2.997	0.024
	13		0.130	0.600	<u> 000.66</u>	64.500	32.800	2.700	0.001	0.645	0.178	0.663	-2.882	0.294
	14		0.200	0.750	99.050	79.000	18.850	2.350	0.002	0.790	0.211	0.807	-2.695	0.622
23	15	• •	0.300	0.750	98.950	90.000	8.200	1.800	0.003	0.900	0.286	0.916	-2.518	1.040
31	16	•	0.100	0.600	99.300	34.000	63.500	2.500	0.001	0.340	0.143	0.349	-2.997	-0.271

-0.385 -0.193 0.222 0.017 0.014 0.030 0.425 0.641 -0.287 -0.301 0.165 -0.053 0.349 0.313-0.300 0.531 H, -2.819 -2.450 -0.979 -2.089 -1.813 -1.705 2.179 -2.597 -2.694 1.203 -0.862 -1.017 -0.941 -1.131 -1.991 Щ 0.510 0.508 0.517 0.814 0.673 0.334 0.727 0.333 0.594 0.772 0.470 .292 0.625 0.341 0.391 169.0 ທີ for the Quaternary System : Xylene(X)- Hexane (H)-Dmso(D') + Water(W) at 30°C 0.705 0.766 0.787 0.808 0.708 0.781 0.500 0.625 0.714 0.371 0.138 0.207 0.278 0.174 0.244 0.421 5 0.310 0.645 0.325 0.490 0.470 0.315 0.542 0.740 0.285 0.380 0.460 0.665 0.767 0.444 0.601 .656 \mathbf{D}_2 0.019 0.058 0.085 0.100 0.118 0.067 0.093 0.008 0.010 0.015 0.007 0.002 0.003 0.004 0.002 0.003 ā X_{D'R+WR} 5.600 2.420 2.700 3.940 4.150 2.630 3.900 9.500 9.100 8.500 5.750 9.000 5.500 5.700 4.200 5.000 X_{H'R} 44.500 43.900 25.000 60.000 21.800 50.050 31.350 47.100 17.550 63.000 37.100 29.400 59.080 59.300 36.010 64.870 46.000 47.000 76.700 31.000 31.500 74.000 44.350 X_{XR} 50.050 54.500 2.500 000[°]6t 56.500 54.200 65:600 38.000 28.500 X_{D'E+WE} 98.250 97.310 88.150 98.100 98.000 97.600 98.910 98,790 98.740 98.850 91.850 98.770 88.400 87.300 85.450 90.540 0.910 2.700 0.900 1.100 0.940 0.960 X_{H'E} 2.410 2.600 2.800 2.760 1.100 1.000 0.950 0.930 10,000 11.750 5.750 8.500 6.700 9.250. 0.800 1.000 1.920 0.650 0.150 0.250 0.350 0.200 0.300 X_{XE} %Dmso+Water 90+10 80+20 0+00 Sr.No \mathbf{C} 4

Table. -23

Data processing Table of parameters for Distribution, Selectivity diagrams and Hand's plots

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-1.114 -0.839 -1.109 0.600 -0.005 -0.120 -1.256 -1.004 -0.623 -0.903 -0.649 -0.996 0.501 0.351 -0.234 H, 0.917 -0.835 -0.772 -0.694 -0.617 -0.640 -1.757 -1.587 -1.378 -1.663 -1.471 -1.837 -1.732 -1.626 -1.784 1.677 H, 0.240 0.308 0.368 0.053 0.090 0.127 0.072 0.201 0.497 0.431 0.192 0.071 0.111 0.183 0.147 0.092 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots 5 for the Quaternary System : Xylene(X)- Hexane (H)-Dmso(D') + Water(W) at 40°C 0.937 0.646 0.412 0.856 0.816 0.842 0.899 0.574 0.714 0.879 0.823 0.643 0.862 0.821 0.615 0.804 S 0.194 0.235 0.295 0.410 0.180 0.068 0.133 0.065 0.100 0.165 0.083 0.350 0.475 0.050 0.086 0.133 ñ 0.125 0.140 0.160 0.192 0.183 0.017 0.025 0.040 0.021 0.033 0.014 0.018 0.023 0.016 0.106 0.021 Ā X_{D'R+WR} 5.000 10.000 10.000 0.000 0.000 4.950 4.700 6.400 4.800 0.000 3,310 5.000 4.500 4.910 3.000 4.350 X_{H'R} 90.050 86.700 75.600 88.400 91.700 83.500 81.750 74.500 60.000 48.000 54.090 80.000 73.500 76.750 Table. -24 77.290 66.150 47.500 41.000 8.000 13.300 X_{XR} 23.500 29.500 35.000 5.000 8.600 6.800 6.500 0.000 6.500 8.250 3.250 19.40<u>0</u> X_{D'E+WE} 87.600 85.500 82.840 79.000 79.500 79.690 97.040 96.500 95.450 96.750 96.050 96.100 97.200 97.200 97.400 97.450 X_{H'E} 1.300 2.000 3.160 3.000 2.050 1.260 0.550 1.150 0.700 2.000 1.000 0.500 1.790 1.000 0.500 10.600 12.500 14.000 16.000 19.200 18.250 X_{XE} 1:700 2.500 4.000 1.400 1.800 2.300 2.100 3.250 1.600 2.050 %Dmso+Water 90+10 100+080+20 Sr.No

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-1.112 -0.596 -0.360 0.512 -0.086 0.352 0.010 -0.716 0.217 -0.195 0.019 0.050 -0.421 0.374 H, -1.379 -1.260 -1.157 -0.848 -0.650 -0.559 -0.479 -2.296 -1.184 -0.659 -0.475 -0.387 -1.647 -1.206 -1.091 -0.901 H, 0.308 0.389 0.072 0.304 0.529 0.235 0.494 0.514 0.275 0.624 0.703 0.511 0.451 0.377 0.161 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots Ś for the Quaternary System : Benzene(B)- Hept (H')-Dmso(D') + Water(W) at 20°C 0.810 0.779 0.809 0.853 0.400 0.975 0.988 0.963 0.977 0.987 0.975 0.904 0.952 0.991 0.880 0.941 5 0.230 0.300 0.200 0.445 0.490 0.373 0.486 0.667 0.300 0.157 0.266 0.427 0.591 0.071 0.373 0.521 D, 0.179 0.040 0.120 0.206 0.250 0.065 0.075 0.005 0.179 0.290 0.052 0.059 0.061 0.111 0.022 Ā X_{D'R+WR} 2.300 2.550 4.650 .100 .300 3.600 2.620 3.350 4.200 4.910 5.250 5.100 1.000 .200 .500 300 91.900 78.900 68:800 54.200 46.400 74.700 67.450 43.700 46.350 70.050 58.500 46.490 35.650 28.200 61.450 X_{H'R} 81.680 Table. -25 23.000 30.000 26.600 37.300 30.000 44.500 f2.700 19.000 5.700 48.600 9.100 66.700 20.000 52.100 37.250 7.100 X_{BR} X_{D'E+WE} 84.600 79.900 93.350 98.750 95.750 94.600 71.980 93.250 88.340 81.650 74.700 70.750 97.500 92.400 74.540 94.000 X_{H'E} 3.400 4.200 4.110 0.750 0.300 0.300 0.250 0.200 0.150 0.100 0.650 0.560 0.450 0.250 0.150 4.860 12.000 20.600 23.900 17.900 11.100 25.000 29.000 5.200 7.500 0.500 6.100 2.200 4.000 6.500 5.850 X_{BE} %Dmso+Water 1 1 1 90+10 0+001 80+20 Sr.No 4 16 3 2

0.191 0.652 0.299 0.219 0.366 0.366 0.366 0.366 0.366 0.366 -0.054 0.392 0.321 0.209 0.091 0.110 H2 -0.778 -0.616 -0.308 -1.207 -0.904 -0.599 -0.522 -1.688 -1.378 -0.906 -0.672 -0.381 -1.121 0.728 H, 0.448 0.608 0.182 0.335 0.440 0.623 0.699 0.323 0.563 0.067 0.181 0.287 0.469 0.289 0.651 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots ິ for the Quaternary System : Benzene(B)- Hept (H')-Dmso(D') + Water(W) at 30°C 0.875 0.932 0.963 0.972 0.838 0.981 0.800 0.889 0.722 0.774 0.781 0.792 0.811 0.933 0.957 ā 0.315 0.360 0.430 0.500 0.520 0.175 0.322 0.425 0.605 0.681 0.065 0.177 0.280 0.459 0.280 0.637 \mathbf{D}_2 0.310 0.058 0.110 0.160 0.200 0.230 0.020 0.040 0.110 0.167 0.185 0.210 0.275 0.070 0.160 0.130 ค์ X_{D'R+WR} 4.000 2.600 4.000 11.180 4.050 3.740 3.400 2.950 2.600 2.500 2.400 2.300 2.200 2.100 3.000 36.550 29.300 91.000 79.900 69.700 X_{H'R} 69.000 65.890 58.250 53.000 38.820 33:500 78.450 64.060 54.100 51.950 34.200 52.000 17.500 32.200 42.500 60.500 43.000 50.000 68.100 17.700 28.000 31.500 45.850 63.700 28.000 6.500 X_{BR} XD'E+WE 88.200 79.420 97.500 95.500 92.500 85.500 66.100 63.000 93.370 83.380 76.550 88.500 78.400 73.500 78.000 X_{H'E} 6.000 0.830 0.800 0.620 5.200 5.390 0.570 0.450 0.500 0.500 0.500 5.000 4.890 5.500 0.500 0.500 20.000 23.000 11.000 16.000 13.000 16.700 18.500 21,000 27.500 31.000 5.800 2.000 4.000 7.000 1.000 6.000 X_{BE} %Dmso+Water 100+0 90+10 80+20 Sr.No

Table. -26

-0.549 -0.5729 -0.057 -0.057 -0.050 -0.420 -0.420 -0.420 -0.420 -0.420 -0.143 -0.143 -0.050 -0.339 -0.050 -0.614 -0.614 -0.051 -0.051 -0.057 -0.0500 -0.0500 -0.0500 -0.0500 -0.0500 -0.0500 -0.0500 -H, -0.550 -1.229 -666.0--0.639 -0.352 -0.629 -0.301 -0.682 -2.036 -1.272 -1.054 -0.746 0.567 0.751 0.651 H, 0.319 0.078 0.418 0.686 0.552 0.130 0.196 0.401 0.467 0.619 0.535 0.275 0.171 0.082 0.586 0.493 0.220 Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots Ś for the Quaternary System : Benzene(B)- Hept (H')-Dmso(D') + Water(W) at 40°C 0.750 0.722 0.675 0.878 0.686 0.690 0.797 0.949 0.965 0.429 0.667 0.769 0.842 0.909 0.933 .923 5 0.205 0.430 0.520 0.480 0.255 0.075 0.165 0.405 0.667 0.536 0.126 0.080 0.190 0.390 0.570 .480 ń 0.175 0.200 0.300 0.260 0.159 0.055 0.090 0.185 0.305 0.245 0.009 0.050 0.080 0.150 0.140 0.210 0.180 ด์ X_{D'R+WR} 6.000 16.000 9.200 3.150 2.750 2.850 8.000 7.390 3.600 3.500 3.200 7.000 3.000 2.900 2.800 2.700 2.700 X_{H'R} 80.000 30.550 43.550 84.200 41.800 67.100 56.350 89.000 78.100 58.200 40.300 72.500 49.000 32.000 88.880 l9.300 64.000 Table. -27 16.500 40.500 43.000 52.000 48.000 25.500 66.700 53.600 12.600 .000[°] 30.000 7.520 8.000 39.000 57.000 F8.000 20.500 X_{BR} X_{D'E+WE} 80.500 68.600 79.000 74.500 71.000 60.000 64,000 76.440 93.100 89.750 74.600 97.850 93.500 90.500 83.500 77.500 80.500 X_{H'E} 8.000 9.000 0.000 0.000 7.650 1.400 1.250 1.000 0.900 0.900 1.200 1.500 .500 1.500 1.500 7.000 26.000 15.900 5.500 9.000 18.500 30.500 24.500 15.000 14.000 17.500 20.000 30.000 0.900 5.000 21.000 8.000 8.000 X_{BE} %Dmso+Water 100+0 01+06 80+20 Sr.No í
0.626 0.379 0.135 0.108 0.111 0.111 0.291 0.163 0.317 0.595 0.124 0.509 0.127 0.127 0.640 H, -1.140 -1.362 -1.952 -1.539 -1.991 -1.535 -1.063 -0.709 -0.311 -1.409 -1.278 -1.278 -0.688 -0.288 -1.234 1.704 H, Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots 0.191 0.295 0.423 0.438 0.564 0.339 0.497 0.593 0.571 0.571 0.571 0.573 0.573 0.573 0.573 0.573 0.643 ິ for the Quaternary System : Benzene(B)- Oct (O)-Dmso(D') + Water(W) at 20°C 0.856 0.887 0.721 0.984 0.983 0.993 0.998 0.988 0.933 0.710 0.889 0.830 0.500 0.700 0.842 ō. 0.190 0.293 0.425 0.435 0.435 0.435 0.495 0.495 0.495 0.495 0.570 0.570 0.570 0.570 0.570 0.570 0.570 0.810 ñ 0.028 0.160 0.315 0.037 0:050 0.085 0.170 0.340 0.068 0.068 0.055 0.010 0.080 0.011 X_{D'R+WR} 0.740 2.200 0.500 0.450 6.000 1.070 0.500 0.500 0.450 0.450 0.450 0.650 0.680 0.750 0.450 30.350 70.150 57.320 55.750 41.000 65.430 50.000 42.550 28.550 18.550 35.550 40.500 32.260 19.800 40.750 23.550 Xor 49.500 59.000 67.000 78.000 54.250 57.000 71.000 81.000 43.500 53.000 33.500 76.000 19.000 29.300 42.000 54.000 X_{BR} X_{D'E+WE} 98.000 96.000 92.500 81.800 64.500 94.870 94.930 91.360 82.880 65.930 93.170 98.450 96.850 95.550 94.250 98.650 1.000 1.200 1.500 2.700 4.000 0.450 0.350 1.430 0.010 0.140 0.120 0.070 0.080 0.300 0.250 XOE .400 1.000 2.800 8.000 8.000 31.500 31.500 31.500 5.000 5.000 8.500 34.000 34.000 34.000 34.150 11.100 2.800 2.800 5.500 X_{BE} %Dmso+Water 90+10 100+0 80+20 Sr.No

Table. -28

Table. -28

-0.339 -0.214 -0.228 -0.328 0.061 -0.416 0.041 0.309 0.433 0.172 0.172 0.172 0.172 0.172 0.172 0.255 0.400 H, -0.957 0.964 -0.507 -1.988 -1.689 -0.886 -0.367 -0.176 -1.880 -1.509 -1.327 -1.032 -0.327 1.658 H Data processing Table of parameters for Distribution ,Selectivity diagrams and Hand's plots 0.314 0.379 0.320 0.458 0.535 0.238 0.277 0.523 0.598 0.433 0.552 0.643 0.671 0.731 0.492 ົ for the Quaternary System : Benzene(B)- Oct (O)-Dmso(D') + Water(W) at 30°C 0.835 0.880 0.847 0.858 0.357 0.909 766.0 9999 0.995 0.991 0.963 0.987 0.993 0.998 779.0 5 0.310 0.315 0.450 0.525 0.235 0.275 0.520 0.665 0.720 0.593 0.430 0.550 0.640 0.710 0.490 D2 0.105 0.160 0.102 0.230 0.306 0.010 0.020 0.115 0.300 0.400 0.208 0.013 0.030 0.045 0.085 ď X_{D'R+WR} 0.850 1.400 1.600 1.420 1.800 1.100 0.850 0.650 1.450 0.900 0.600 0.400 0.400 0.750 0.500 Xor 47.350 32.650 67.600 61.100 67.080 53.200 45.600 26.550 39.850 35.600 28.250 75.400 71.650 56.400 44.600 50.500 31.000 37.300 31.500 45.000 52.500 27.500 23.500 52.000 66.500 72.000 59.250 43.000 55.000 64.000 71.000 49.000 X_{BR} X_{D'E+WE} 95.100 81.550 93.400 73.850 65.000 97.200 97.800 88.390 69.910 59.950 78.250 98.650 96.960 95.470 91.480 97.800 2.000 X_{OE} 1.900 2.650 4.400 1.800 0.200 0.110 0.090 0.050 0.040 0.100 0.050 0.030 0.020 er viene 0.050 10.500 16.000 10.150 23.000 30.600 1.000 2.000 11.500 30.000 40.000 20.750 1.300 3.000 4.500 XBE 8.500 %Dmso+Water 90+10 0+00] 80+20 Sr.No <u>m</u> 14 2

Table. -29

Table. -30

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Data processing Table of parameters for Distribution , Selectivity diagrams and Hand's plots 1.5. 1.7. 1.7. 1.7.

for the Quaternary System : Benzene(B)- Oct (O)-Dmso(D') + Water(W) at 40°C

Sr.No	%Dmso+Water	XBE	XOE	X _{D'E+WE}	X _{BR}	X _{OR}	X _{D'R+WR}	D1	\mathbf{D}_2	S,	S_2	Нı	H,
		· ·	• •						•	•		•	
	100+0	5.350	0.790	93.850	24.700	74.620	0.670	0.054	0.247	0.871	0.249	-1.244	-0.48
7		18.200	1.970	79.820	44.000	55.210	0.790	0.182	0.440	0.902	0.444	-0.642	-000
ŝ	•	36,500	6.370	57.120	52.200	32.260	15.530	0.365	0.522	0.851	0.618	-0.194	0.200
4		3.000	2.550	94.450	19.500	79.150	1.350	0.030	0.195	0.541	0.198	-1.498	-0.60
ŝ		17.500	2.950	79.550	31.500	66.650	1.850	0.175	0.315	0.856	0.321	-0.658	-0.32
9		21.300	3.150	75.550	35.500	62.650	1.850	0.213	0.355	0.871	0.362	-0.550	-0.24
7		36.500	6.370	57.120	42.000	56.150	1.950	0.365	0.420	0.851	0.428	-0.194	-0.12
×	00+10	1.700	0.240	98.060	18.000	79.840	2.160	0.017	0.180	0.876	0.184	-1.761	-0.64
6		19.400	0.200	80.400	56.500	42.250	1.250	0.194	0.565	0660	0.572	-0.617	0.12
10		7.000	0.220	92.780	36.500	61.800	1.700	0.070	0.365	0.970	0.371	-1.122	-0.22
11		4.350	0.220	95.430	27.200	70.750	2.000	0.044	0.272	0.952	0.278	-1.341	-0.41
12		13.200	0.200	86.600	46.500	52.000	1.500	0.132	0.465	0.985	0.472	-0.817	-0.04
13	80+20	2.090	0.110	97.800	42.000	57.200	0.800	0.021	0.420	0.950	0.423	-1.670	-0.13
14		3.800	0.070	96.100	54.000	45.350	0.650	0.038	0.540	0.982	0.544	-1.403	0.07
15		10.000	0.080	89.200	71.000	28.510	0.490	0.100	0.710	0.992	0.713	-0.950	0.39
16		7.040	0.050	92.900	83.500	16.100	0.400	0.070	0.835	0 993	0 838	-1 120	0.71

(ii) Effect of anti solvent concentration.

(iii)Effect of molecular weight of aromatics.

(iv)Effect of molecular weight of aliphatics.

Hence present discussion however happens to be qualitative in nature.

5.2.1 Discussion for Tie line data diagrams for mixed solvent Dmf+W:-

Diagrams depicted in Figurs- T-1 to T-15 having been divided in five groups as under:-

(i) Diagrams for Systems-B-H-Dmf+W at different temperatures and antisolvent concentrations.

(ii) Diagrams for Systems-T-H-Dmf+W at different temperatures and antisolvent concentrations.

(iii)Diagrams for Systems-X-H-Dmf+W at different temperatures and antisolvent concentrations.

(iv)Diagrams for Systems-B-Hep-Dmf+W at different temperatures and antisolvent concentrations.

(v) Diagrams for Systems-B-Oct-Dmf+W at different temperatures and antisolvent concentrations.

Following are the important conclusions from these diagrams:

(1) Whether solute is Benzene or Toluene or Xylene and non-solute is Hexane or Heptane or Octane for anti solvent concentration of the order of 0%W, all the Binodal curves obtained are of closed type. However when anti solvent concentration increases nature of Binodal curve changes from closed type to open type.

(2) As temperature increases, miscibility region increases and as a result area under the Binodal curve decreases. This is observed for all the systems under considerations consisting of 45 systems for mixed solvent- Dmf+Water.



<u>Fig-T-1</u> <u>Tie line data_for the Quaternary system:</u> <u>B-H-Dmf-W at 20 ° C with anti solvent concentration as a parameter</u>



















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90%Dmf+10%W



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<u>Fig-T-13 Tie line data for the Quaternary system:</u> B-Oct-Dmf-W at 20 ° C with anti solvent concentration as a parameter











(3) When systems under consideration are of closed type, the value of plait point composition can be estimated by graphical technique. Effect of various parameters like temperature, molecular weight of aromatics and molecular weight of aliphatics on the values of plait point composition has been discussed separately.

(4) Tie line data obtained in this investigation can be correlated by different Tie line correlations available in the literature out of which Hand's correlation appear to be more appropriate and sound for correlating the data. This aspect has also been discussed separately later on under heading 5.5.0: Correlating quaternary liquid-liquid phase equilibrium data.

(5) Nature of slopes of tie line data straight lines can be analyzed which offers explanation for effect of different parameters on the values of plait points which has been discussed under Subsection- 5.2.3 for all the systems which are of closed type.

(6) The lines can be utilized conveniently to estimate compositions of extract phase and raffinate phase for a fixed value of feed composition. It can also utilize to calculate limiting values of % aromatics extracted.

Based on Tie line data, the values of extraction capacity and selectivity of mixed solvent Dmf+W can also be estimated under different sets of conditions inclusive of values of distribution coefficients. This aspect has been also discussed in detail under sub section-5.4.0 and 5.4.1.

5.2.2 Discussion for Tie line data diagrams for mixed solvent Dmso+W:-

Diagrams depicted in Figurs- T-16 to T-30 having been divided in five groups as under:-

(i)Diagrams for Systems-B-H-Dmso+W at different temperatures and antisolvent concentrations.

(ii)Diagrams for Systems-T-H-Dmso+W at different temperatures and antisolvent concentrations.



<u>Fig-T-16 Tie line data for the Quaternary system:</u> <u>B-H-Dmso-W at 20 ° C with anti solvent concentration as parameter</u>



Fig-T-17 Tie line data for the Quaternary system: B-H-Dmso-W at 30 ° C with anti solvent concentration as a parameter





<u>Fig-T-18 Tie line data for the Quaternary system:</u> B-H-Dmso-W at 40 ° C with anti solvent concentration as a parameter

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<u>Fig-T-19 Tie line data for the Quaternary system:</u> <u>T-H-Dmso-W at 20 ° C with anti solvent concentration as parameter</u>



<u>Fig-T-20 Tie line data for the Quaternary system:</u> <u>T-H-Dmso-W at 30 ° C with anti solvent concentration as parameter</u>



Fig-T-21 Tie line data for the Quaternary system: T-H-Dmso-W at 40 ° C with anti solvent concentration as parameter



<u>Fig-T-22 Tie line data for the Quaternary system:</u> X-H-Dmso-W at 20 ° C with anti solvent concentration as parameter

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<u>Fig-T-24 Tie line data for the Quaternary system:</u> X-H-Dmso-W at 40 ° C with anti solvent concentration as parameter



Fig-T-25 Tie line data for the Quaternary system: B-Hep-Dmso-W at 20 ° C with anti solvent concentration as parameter







Fig-T-26 Tie line data for the Quaternary system: B-Hep-Dmso-W at 30 ° C with anti solvent concentration as parameter









80%Dmso+20%W



<u>Fig-T-29 Tie line data for the Quaternary system:</u> B-Oct-Dmso-W at 30 ° C with anti solvent concentration as parameter

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<u>Fig-T-30 Tie line data for the Quaternary system:</u> <u>B-Oct-Dmso-W at 40 ° C with anti solvent concentration as parameter</u>

(iii)Diagrams for Systems-X-H-Dmso+W at different temperatures and antisolvent concentrations.

(iv)Diagrams for Systems-B-Hep-Dmso+W at different temperatures and antisolvent concentrations.

(v)Diagrams for Systems-B-Oct-Dmso+W at different temperatures and antisolvent concentrations.

Following are the important conclusions from these diagrams:

(1)Whether solute is Benzene or Toluene or Xylene and non-solute is Hexane or Heptane or Octane for anti solvent concentration of the order of 0%W all the Binodal curves obtained are of closed type. However when anti solvent concentration increases nature of Binodal curve changes from closed type to open type.

(2)As temperature increases, miscibility region increases and as a result area under the Binodal curve decreases. This is observed for all the systems under considerations consisting of 45 systems for mixed solvent- Dmso+Water.

(3)When systems under consideration are of closed type, the value of plait point composition can be estimated by graphical technique. Effect of various parameters like temperature, molecular weight of aromatics and molecular weight of aliphatics on the values of plait point composition has been discussed separately.

(4)Tie line data obtained in this investigation can be correlated by different Tie line correlations available in the literature out of which Hand's correlation appear to be more appropriate and sound for correlating the data. This aspect has also been discussed separately later on under heading 5.5.0: Correlating quaternary liquid-liquid phase equilibrium data.

(5)Nature of slopes of different tie line data straight lines can be analyzed which offers explanation for effect of different parameters on plait points which has been discussed Subsection 5.2.4 for all the systems which are of closed type.

(6)Tie lines can be utilized conveniently to estimate compositions of extract phase and raffinate phase for a fixed value of feed composition. Tie line data can also utilize to calculate limiting values of % aromatics extracted.
Based on Tie line data, the values of extraction capacity and selectivity of mixed solvent Dmso+W can also be estimated under different sets of conditions inclusive of values of distribution coefficients. This aspect has been also discussed in detail under sub section- 5.5.0 and 5.5.1

5.2.3 Data for plait points for systems consisting of

B/T/X-H/H'/O-Dmf-W:-

Quaternary liquid- liquid phase equilibrium data can be converted into equivalent ternary data by introducing concept of mixed solvent.

Mixed solvent in the present case is Dimethyl formamide (Dmf) along with anti solvent water. Thus anti solvent concentration of water has been varied from 0% W, 10%W and 20%W. Accordingly mixed solvent consisting of three anti solvent concentrations have been utilized as under.

- (i) Mixed solvent 100% Dmf + 0% W
- (ii) Mixed solvent 90% Dmf + 10% W
- (iii) Mixed solvent 80%Dmf + 20%W

These three mixed solvents have been investigated for three different fixed temperatures namely 20 0 C, 30 0 C and 40 0 C with solute being changed from Benzene to Toluene and subsequently to Xylene. Further non solute also has been changed from Hexane to Heptane and subsequently to Octane.

Accordingly tie line data which have been obtained under different sets of conditions and rectangular coordinate diagrams for fixed anti solvent concentrations have been constructed and shown in Figures T-1 to T-15.

Based on these various diagrams it is observed that only for anti solvent concentrations 0% water different system under considerations are of close curve type.

For all such system plait points have been determined by graphical technique and corresponding values of plait points composition have been reported in Tables-(1.2), (1.3) and (1.4).

(i) Effect of temperature on plait point:-

Data reported in Table 1.2 indicates that as temperature is increased from 20 °C to 30 °C and up to 40 °C, composition of solute Benzene in plait point decreases. Five illustrations depicting temperature effect are as under:-

(1)For system B- H-100%Dmf- 0%W as temperature is increased from 20 0 C to 30 0 C and up to 40 0 C, plait point composition of solute component- Benzene decreases from 23.5%, 19.5% to 17.5% respectively.

(2)For examples for system T-H-100%Dmf-0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C, plait point composition of solute component-Toluene decreases from 25%, 21% to 18.5% respectively.

(3)For system X- H-100%Dmf- 0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C plait point composition of solute component- Xylene decreases from 28.5%, 26% to 24% respectively.

(4)For system B- Hep-100%Dmf- 0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C, plait point composition of solute component- Benzene decreases from 16.5%, 15.5% to 13.5% respectively.

(5)For system D- Oct-100%Dmf- 0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C plait point composition of solute component- Benzene decreases from 34%, 32% to 31% respectively.

As temperatures increases area under the curve Binodal curve (two phase region) decreases. As a result composition of Benzene (% XB) in plait point value decreases.

As temperatures increases, solubility of Benzene in extract phase increases. Thus miscibility region increases. As a result area under the of Binodal curve decreases.

(ii)Effect of molecular weight of aromatics on plait point:-

Data reported in Table 1.3 indicates that at constant temperature as solute Benzene is changed to Toluene and further changed to Xylene, composition of Benzene

Table-1.2

Values of plait points for different systems consisting of B/T/X-H/H'/O-100%Dmf-0%W under different sets of conditions.

System		Хв/%Хт/%Хх	%ХН%Хнер/%	%Xoct %X Dmf	+ W
B-H-100%Dmf-0%W	20°C	23.500	48.000	28.500	
B-H-100%Dmf-0%W	30°C	19.500	46.000	34.500	
B-H-100%Dmf-0%W	40°C	17.500	58.500	24.000	
T-H-100%Dmf-0%W	20°C	25.000	50.000	25.000	•
T-H-100%Dmf-0%W	30°C	21.000	44.000	35.000	
1-H-100%DMI-0%W	40°C	18.500	47.000	34.300	
X-H-100%Dmf-0%W	20°C	28.500	46.000	25.500	
X-H-100%Dmf-0%W	:- 30°C	26.000	45.000	29.000	
X-H-100%Dmf-0%W	40°C	24.000	54.000	22.000	
B-Hep-100%Dmf-0%V	V 20°C	16.500	43.000	40.500	
B-Hep-100%Dmf-0%V	V 30°C	15.000	45.000	40.000	
B-Hep-100%Dmf-0%V	V 40°C	13.500	54.000	32.500	
B-Oct -100%Dmf-0%V	V 20°C	34.000	30.000	36.000	• •
B-Oct -100%Dmf-0%V	V 30°C	32.200	42.500	25.300	
- B-Oct -100%Dmf-0%W	V 40°C	31.000	45.000	24.000	-
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Table-1.3

Values of plait points for different systems consisting of B/T/X-H -100%Dmf-0%W under different sets of conditions.

System	%Хв/%Хт/%Хх %Хн		%XDmf+W
B-H-100%Dmf-0%W 20°C	23.500	48.000	28.500
T-H-100%Dmf-0%W 20°C	25.000	50.000	25.000
X-H-100%Dmf-0%W 20°C	28.500	46.000	25.500
B-H-100%Dmf-0%W 30°C	19.500	46.000	34.500
T-H-100%Dmf-0%W 30°C	21.000	44.000	35.000
X-H-100%Dmf-0%W :- 30°C	26.000	45.000	29.000
B-H-100%Dmf-0%W 40°C	17.500	58.500	24.000
T-H-100%Dmf-0%W 40°C	18.500	47.000	34.500
X-H-100%Dmf-0%W 40°C	24.000	54.000	22.000

(%XB) in plait point increases. Thus for example at constant temperature of 20 0 C in a system B/T/X- H --Dmf-W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 23.5% to 25% to 28.5% respectively.

Further for example at constant temperature of 30 0 C in a system B/T/X- H – Dmf-W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 19.5% to 21% to 26% respectively.

Further for example at constant temperature of 40 $^{\circ}$ C in a system B/T/X- H – Dmf-W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 17.5% to 18.5% to 24% respectively.

It appears that in a system when solute Benzene is changed to Toluene and subsequently to Xylene the slope of tie line increases in clock wise directions. Thus when shifts from $B \rightarrow T \rightarrow X$ i.e. as molecular weight increases, slope of tie line for a particular set of tie lines for a fixed solute component- B/T/X increases in clock wise direction. As a result plait point composition of solute B/T/X (%XB/T/X) in plait point increases.

(iii)Effect of molecular weight of aliphatics on plait point:-

Effect of temperature and effect of molecular weight of aromatics on plait point which has been already discussed follows a peculiar trend i.e. with an increase in temperature the value of % XB in plait point decreases and with an increase in molecular weight of aromatics, the value of %XB in plait point increases.

As could be seen from Table-1.4, with respect to effect of increase in molecular weight of aliphatics, a peculiar trend- which is a combination of above two trends- is followed.

When one compares plait point values for systems consisting of Benzene-Hexane- Dmf with systems consisting of B-Hept- Dmf under different sets of conditions of temperatures, the composition of Benzene (%XB) in plait point value decreases.

Table-1.4

Values of plait points for different systems consisting of B-H/H'/O-100%Dmf-0%W under different sets of conditions.

System%XB %XH%XHep/%Xoct %XDmf+			t %XDmf+w	
B-H-100%Dmf-0%W 20°C	23.500	48.000	28.500	
B-Hep-100%Dmf-0%W 20°C	16.500	43.000	40.500	
B-Oct -100%Dmf-0%W 20°C	34.000	30.000	36.000	
B-H-100%Dmf-0%W 30°C	19.500	46.000	34.500	
B-Hep-100%Dmf-0%W 30°C	15.000	45.000	40.000	
B-Oct -100%Dmf-0%W 30°C	32.200	42.500	25.300	
			•	
B-H-100%Dmf-0%W 40°C	17.500	58.500	24.000	
B-Hep-100%Dmf-0%W 40°C	13.500	54.000	32.500	
B-Oct -100%Dmf-0%W 40°C	31.000	45.000	24.000	-

However when one compares plait point value for systems consisting of B-Hept-Dmf with systems consisting of B-Oct-Dmf under different sets of conditions of temperature the composition of Benzene (%XB) in plait point values increases.

Thus for example at 20 0 C when non solute Hexane is replaced by Heptane the value of %XB decreases from 23.5% to 16.5% respectively.However when non solute Heptane is replaced by Octane the value of %XB increases from 16.5% to 34% respectively.

Further for example at 30 0 C when non solute Hexane is replaced by Heptane %XB value decreases from 19.5% to 15% respectively.However when non solute Heptane is replaced by Octane, the value of %XB increases from 15% to 32.2 % respectively.

Also for example at 40 0 C when non solute Hexane is replaced by Heptane %X_B decreases from 17.5% to 13.5 % respectively.However when non solute Heptane is replaced by Octane, the value of %X_B increases from 13.5% to 31 % respectively.

This peculiar behavior can be explained as under :- In a system when non solute Hexane is replaced by Heptane, area under the Binodal curve decreases. As a result miscibility region increases and subsequently value of solute composition (XB) in plait point decreases.

However, when non-solute Heptane in a system is replaced by Octane, area under the Binodal curve increases. As a result, miscibility region relatively decreases. And subsequently the value of composition of solute Benzene in plait point increases.

Further, when non solute Heptane is replaced by non solute Octane, slope of Tie lines for particular set of Tie lines decreases in a clockwise direction. As a result the value of % XB in plait point composition increases.

5.2.4 Data for plait points for systems consisting of

B/T/X-H/H'/O-Dmso-W:

Quaternary liquid- liquid phase equilibrium data can be converted into equivalent ternary data by introducing concept of mixed solvent. Mixed solvent in the present case is Dimethyl Sulfoxide(Dmso) along with anti solvent water. Thus anti solvent concentration of water has been varied from 0% W, 10%W to 20% W. Accordingly mixed solvent consisting of three anti solvent concentrations have been utilized as under:--

(i) Mixed solvent 100%Dmso + 0%W

(ii) Mixed solvent 90%Dmso + 10%W

(iii) Mixed solvent 80%Dmso + 20%W

These three mixed solvents have been investigated for three different fixed temperatures namely 20 °C, 30 °C and 40 °C with solute being changed from Benzene to Toluene and subsequently to Xylene. Further non solute also has been changed from Hexane to Heptane and subsequently to Octane

Accordingly tie line data which have been obtained under different sets of conditions and rectangular coordinate diagrams for fixed anti solvent concentrations have been constructed and shown in Figures T-16 to T-30.

Based on these various diagrams it is observed that only for anti solvent concentrations 0% water, different system under considerations are of close curve type.

For all such system plait points have been determined by graphical technique and corresponding values of plait point compositions have been reported in Table 2.2 2.3 and 2.4

(i)Effect of temperature on plait point:-

Data reported in Table 2.2 indicates that as temperature is increased from 20 0 C to 30 0 C and up to 40 0 C, composition of solute Benzene in plait point decreases. Five illustrations depicting temperature effect are as under:-

(1)For system B- H-100%Dmso - 0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C, plait point composition of solute component- Benzene decreases from 50.5%,45.1% to 38.0% respectively.

Table- 2.2

Values of plait points for different systems consisting of B/T/X-H-Dmso-W under different sets of conditions. System :%XB/%XT/%Xx %XH%/XHep/%Xoct XDmso + W

B-H-100%Dmso-0%W20°C	50.500	16.000	33.500
B-H-100%Dmso-0%W30°C	45.148	26.164	28.688
B-H-100%Dmso-0%W40°C	38.090	12.010	49.899
	•		
T-H-100%Dmso-0%W20°C	53.257	06.751	39.992
T-H-100%Dmso-0%W30°C	47.654	20.800	31.548
T-H-100%Dmso-0%W40°C	41.412	15.305	43.283
X-H-100%Dmso-0%W20°C	, . .	-	-
X-H-100%Dmso-0%W30°C	63.693	02.167	34.320
X-H-100%Dmso-0%W40°C	45.258	06.474	48.268
B-Hep-100%Dmso-0%W20°C	44.500	11.500	44.000
B-Hep-100%Dmso-0%W30°C	42.3	12.1	45.6
B-Hep-100%Dmso-0%W40°C	35.500	24.000	40.500
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B-Oct-100%Dmso-0%W20°C	52.091	08.401	39.508
B-Oct-100%Dmso-0%W30°C	48.964	11.628	39.408
B-Oct-100%Dmso-0%W40°C	45.10	7.6	47.30

Table- 2.3

Values of plait points for different systems consisting of B/T/X-H -Dmso-W under different sets of conditions.

System

%XB/%XT/%XX %XH %XDmso+W

	.B-H-100%Dmso-0%W20°C	50.500	16.000	33.500	
	T-H-100%Dmso-0%W20°C	53.257	06.751	39.992	
	X-H-100%Dmso-0%W20°C	-		-	
		•		,	
	B-H-100%Dmso-0%W30°C	45.1482	26.164	28.688	
	T-H-100%Dmso-0%W30°C	47.654	20.800	31.548	
	X-H-100%Dmso-0%W30°C	63.693	02.167	34.320	
	B-H-100%Dmso-0%W40°C	38.090	12.010	49.899	
	T-H-100%Dmso-0%W40°C	41.412	15.305	43.283	
4	X-H-100%Dmso-0%W40°C	45.258	06.474	48.268	
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(2)For examples for system T-H-100%Dmf-0%W as temperature is increased from 20 $^{\circ}$ C to 30 $^{\circ}$ C and up to 40 $^{\circ}$ C, plait point composition of solute component-Toluene decreases from 25%, 21% to 18.5% respectively.

(3)For system X- H-100%Dmf- 0%W as temperature is increased from $20 \ {}^{0}C$ to 30 ${}^{0}C$ and up to 40 ${}^{0}C$ plait point composition of solute component- Xylene decreases from 28.5%, 26% to 24% respectively.

(4)For system B- Hep-100% Dmi^2 0%W as temperature is increased from 20 $^{\circ}C$ to 30 $^{\circ}C$ and up to 40 $^{\circ}C$, plait point composition of solute component- Benzene decreases from 16.5%, 15.5% to 13.5% respectively.

(5)For system B- Oct-100%Dmf- 0%W as temperature is increased from 20 0 C to 30 0 C and up to 40 0 C plait point composition of solute component- Benzene decreases from 34%, 32% to 31% respectively.

As temperatures increases area under the curve Binodal curve (two phase region) decreases. As a result composition of Benzene (% XB) in plait point value decreases.

As temperatures increases, solubility of Benzene in extract phase increases. Thus miscibility region increases. As a result area under the of Binodal curve decreases.

(ii)Effect of molecular weight of aromatics on plait point:-

Data reported in Table 1.3 indicates that at constant temperature as solute Benzene is changed to Toluene and further changed to Xylene, composition of Benzene (%XB) in plait point increases. Thus for example at constant temperature of 20 0 C in a system B/T/X- H –Dmf-W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 23.5% to 25% to 28.5% respectively.

Further for example at constant temperature of 30 $^{\circ}$ C in a system B/T/X- H – Dmf-W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 19.5% to 21% to 26% respectively.

Further for example at constant temperature of 40 0 C in a system B/T/X- H – Dmso -W, when Benzene is changed to Toluene and subsequently to Xylene, the composition of Benzene in plait point data increases from 38.0 to 41.4 to 45.2 respectively.

It appears that in a system when solute Benzene is changed to Toluene and subsequently to Xylene, the slope of tie line increases in clock wise direction. Thus when shifts from $B \rightarrow T \rightarrow X$ i.e. as molecular weight increases, slope of tie line for a particular set of tie lines for a fixed solute component-B/T/X increases in clock wise direction. As a result plait point composition of solute B/T/X (%XB/T/X) in plait point increases.

(iii)Effect of molecular weight of aliphatics on plait point:-

Effect of temperature and effect of molecular weight of aromatics on plait point which has been already discussed follows a peculiar trend i.e. with an increase in temperature, the value of % XB in plait point decreases and with an increase in molecular weight of aromatics, the value of %XB in plait point increases.

As could be seen from Table-2.4, with respect to effect of increase in molecular weight of aliphatics a peculiar trend which is a combination of above two trends is followed.

When one compares plait point values for systems consisting of Benzene-Hexane- Dmso with systems consisting of B-Hept - Dmso under different sets of condition of temperature, the composition of Benzene (%XB) in plait point value decreases.

However when one compares plaits points value for systems consisting of B-Hept-Dmso with system consisting of B-Oct-Dmso under different sets of conditions of temperatures the composition of Benzene (%XB) in plait point values increases.

Thus for example at 20 $^{\circ}$ C when non solute Hexane is replaced by Heptane , the value of %XB decreases from 23.5% to 16.5% respectively. However when non solute Heptane is replaced by Octane the value of %XB value increases from 16.5% to 34% respectively.

Table- 2.4

Values of plait points for different systems consisting of B -H/H'/O-Dmso-W under different sets of conditions.

System	%XB % XH%XHep/%Xoct %XDmso + W			
B-H-100%Dmso-0%W20°C	50.500	16.000	33.500	
B-Hep-100%Dmso-0%W20°	C 44.500	11.500	44.000	
B-Oct-100%Dmso-0%W20°C	C 52.091	08.401	39.508	
B-H-100%Dmso-0%W30°C	45.148	26.164	28.688	
B-Hep-100%Dmso-0%W30%	C 42.3	12.1	45.6	
B-Oct-100%Dmso-0%W30°C	C 48.964	11.628	39.408	
B-H-100%Dmso-0%W40°C	38.090	12.010	49.899	
B-Hep-100%Dmso-0%W40%	C 35.500	• 24.000	40.500	
B-Oct-100%Dmso-0%W40°C	2 45.10	7.6	43.30	

Further for example at 30 $^{\circ}$ C when non solute Hexane is replaced by Heptane %XB value decreases from 45.1% to 42.3% respectively. However when non solute Heptane is replaced by Octane, the value of %XB increases from 42.3% to 48.9 % respectively.

Also for example at 40 0 C when non solute Hexane is replaced by Heptane the value of %XB decreases from 38.0% to 35.5 % respectively. However when non solute Heptane is replaced by Octane, the value of %XB increases from 35.5 % to 45.1 % respectively.

This peculiar behavior can be explained as under:-.

In a system non solute Hexane is replaced by Heptane, area under the Binodal curve decreases. As a result miscibility region increases and subsequently value of solute composition (XB) in plait point decreases.

However, when non-solute Heptane in a system is replaced by Octane, area under the Binodal curve increases. As a result miscibility region relatively decreases and subsequently the value of composition of solute Benzene in plait point increases.

Further, when non solute Heptane is replaced by non solute Octane, slope of Tie line for particular set of Tie lines decreases in a clockwise direction. As a result the value of % XB in plait point composition increases.

CHAPTER-5

5.3.0

Extraction Capacity

&

Selectivity

of

Mixed Solvents-

(Dmf+W)&(Dmso+W)

5.3.0 EXTRACTION CAPACITY AND SELECTIVITY OF SOLVENT FOR LIQUID - LIQUID EXTRACTION OF AROMATICS

Extraction Capacity and Selectivity of any solvent can be estimated conveniently by the carefull study of distribution and selectivity diagrams. Hence, distribution and selectivity diagrams have been constructed for two solvents namely Dimethyl formamide (Dmf) and Dimethyl sulfoxide (Dmso) under different sets of conditions. Suitability of these two newer solvents for liquid-liquid extraction of aromatics has been investigated in this investigation under different sets of conditions like the following.:-

(i) Anti solvent concentration variation from 0% by weight, 10% by weight to 20% by weight.

(ii) Temperature variation from 20 °C ,30 °C to 40 °C .

(iii)Changing solute aromatics from Benzene (B) to Toluene(T) and to Xylene(X).

(iv) Changing non-solute from Hexane (H) to Heptane(H') and to Octane(O).

5.3.1 Data Tables and figures for distribution and selectivity diagrams :-

Data required for construction of distribution and selectivity diagrams for the quaternary systems consisting of aromatics (B/T/X)-aliphatics(H/H³/O)-Dmf-W where in temperature has been varied from 20 °C , 30 °C to 40 °C and anti solvent concentration has been varied from 0%W, 10% W to 20% W have been reported in Tables D-1 to D-5 and Tables S-1 to S-5 respectively in appendix where in parameter investigated is anti solvent concentration under constant temperature conditions.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures D-1 to D-5 and Figures S-1 to S-5 respectively for different system under consideration for solvent- Dimethyl formamide (Dmf) where in parameter is anti solvent concentration.

(ii)Further, Data required for construction of distribution and selectivity diagrams for the quaternary systems consisting of aromatics (B/T/X)-aliphatics (H/H'/O)-Dmso-W where in temperature has been varied from 20 °C, 30 °C to 40 °C and anti solvent concentration has been varied from 0%W, 10% W to 20% W have been reported in Tables D-6 to D-10 and Tables S-6 to S-10 respectively in appendix where in parameter investigated is anti solvent concentration.

Also, distribution diagrams and selectivity diagrams have been plotted in Figures. D-6 to D-10 and Tables S-6 to S-10 for different systems under consideration for solvent Dimethyl sulfoxide (Dmso) where in parameter investigated is anti solvent concentration.

(iii) Data required for construction of distribution and selectivity diagrams for the quaternary systems consisting of aromatics (B/T/X)-aliphatics(H/H'/O)-Dmf-W have been reported in Tables D-11 to D-15 and Tables S-11 to S-15 in appendix respectively, where in temperature has been varied from 20 °C, 30 °C to 40 °C and anti solvent concentration has been varied from 0%W, 10% W to 20% W.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-11 to D-15 and Tables S-11 to S-15 for different system under consideration for solvent Dimethyl formamide (Dmf) where in parameter is temperature of extraction.

(iv) Data required for construction of distribution and selectivity diagrams for the quaternary systems consisting of aromatics (B/T/X)-aliphatics(H/H^{*}/O)-Dmso-W where in temperature has been varied from 20 °C, 30 °C to 40 °C and anti solvent concentration has been varied from 0%W, 10% W to 20% W have been reported in Tables D-16 to D-20 and Tables S-16 to S-20 respectively in appendix.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-16 to D-20 and Figures S-16 to S-20 for different system under consideration for solvent Dimethyl sulfoxide (Dmso) where in parameter is temperature of extraction. (v) Data required for construction of distribution and selectivity diagrams for different quaternary systems for solvent Dmf have been reported in Tables D-21 to D-23 and Tables S-21 to S-23 respectively in appendix where in parameter investigated is molecular weight of aromatics. i.e. benzene changed to toluene replaced by Xylene.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-21 to D-23 and Tables S-21 to S-23 for different system under consideration for solvent Dimethyl formamide (Dmf) to consider aromatic effect.

(vi) Data required for construction of distribution and selectivity diagrams for different quaternary systems for solvent Dmso have been reported in Tables D-24 to D-26 and Tables S-24 to S-26 respectively in appendix where in parameter investigated is molecular weight of aromatics. i.e. benzene changed to toluene replaced byXylene.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-24 to D-26 and Tables S-24 to S-26 for different system under consideration for solvent Dimethyl sulfoxide (Dmso) to consider aromatic effect.

(viii)Data required for construction of distribution and selectivity diagrams for different quaternary systems for solvent Dmf have been reported in Tables D-27 to D-29 and Tables S-27 to S-29 respectively in appendix where in parameter investigated is molecular weight of aliphatics i.e. hexane changed to and heptane replaced by octane.

(vii)Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-27 to D-29 and Tables S-27 to S-29 for different system under consideration for solvent Dimethyl formamide (Dmf) to consider aliphatic effect

Data required for construction of distribution and selectivity diagrams for different quaternary systems for solvent Dmso have been reported in Tables D-30 to D-32 and Tables S-30 to S-32 respectively where in parameter investigated is molecular weight of aliphatics i.e. hexane changed to and heptane replaced by octane.

Accordingly, distribution diagrams and selectivity diagrams have been plotted in Figures. D-30 to D-32 and Figures S-30 to S-32 for different system under consideration for solvent Dimethyl sulfoxide (Dmso) to consider aliphatic effect

5.3.2 Effect of Anti solvent concentration on extraction capacity and selectivity of solvent Dmf:-

(i)System: B-H- Dmf-W at three temperatures with anti solvent concentration as a parameter.

For the System B-H-Dmf at 20°C, the values of aromatics fraction in extract phase (D1) have been plotted against aromatics fraction in raffinate phase (D2) in Fig-D-1 with anti solvent concentration as a parameter.

As could be seen from the graph with an increase in anti solvent concentration, from 0 % to 10% and up to 20 % for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0. 5 to 0.25 and upto 0.2 respectively.

The values of selectivity for the same system under consideration have been plotted in Fig-S-1 which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentrations from 0 % to 10% and up to 20 % for a fixed value of S2=0.4, the values of selectivity increase from 0.5 to 0.6 and up to 0.75 respectively.

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. Consequently, since extraction capacity and selectivity behave in the opposite manner, selectivity of the solvent increases. Similar observation are available in literature by Deshpande and coworkers,³⁶ Tare and coworkers and Bansod and coworkers.⁷²

From the same Fig-D-1, it can be observed that for the system B-H- Dmf at 30° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 20 % for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0.24 to 0.10 respectively.

From the same Fig-S-1where in value of selectivity have been plotted for a fixed temperature of 30 °C, it can be observed that with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of S2=0.4, the value of selectivity of solvent-Dmf remains 0.40

Thus at 30 °C as the water concentration increases the value of selectivity is expected to decrease. However selectivity of solvent practically remains same for all anti solvent concentration values. As such selectivity should have been increased with an increase in anti solvent concentration. The reason for this behavior is not clear.

From the Fig-D-1 it can be observed that for the system B-H- Dmf at 40° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.5, the value of aromatics in extract phase decreases from 0.40 to 0.38 and up to 0.2 respectively.

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.

From the same Fig-S-1 where in selectivity have been plotted for a fixed temperature of 40 $^{\circ}$ C , it can also be observed that with an increase in anti solvent concentration from 0% to 10% for a fixed value of S2=0.7, the value of selectivity of solvent increases from 0.25 to 0.75 As the anti solvent concentration is increased further , the selectivity practically remains the same in the range of 0.75. This trend is practically similar to the trend observed for temperature 30 $^{\circ}$ C where in the value of selectivity has remain practically constant.

Further for some points for the case of anti solvent concentration being 20%, lower values of selectivity are observed which may be because of some experimental error and can be ignored.

Thus it can be concluded tha under otherwise identical conditions, as extraction capacity of solvent increases, the selectivity of solvent decreases and vice versa. i.e. as extraction capacity of solvent decreases, its selectivity increases.





Distribution diagrams for system: B-H-Dmf+W at different temperatures with anti solvent concentrations as a parameter.





(ii)System: T –H- Dmf-W at three temperatures with anti solvent concentration as a parameter:

For the System T-H-Dmf at 20°C, the values of aromatics fraction in extract phase(D1) have been plotted against aromatics fraction in raffinate phase(D2)in Fig-D-2 with anti solvent concentration as a parameter. As could be seen from the graph with an increase in anti solvent concentration, from 0 % to 20 % for a fixed value of D2=0.2 the value of aromatics in extract phase decreases from 0.2 to 0.0 2 respectively.

The values of selectivity for the same system under consideration have been plotted in Fig-S-2. Thus the value of selectivity practically remains the same when anti solvent concentration is increased from 0% and 10% up to 20%.

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. However, on selectivity anti solvent concentration appears to have practically no effect.

Based on data at 30 °C, distribution diagram and selectivity diagram have also been plotted in Fig D2 and S2 respectively. Similar observations with respect to anti solvent concentration effect can be drawn from these figures.

Further distribution diagram and selectivity diagram at temp 40 °C have also been plotted in the same Fig. D2 and S2 respectively.

Similar observations and conclusions with respect to anti solvent concentration effect can be observed from these figures.

Thus it can be concluded that in general, as anti solvent concentration increases extracted capacity decreases. However selectivity practically remains same.









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(iii)System: X-H-Dmf-W at three temperatures with anti solvent concentration as a parameter:

For the System X-H-Dmf at 20°C, the values of aromatics fraction in extract phase(D1) have been plotted against aromatics fraction in raffinate phase(D2)in Fig-D-3 with anti solvent concentration as a parameter.

The values of selectivity for the same system under consideration have been plotted in Fig-S-3 at constant temperature 20 °C when anti solvent concentration is increased from 0%W to 20 %W selectivityremains practically in the same range. However when anti solvent concentration is increased from 10% to 20 % selectivity increases further. Thus for example, for a fixed value of S2=0.7 the values of S1 increases from 0.62 to 0.82. the corresponding anti solvent concentration being 10% W to 20%W respectively.

From the same Fig-D-3 it can be observed that for the system X-H-- Dmf at 30° C under otherwise identical conditions with an increase in anti solvent concentration, from 0 % to 10% and up to 20 % for a fixed value of D2=0.2 the value of aromatics in extract phase decreases from 0.2 to 0.05 and up to 0.02 respectively.

The values of selectivity for the same system under consideration have also been plotted in Fig-S-3 at 30 °C it can also be observed that selectivity of solvent practically remains same for all anti solvent concentration, When anti solvent concentration, is increased from 0%W, 10% W to 20%W.

Distribution diagram at 40 °C are also depicted in Fig. D3 where in anti solvent concentration of water appears to have marginal effect on extraction capacity.

Selectivity diagram drawn for the same system at 40 °C follow similar trend which have been indicated at 30 °C.

Thus in summary it can be concluded that in general as anti solvent concentration increases extracted capacity decreases. However selectivity values do not increase with increase in anti solvent and they remain practically same.













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(iv) System: B- Hep - Dmf-W at three temperatures with anti solvent concentration as a parameter:-

From the data reported in Tables. D4 and S4, distribution diagrams and selectivity diagrams have been constructed at three temperatures where in parameter is anti solvent concentrations of water.

It is observed that abnormal trend is noticed for all the data with respect to extraction capacity for all three temperatures and for all the values of anti solvent concentrations (water).

With an increase in anti solvent concentration, it has been observed previously that extraction capacity of the solvent decreases. However, for the preset system under consideration, it appears that there is practically no effect of anti solvent concentration on extraction capacity. Distribution diagram at three differently temperatures with anti solvent concentration as a parameter also follow single straight line. Hence it appears that there is no major change in solubility of benzene in solvent Dmf+W where in non solute has been altered to heptane instead of hexane .Hence it can be considered that due to heptane, solubility of benzene in solvent does not decrease . If at all it decreases, it decreases marginally only.

Selectivity diagrams also follow the similar trend except at temperature 40 °C. Selectivity values for 20 % W are higher than that for 0% W and 10 % W. Thus selectivity values also follow a single straight line for varying anti solvent concentration at different constant temperature

In summary, for the present system under consideration based on critical analysis performed in this investigation deviates from normal trend with respect to extraction capacity and selectivity. Probable reason may be effect of aliphatic (non solute) on solubility of aromatics in solvents (Dmf-W) at all three temperatures and anti solvent concentrations.





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(v) System: B-Oct-Dmf-W at three temperatures with anti solvent concentration as a parameter:-

From the data reported in Tables. D- 5 and S-5, distribution diagram and selectivity diagrams have been constructed at three temperatures where in parameter is anti solvent concentrations of water.

It is observed that abnormal trend is noticed for all the data with respect to extraction capacity for all three concentrations except for temperature 40 °C and anti solvent concentration 20 % W.

With an increase in anti solvent concentration, it has been observed previously that extraction capacity of the solvent decreases. However, for the preset system under consideration, it appears that practically no effect of anti solvent concentration on extraction capacity. Distribution diagram at three differently temperatures with anti solvent concentration concern as parameter follow single straight line. Hence it appears that there is no major change in solubility of benzene in solvent Dmf+W where in non solute has been altered from hexane to octane .Hence it can be considered that due to octane, solubility of benzene in solvent does not decrease . If at all it decreases, it decreases marginally only.

Selectivity diagram also follow the similar trend except at temperature 40 $^{\circ}$ C and 20% W. Selectivity values for 20 % W are higher than that for 0% W and 10 % W. Thus selectivity values also follow a single straight line for varying anti solvent concentration at different constant temperature. Similar trend was observed for system B-H-Dmf- W at three temperatures varied from 20 $^{\circ}$ C,30 $^{\circ}$ C and 40 $^{\circ}$ C.also varying anti solvent concentrations.

In summary, the present system under consideration also deviates from normal trend with respect to extraction capacity and selectivity. Probable reason may be effect of aliphatic (non solute) on solubility of aromatics in solvents (Dmf-W) at all three temperatures and anti solvent concentrations.













5.3.3 Effect of Anti solvent concentration on extraction capacity and selectivity of solvent Dmso:-

(i)System: B-H- Dmso -W at three temperatures with anti solvent concentration as a parameter:

For the System B-H-Dmso at 20°C, the values of aromatics fraction in extract phase (D1) have been plotted against aromatics fraction in raffinate phase (D2)in Fig-D-6 with anti solvent concentration as a parameter. As could be seen from the graph with an increase in anti solvent concentration, from 0 % to 10% for a fixed value of D2=0.5 the value of aromatics in extract phase decreases from 0.38 to 0.13.

The values of selectivity for the same system under consideration have been plotted in Fig-S-6 which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.5 the values of selectivity increase from 0.80 to 0. 95 with a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.95

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. Consequently, since extraction capacity and selectivity behave in the opposite manner, selectivity of the solvent increases. Similar observation are available in literature by Deshpande and coworkers, Tare and coworkers and Bansood and coworkers.

From the same Fig-D-6 it can be observed that for the system B-H- Dmso at 30° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.5 the value of aromatics in extract phase decreases from 0.45 to 0.20 and up to 0.05 respectively.

From the Fig-S-6 where in value of selectivity have been plotted for affixed temp of 30 °C it can be observed that with an increase in anti solvent concentration, from 0 % to 10% for a fixed value of S2=0.5 the values of selectivity increase from








0.80 to 0. 95 with a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.98.

From the Fig-D-6 it can be observed that for the system B-H- Dmso at 40°C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.5 the value of aromatics in extract phase decreases from 0.5 to 0.3 and up to 0.1 respectively

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.

From the same Fig-S-6 it can be observed that with an increase in anti solvent concentration, from 0 % to 10% and up to 20 % for a fixed value of S2=0.4 The values of selectivity increase from 0.5 to 0.6 and up to 0.75 respectively.

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. Consequently since extraction capacity and selectivity behave in the opposite manner, selectivity of the solvent increases.

Thus it can be concluded that under otherwise identical conditions, as extraction capacity of solvent increases, the selectivity of solvent decreases and vice versa. i.e. as extraction capacity of solvent decreases its selectivity increases.

(ii)System: T-H-Dmso-W at three temperatures with anti solvent concentration as a parameter:

For the System T-H-Dmso at 20°C, the values of aromatics fraction in extract phase (D1) have been plotted against aromatics fraction in raffinate phase (D2) in Fig-D-7 with anti solvent concentration as a parameter. As could be seen from the graph with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0. 25 to 0.04 and up to 0.005 respectively.

The values of selectivity for the same system under consideration have been plotted in Fig-S-7 which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus with an increase in anti solvent from the same Fig-S-1 wherein selectivity values have been plotted for a fixed temperature of 20 °C, it can also be observed that with an increase in anti solvent the values of selectivity increase from 0.7 to 0.96 and up to 0.98 respectively.

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. Consequently, since extraction capacity and selectivity behave in the opposite manner, selectivity of the solvent increases.

From the Fig-D-7 it can be observed that for the system T-H-Dmso at 30 $^{\circ C}$ under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.23 to 0.075 and up to 0.01 respectively.

From the Fig-S-7 where in value of selectivity have been plotted for a fixed temperature of 30 °C, it can be observed that with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of S2=0.8 the value of its selectivity remains constant in the range of 0.8.

Thus at 30 °C as the water concentration increases the value of aromatic extracted is expected to decrease. However selectivity of solvent practically remains same. For all anti solvent concentration. As such selectivity should have been increased with increase in anti solvent concentration the reason for this behavior is not clear.

From the Fig-D-7 it can be observed that for the system T-H-Dmso at 40° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.28 to 0.0 8 and up to 0.04 respectively.

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.





20 °C 1.2 1 0.8 ♦ 0%W ⊽ 0.6 M 10%W 0.4 **▲** 20%W 0.2 0 0.2 0 0.4 0.6 0.8 1 **S**2 30 °C 1.2 ₇ 1 0.8 ♦ 0%W 5 0.6 **5** 10%W 0.4 **▲** 20%W . 0.2 0 1 0.2 0.6 1.2 0 0.4 0.8 1 S2 40 ℃ 1.2 1 ¢0%₩ 0.8 5.0 5 10%W 0.4 **▲**20%W 0.2 0 0 0.2 0.4 0.6 0.8 1 4 S2



The values of selectivity for the same system under consideration have been plotted in Fig-S-7 which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.5 the values of selectivity increase from 0.80 to 0.95. With a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.95

This trend is practically similar to the trend observed for temperature 30 °C where in the value of selectivity has remained practically constant.

Thus it can be concluded that under otherwise identical conditions, as extraction capacity of solvent increases, the selectivity of solvent decreases and vice versa. i.e. as extraction capacity of solvent decreases its selectivity increases

(iii)System: X-H-Dmso-W at three temperatures with anti solvent concentration as a parameter:

For the System X-H-Dmso at 20°C, the values of aromatics fraction in extract phase(D1) have been plotted against aromatics fraction in raffinate phase(D2)in Fig-D-8 with anti solvent concentration as a parameter.

As could be seen from the graph with an increase in anti solvent concentration, from 0 % to 10% for a fixed value of D2=0.7 the value of aromatics in extract phase decrease from 0.035 to 0.001 respectively. With a further increase in water concentration from 10% to 20%, it seems that extraction capacity practically remains constant..

The values of selectivity for the same system under consideration have been plotted in Fig. S-8 at 20 °C which depicts abnormal behaviour which is observed in this thesis and can be considered as an exception to normal trend.

It is observed that selectivity for 0% water is highest of the order of S1=0.6 and selectivity values for 10% water and 20 % water being lowest in the range of S1=0.1 to 0.2







Fig .S-8 Selectivity diagrams for system: X-H-Dmso+W at different temperatures with anti solvent concentrations as a parameter.

From the same figure D-8 at 30 $^{\circ}$ C as could be seen from the graph with an increase in anti solvent concentration, from 0 % to 10% for a fixed value of D2=0.7 the value of aromatics in extract phase decrease from 0.11 to 0.01 respectively. With a further increase in water concentration from 10% to 20%, extraction capacity remains same. It seems that extraction capacity practically remains constant.

The values of selectivity for the same system under consideration have been plotted in Fig. S-8 at 30 °C which depicts abnormal behaviour which is observed in this thesis and can also be considered as an exception to normal trend.

It is observed that selectivity for anti solvent concentration of 0% water is highest of the order of S1=0.8 and selectivity values for 10% water and 20 % water being lowest in the range of S1=0.1 to 0.2.

From the Fig-D-8 it can be observed that for the system X-H-Dmso at 40° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.17 to 0.07 and up to 0.05 respectively

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.

From the Fig-S-8 where in selectivity values have been plotted for a fixed temperature of 40 °C, it can also be observed that with an increase in anti solvent concentration the value of its selectivity practically remains same i.e. about 0.90 .As the anti solvent concentration is increased further, the selectivity practically remains s the same in the range of 0.90

Further for some points for the case of anti solvent concentration being 20%, lower values of selectivity are observed which may be because of some experimental error and can be ignored.

Thus it can be concluded that for the system under consideration X-H-Dmso-W at three different temperature and three different anti solvent concentration values,

nature of the distribution diagram is similar to whatever is observed by different researchers [®] However, with respect to selectivity abnormal behavior is observed i.e.with increase in anti solvent concentration along with extraction capacity, selectivity also decreases at temp 20 °C. and 30 °C. which may be considered exception from normal trend.

(iv)System: B-Hep-Dmso-W at three temperatures with anti solvent concentration as a parameter:

For the System B-Hep-Dmso at 20°C, the values of aromatics fraction in extract phase(D1) have been plotted against aromatics fraction in raffinate phase(D2)in Fig-D-9 with anti solvent concentration as a parameter.

As could be seen from the graph with an increase in anti solvent concentration, from 0 % to 10% up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.2 to 0.1 up to 0.05 respectively.

The values of selectivity for the same system under consideration have been plotted in Fig-S-9 at 20 $^{\circ}$ C which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.5, the values of selectivity increase from 0.80 to 0. 95. With a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.95

Thus at 20 °C as the concentration of anti solvent (W) increases extraction capacity of the solvent decreases. Consequently, since extraction capacity and selectivity behave in the opposite manner, selectivity of the solvent increases.

As could be seen from the Fig-D-9 it can be observed that for the system B-HEP-Dmso at 30° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0.22 to 0.13 and up to 0.09 respectively.



Fig D-9 Distribution diagrams for system: B-Hep-Dmso+W at different temperatures with anti solvent concentration as a parameter.





The values of selectivity for the same system under consideration have been plotted in Fig-S-9 at 30 0 C which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.5, the values of selectivity increase from 0.75 to 0. 85. With a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.90.

As could be seen from the Fig-D-9 it can be observed that for the system B-Hep—Dmso at 40°C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0.23 to 0.18 and up to 0.1 respectively.

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.

From the Fig-S-9 at 40 °C it can also be observed that with an increase in anti solvent concentration from 0% to 10% the value of its selectivity of solvent increases from 72% to 90%. With a further increase in anti solvent concentration from 10% to 20%, the value of selectivity practically remains constant in the range of 0.90.

.Thus it can be concluded that under otherwise identical conditions as extraction capacity of solvent increases, the selectivity of solvent decreases and vice versa. i.e. as extraction capacity of solvent decreases its selectivity increases.

(v)System: B- Oct -Dmso-W at three temperatures with anti solvent concentration as a parameter:

For the System B-Oct-Dmso at 20°C, the values of aromatics fraction in extract phase(D1) have been plotted against aromatics fraction in raffinate phase(D2)in Fig-D-10 with anti solvent concentration as a parameter.



Fig D-10 Distribution diagrams for system: B-Oct-Dmso+W at different temperatures with anti solvent concentration as a parameter.

As could be seen from the graph with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.1 to 0.02 and up to 0.01 respectively.

From the Fig-S-10 at 40 $^{\circ}$ C where in value of selectivity have been plotted for a fixed temperature of 20 $^{\circ}$ C, it can be observed that with an increase in anti solvent concentration, from 0 % to 10% and up to 20 % for a fixed value of S2=0.8 the value of its selectivity remains in the range of 0.8.

Thus at 20 °C as the water concentration increases the value of aromatic extracted is expected to decrease. However selectivity of solvent practically remains same for all anti solvent concentrations. As such selectivity should have been increased with increase in anti solvent concentration. The reason for this behavior is not clear.

From the Fig-D-10 it can be observed that for the system B-Oct-Dmso at 30° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20 % for a fixed value of D2=0.4 the value of aromatics in extract phase decreases from 0.18 to 0.05 and up to 0.01 respectively.

The values of selectivity for the same system under consideration have been plotted in Fig-S-10 at 30 $^{\circ}$ C which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.4 the values of selectivity increase from 0.82 to 0. 90. With a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.98

From the Fig-D-10 it can be observed that for the system B-Oct-Dmso at 40° C under otherwise identical conditions with an increase in anti solvent concentration from 0 % to 10% and up to 20% for a fixed value of D2=0.4, the value of aromatics in extract phase decreases from 0.14to 0.010 and up to 0.02 respectively.

Thus for 40 °C also the same trend is observed i.e. as anti solvent concentration increases, extraction capacity decreases.



Fig S -10 Selectivity diagrams for system: B-Oct-Dmso+W at different temperatures with anti solvent concentrations as parameters.

The values of selectivity for the same system under consideration have been plotted in Fig-S-10 at 40 0 C which depicts effect of anti solvent concentration on selectivity under otherwise identical conditions. Thus for example with an increase in anti solvent concentration from 0 % to 10% for a fixed value of S2=0.4 the values of selectivity increase from 0.8 to 0. 88. With a further increase in anti solvent concentration from 10% to 20% the value of selectivity practically remains constant in the range of 0.95.

5.3.4 Effect of temperature on extraction capacity and selectivity of solvent Dmf:-

(i)System: B-H-Dmf-W at three values of anti solvent concentrations with temperature as a parameter:

For the System B-H-Dmf at 0% W being anti solvent concentration, the values of aromatic fraction in extract phase (D1) have been plotted against aromatic fraction in raffinate phase (D2) in Figs.D 11 with temperature as a parameter.

As could be seen from the graph (Fig.D-11) with an increase in temperature from 20° C to $30^{\circ C}$ and up to 40° C for a fixed value of D2of0.05, the value of aromatics in extract phase increase 0.075 to 0.085 and up to 0.1 respectively. As temperature increases solubility of aromatic in solvent increases, as a result value of D increases. Since D increases, extraction capacity of solvent increases. However relative increase in value of extraction capacity is marginal only.

In previous section, where in anti solvent effect has been considered relative increase in extraction capacity was substantial. In comparison to anti solvent effect, effect of temperature on the value of extraction capacity appears to be substantially small. Thus extraction capacity happen to be a strong function of anti solvent concentration and weakest function of temperature.

The values of selectivity for the same System under consideration have been plotted in Figs.S -11 which depicts effect of temperature on selectivity under otherwise







Fig D11 Distribution diagram for system: B-H-Dmf+W at different anti solvent concentrations with temperature as a parameter.





identical conditions. Thus for example, with an increase temperature from 20^{0} C to 30^{0} C and up to 40^{0} C for a fixed value of S2of0.1 values of selectivity decrease from 0.38 to 0.25 and up to 0.22 respectively. Thus since as temperature increases, extraction capacity also increases .Hence as expected, consequently, selectivity decreases with an increase in temperature.

Thus at 0 %W concentration as temperature increases, extraction capacity of the solvent increases. An onsequently selectivity of the solvent decreases. Available information in the literature of different researchers Deshpande and coworkers, Tare and coworkers and Bansod and coworkers is in good agreement with present investigations conclusion.

From the same Fig.D-11 where in anti solvent concentration is 10 % w, it is observed that as temperature increases from 20 °C to 30 °C effect happens to be marginal ;however when temperature increases from 30 °C to 40 °C, effect of temperature appears to be relatively large in comparison to temperature range 20 °C to 30 °C.

From the same Fig.S-11 where in value of selectivity have been plotted for a fixed value of anti solvent concentration 10%W, it can be observed that when temperature is increased from 20 °C to 40 °C selectivity remains practically the same, even though extraction capacity have increased with an increase in temperature. Relative increase in solubility when temperature is increased from 20 °C to 40 °C practically remains the same for Benzene as well as Hexane. As a result selectivity values practically remain the same.

From Fig.D-11 where in anti solvent concentration is 20 % W, it is observed that when temperature is increased from 20 °C to 30 °C extraction capacity increases. However, at 40 °C abnormal behavior is observed where in extraction capacity has decreased at highest temperature utilized in this investigation which can be considered as exception. From the same Fig.S-11 at constant value of 20% W it is observed that selectivity is highest at 20 °C and as temperature is increased from 20 °C to 30 °C ,selectivity decreases. However, with a further increase in temperature there is no appreciable decrease in selectivity.

This behavior is very similar to what has been observed at anti solvent concentration value of 10% W

(ii)System: T-H-Dmf-W at three values of anti solvent concentrations with temperature as a parameter:

For System T-H-Dmf at 0% W being ant solvent concentration the value of aromatic in extract phase D1 have been plotted against aromatic in raffinate phase D2 in Fig D12 with temperature as a parameter . As could be seen from fig effect of temperature on extraction capacity appears to be negligible and extraction capacity practically remains in the same range for all the three temperatures under consideration for previous System where in the Benzene was solute effect of temperature on extraction capacity was marginal only. When Benzene is replaced by Toluene, effect of temperature which was marginal in previous case, shifts to very marginal as if negligible.

Selectivity diagram for System under consideration has been shown in Fig S-12 at constant value of ant solvent concentration 0% W. With increasing temperature from 20 °C to $30^{\circ C}$ selectivity values decrease very marginally however when temperature is increase from 30 °C to $40^{\circ C}$ selectivity decreases as per expectation.

From the same Fig.D-12, where in graph has been shown for water concentration of 10 % W, normal behavior is observed i. e. as temperature increases extraction capacity increases.

Selectivity diagram for the same System has been shown also in Fig-S-12 at affixed value of anti solvent concentration 10 % with an increase in temperature selectivity values as such should decrease but from fig they appear to be practically in the same range. The reasoning given for the System involving solute Benzene is equally valid. For the System under consideration. Where in solute has been changed from Benzene to Toluene.







Fig D-12 Distribution diagrams for system: T-H-Dmf+W at different anti solvent concentrations with temperature as a parameter.





Distribution diagram and corresponding selectivity diagram at constant value of anti solvent concentration 20% W have been plotted in Fig. D-12 and S-12 respectively.

The conclusion which have been drawn fro the System under consideration at constant value of anti solvent concentration of 10 %W are valid for the System where in anti solvent concentration is increased to 20 % W.

(iii)System: X-H-Dmf-W at three values of anti solvent concentrations with temperature as a parameter:

Distribution diagram for the System X-H-Dmf-W at three constant values of anti solvent concentration (0%W, 10%W and 20 %W) with temperature as a parameter have been plotted in Fig. D-13. At constant value of water concentration 0% and 20 % W with increase in temperature extraction capacity of solvent increases under other wise identical conditions for all the observation.

At a fixed value of anti solvent concentration of10%W when temperature is increased from 30 °C to 40 °C extraction capacity increases however very marginally.

At a fixed value of anti solvent concentration of 10% when temperature is increased from 20 °C to 30 °C extraction capacity increases .Thus for example, for affixed value of D2of0.5 as temperature is increased from 20 °C to 30 °C extraction capacity of solvent increases from 0.07 to 0.15 respectively. With a further increase in temperature from 30 °C to 40 °C value increases very marginally from 0.15 to 0.155.

Selectivity diagram drawn for the System under consideration under different sets of conditions have been plotted in Fig.S-13 where in three constant values of anti solvent concentration have been utilized namely 0%, 10% and 20%W.

At 0% W values of selectivity practically remains in the same range indicating that as temperature is increased solubility of Xylene and solubility of Hexane in solvent increase proportionately as a result selectivity values are expected to remain same.







Fig D- 13 Distribution diagrams for system: X-H-Dmf+W at different anti solvent concentrations with temperature as a parameter.





For a fixed value of anti solvent concentration equal to 10%W, value of selectivity in the temperature range 20 °C to 30 °C practically remain in the same range. However, when temperature is further increased to 40°C selectivity values lowered down. Thus as expected selectivity values are lowest at 40 °C.

For a fixed value of anti solvent concentration equal to 20%W, the values of selectivity in the temperature range 30 °C to 40 °C remain practically constant. With an increase in temperature. Even for 20 °C temperature range values do merge in to the same line which has been drawn for temp 30 °C and 40 °C remain practically constant. With an increase in temperature even for 20 °C temperature range values do merge into the same line which has been drawn for temp 30 °C to 40 °C However in the region , where in merging of these two lines does not exist where in as expected , selectivity is highest at 20 °C and 20% W concentration., the selectivity value being in the range of 0.9 to 0.95.

(iv) System: B- Hept - Dmf-W at three values of anti solvent concentrations with temperature as a parameter:

Data for construction of distribution diagram for the System B-Hep-Dmf-W reported in Table-D-14 has been plotted in Fig. D-14. Where in three distribution diagram for three values of anti sovent concentration water have been depicted.

As could bee seen for constant values of anti solvent concentration 0%W, 10%W, and 20 % W with increase in temperature extraction capacity of solvent Dmf increases At 20%W of anti solvent concentration increase in extraction capacity with increase in temperature however appears to be marginal.

Based on data reported in Table S-14 on "for parameter s S1 and S2 has been plotted in Fig .S-14 where in three selectivity diagrams at three values of anti solvent concentrations (0%W, 10%W and 20%W) have been depicted with temperature as parameter.

Selectivity diagram for 10 % W and 20 % W follow practically a single straight line /curve indicating that with increase in temperature, decrease in selectivity appears



Fig D 14 Distribution diagrams for system: B-Hep-Dmf+W at different anti solvent concentrations with temperature as a parameter.





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to be practically negligible. However at 0%W with increase in temperature selectivity values as such should decrease – which is called as normal trend. However for the case under consideration abnormal behavior is observed. With an increase in temperature, selectivity values are increasing.

It appears that when temperature inceases from 20 °C to 30 °C and up to 40 °C relative increase in solubility ofHeptane in solvent i.e. extract phase. Hence it is expected that with increase in temp selectivity also increases which has to be called as abnormal trend. This has been already confirmed in the discussion and conclusion based on mutual solubility data where in such abnormal trend has been observed during discussion.

In summary, the System B-Hep-Dmf-W follow normal trend with respect to effect of temperature on extraction capacity. However it follows totally a different trend with respect to effect of temperature on selectivity.

(v) System: B-Oct-Dmf-W at three values of anti solvent concentrations with temperature as a parameter:

Data for construction of distribution diagram for the system B- Oct - Dmf-W reported in Table-D-15 has been plotted in Fig. D-15. Where in three distribution diagram for three values of anti solvent concentration water have been depicted.

For a constant value of anti solvent concentration of0%W, effect of temperature on extraction capacity follows the normal trend i.e. with an increase in temperature extraction capacity of solvent increases however marginally.

For a constant value of anti solvent concentration of 10% for temperature range 20 °C to 30 °C. Again normal trend is followed. However, when temperature is increased from 30 °C to 40 °C there appears to be substantial increase in solubility of Benzene in solvent in presence of Octane and as a result the value of extraction capacity increase substantially. Thus for example, for a constant value of D2of0.4, as temperature increases from 30 °C to 40 °C the value of D1 increases from 0.15 to 0.4









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At constant value of anti solvent concentration of 20% similar trend is observed i.e. lower temperature range (20 °C to 30 °C) substantial increase in extraction capacity of solvent.

Based on data reported in Table. S-15 on "for parameter S-1 and S-2" has been plotted in Fig.S-15 where in three selectivity diagram at three values of anti solvent concentration (0%, W10%W and 20%W) have been depicted with temperature as a parameter.

For all the three cases under consideration of three constant values of anti solvent concentration namely 0%W, 10%W and 20%W selectivity diagram follow practically straight line./ curve.Thus with an increase in temperature selectivity value do not vary even marginally. As if selectivity remains practically the same. It is expected that as temperature increases the values of relative increase in solubility of Benzene in solvent – extract phase and relative increase in solubility of Octane in solvent – extract phase remain practically constant. As a result selectivity values do not vary (either increase or decrease) and follow a straight nature / single cuve.

5.3.5 Effect of temperature on Extraction capacity and selectivity of Solvent Dmso:-

(i) System : B-H-Dmso-W at three values of anti solvent concentrations with temperature as a parameter :

For the System B-H-Dmso at 0% W being anti solvent concentration as a parameter, the value of aromatic fraction in extract phase (D1) have been plotted against aromatic fraction in raffinate phase (D2) in fig. D-16 with temperature. as a parameter . As could be seen from the graph, effect of temperature at 20°C and 30°C happens to be marginal; however when temperature is increased from 30°C to 40°C, extraction capacity of solvent increases. Thus for example for a fixed value of D2 of 0.4 as temperature is increased from 30°C to 40°C, the value of D1 increase from 0.18 to 0.32 respectively. From Fig. D-16 at constant value of anti solvent concentration of 10 % W and 20%W also, similar behaviour is observed i.e. when temperature is

increased from 20°C to 30°C, there is very marginal effect of temperature; however when temperature is increased from 30°C to 40°C, effect is appreciable.

The values of selectivity for the same system under consideration under different sets of conditions of temperatures and anti solvent concentrations have been plotted in Fig S-16.

The following conclusions can be drawn from Fig. S-16:-

At value of anti solvent concentration of 0 % W, the value of selectivity at 20°C and 40°C are comparable inclusive of some value at 30 °C also. Thus as temperature increases from 20°C to 30°C and up to 40°C, the relative increase in values of solubility of Benzene in extract solvent being Dmso and also Hexane in extract appear to be comparable. Hence selectivity values are likely to remain same when temperature is increased from 20°C to 30°C and up to 40°C.

For some points at 30°C, the values of selectivity are substantially lower which may be due to experimental error.

From the same Fig. S-16 at constant value of anti solvent concentration of10%W, the values of selectivity at 20°C and 30°C, are comparable and the same reasoning given above is valid.

At 40°C as expected, the values of selectivity do decrease in comparison to 30°C temperature.

Similar trend is observed when anti solvent concentration of 20 % W. However again for this case at 30 °C, some points deviate from normal nature which may be due to experimental error.







Fig D-16 Distribution diagrams for system: B-H-Dmso+W at anti solvent concentrations with temperatures as a parameter.

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Fig S-16 Selectivity diagrams for system: B-H-Dmso+W at different anti solvent concentrations with temperatures as parameters.
(ii) System : T-H Dmso- W at three values of anti solvent concentration with temperature as a parameter:

Data required for construction of distribution and selectivity diagrams reported in Tables D-17 and S-17 have been plotted in Figs D-17 and S-17 under different sets of conditions of temperature and anti solvent concentration for system T-H Dmso-W.

As could be seen from Fig. D-17 with increase in temperature from 20°C to 30°C, extraction capacity of solvent increases marginally. However when temperature is increased from 30°C to 40°C, effect of temperature on extraction capacity appears to be appreciable.

For example, for the case of anti solvent concentration of 10 %W, when temperature is increased from 30° C to 40° C for a constant value of D2 of 0.7, the value of D1 increases from 0.09 to 0.18.

Thus it can be concluded that as temperature increases, extraction capacity of solvent also increases, however effect of temperature is more stringent at 40°C.

From selectivity diagrams which have been plotted in fig S-17 following conclusion can be drawn:-

The value of selectivity at 20°C are highest and at 40°C they are lowest. When temperature is changed from 20°C to 30°C, decrease in selectivity value is very marginal.

For the case of anti solvent concentration of 20 %W, selectivity values remain practically constant and the range of selectivity value is of the order of 0.9 to 0.98.

Some observations for the case under considerations at 30°C do not follow this trend. The probable reason may be experimental error.







Fig D -17 Distribution diagrams for system: T-H-Dmso+W at different anti solvent concentrations with temperature as a parameter.

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Fig S- 17 Selectivity diagrams for system: T-H-Dmso+W at different anti solvent concentrations with temperature as a parameter.

(iii) System: X-H-Dmso-W at three values of anti solvent concentration with temperature as a parameter :

The data required for the construction of distribution diagrams and selectivity diagrams reported in Tables D-18 and S-18 could be used effectively for plotting of the distribution diagrams Fig.D-18 and Fig.S-18 respectively.

From Fig. D-18 following conclusion can be drawn:-

(i) Extraction capacity of the solvent Dmso for extracting Xylene at 40°C temperature happens to be highest and at 20°C it happens to be lowest.

Thus for example at constant value of anti solvent concerntration of 0% W when temperature is increased from 20 °C to 40 °C for a constant value of D2=0.5, the values of D1 are 0.02 and 0.2 respectively. Thus effect of temperature for the system consisting of solute Xylene happen to be most stringent in comparison to solutes Benzene and Toluene.

From selectivity diagrams which have been depicted in Fig S-18 the following conclusion can be drawn:-

(i) Selectivity value at 40°C follow highest range of values and selectivity values at 20°C follow lowest range for all the three values of anti solvent concentrations namely 0%w, 10%w and 20%w.

(ii) Normal trend for selectivity values is: "As temperature increases selectivity decreases". Thus at temperature of40°C selectivity will be lowest and at 20°C it will be highest. However in the present case, selectivity values are highest for temperature 40°C and lowest for 20°C.

Since this trend is observed for all the observations for the system under consideration, it can't be labelled as experimental error. This can be considered as exception to normal trend.



Fig D-18 Distribution diagrams for system: X-H-Dmso+W at anti solvent concentrations with temperature as a parameter.









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(iii) Hence while developing a generalized correlation, an index for temperature effect is expected to be of opposite sign for the system under consideration involving Xylene than the other systems under consideration where in solvents are Benzene and Toluene.

(iv) System B – Hept – Dmso – W at three values of anti solvent concentration with temperature as a parameter:

Based on data regarding distribution diagrams and selectivity diagrams reported in Tables D-19 and S-19, distribution diagrams and selectivity diagrams have been plotted in figures D-19 and S-19.

The following are the important conclusions based on the above diagrams:-

(i) Conclusions for distribution diagrams:-

Values of extraction capacity are highest at 40° C and lowest at 20° C. With an increase in temperature from 20° C to 30° C and up to 40° C for the case of anti solvent concentration being 20%W for a constant value of D₂ of 0.4, the values of D₁ increase from 0.06 to 0.11 and up to 0.16 respectively. Thus effect of temperature on extraction capacity appears to follow normal trend. However, when temperature is increased from 20° C to 30° C for constant value of anti solvent concentration 0%W and 10%W effect of temperature on extraction capacity is very marginal.

(ii) Conclusions for selectivity diagrams:

Values of selectivity are lowest at highest temperature of the order of 40° C and highest at temperature of the order 20° C. However, in some cases effect of temperature on selectivity when temperature is in the range of 20° C to 30° C is very marginal. Further at anti solvent concentration of water of 10%W the values of selectivity remains practically the same indicating as if there is no effect of temperature.

This can be explained by following reasons.







Fig D-19 Distribution diagrams for system: B-Hep-Dmso+W at different anti solvent concentrations with temperature as a parameter.



Fig S-19 Selectivity diagrams for system: B-Hep-Dmso+W at different anti solvent concentrations with temperatures as a parameter.

With an increase in temperature from 20° C to 40° C, relative increase in solubility of Benzene in extract phase and solubility of Heptane in extract phase follow practically the same relative increase-identical rise with increase in temperature. Hence selectivity values are expected to remain constant.

(v) System B-Oct-Dmso-W at three values of anti solvent concentration with temperature as a parameter:

Based on data regarding distribution diagrams and selectivity diagrams reported in Tables D-20 and S-20, distribution diagrams and selectivity diagram have been plotted in Figs D-20 and S -20 respectively.

(i) Conclusions from distribution diagrams for system B-Oct-Dmso-W:-

It is interesting to observe that solubility of Benzene when Hexane is replaced by Octane decreases substantially under otherwise identical conditions. With an increase in temperature extraction capacity increases which is a normal trend observed in this investigation.

However, when Hexane is replaced by Octane the range of extraction capacity is substantially lower than that for B-H-Dmso-W system under otherwise identical conditions. Thus for example, for a constant anti solvent value of 0%W for a constant values of D2 of 0.4, the value of D1 increases from 0.05 to 0.15 and up to 0.18 when temperature is increased from 20° C to 30° C and up to 40° C. However, for the case of anti solvent concentration of water of 20%W with an increase in temperature from 30° C to 40° C effect of temperature appears to be practically marginal.

(ii) Conclusions for selectivity diagrams for System B-Oct-Dmso-W:

Effect of temperature on the values of selectivity appears to be practically negligible indicating that selectivity remains practically constant when temperature is increased from 20° C to 40° C.









The range of values of selectivity is practically 0.95 to 0.99 indicating that % purity of extract is expected to be practically cent percent for the case wherein along with solute Benzene non solute present is Octane instead of Hexane.

However, critical survey of different selectivity diagrams under different sets of conditions also indicates that at 40° C for some observations, the values of selectivity does not follow a single straight line. For these two/three observations reason can be attributed as experimental error.

Thus in conclusion, it can be concluded that effect of temperature on the values of selectivity appears to be very marginal as if no effect and selectivity obtained is of the order of 0.95 to 0.99.

The same reasoning which has been given for other systems where in a single straight line/single curve is observed is valid for this present system under considerations. Relative increase in solubility values of Benzene in extract and also Octane in extract phase remains practically the same when temperature is increased from 20 °C to 30 °C and then from 30 °C to 40 °C. As a result, selectivity diagram for all the three temperatures follow a single line/curve.

5.3.6 Effect of molecular weight of aromatics on extraction capacity and selectivity of solvent Dmf:

(i)System : B/T/X - H - 100% Dmf - 0%W at three values of temperature with molecular weight of aromatics as a parameter :

For the system B/T/X - H - Dmf -W at fixed value of anti solvent concentration of 0%. W, the values of aromatics in extract phase (D.1) have been plotted against aromatic fraction in raffinate phase (D₂) in Fig. D21 at three temperatures namely 20°C, 30°C and 40°C with molecular weight of aromatics as a parameter:



Fig D-21 Distribution diagrams for system: B/T/X-H-100%Dmf+0%W at different temperatures with Aromatic effect as a parameter.





As molecular weight of aromatic increases which is happening in present case. When Benzene is changed to Toluene and Toluene is changed to Xylene, the solubility of aromatics in extract phase is likely to decrease as a result extraction capacity for system containing aromatic Xylene is expected to be lowest and expected to be highest for Benzene.

As temperature is increased from 20°C to 30°C and upto 40°C effect of temperature on solubility values of Benzene, Toluene and Xylene appear to be practically same.

Selectivity diagrams for different systems under consideration at constant value of anti-solvent concentration of 0% W are plotted in Fig. S-21 from which following conclusions can be drawn :

i)At constant value of temperature of 30°C as the value of molecular weight increases (Benzene changed to Toluene changed to Xylene) selectivity of solvent increases.

ii)For system containing Xylene selectivity is highest and for system containing Benzene selectivity is lowest.

iii)Detailed discussion regarding these conclusion has been done elsewhere.
(ii)System : B/T/X/ - H - 90% Dmf - 10% w at three values of temperature with molecular weight as a parameter :

Based on data required for construction of distribution diagrams and selectivity diagrams reported in Tables D-22 and S-22, distribution diagrams and selectivity diagrams have been depicted in Figs. D-22 and S-22.

Based on distribution diagrams shown in Fig. D-22, the following conclusions can be drawn :



Fig D-22 Distribution diagrams for system: B/T/X-H-90%Dmf+10%W at different temperatures with Aromatic effect as a parameter.



Fig S -22 Selectivity diagrams for system: B/T/X-90%Dmf+10%W at different temperatures with molecular weight of Aromatics as a parameter.

i)As solute component is changed from Benzene to Toluene to Xylene, since molecular weight is in increasing order; correspondingly extraction capacity of solvent decreases.

Thus for example at a constant temperature of 40° C and for a constant value of D2=0.4, the corresponding values of D1 are 0.23, 0.13 and 0.1 respectively when the Benzene is replaced by Toluene and Toluene is replaced by Xylene.

ii)Similar observation can be seen from the same Fig. D-22 for temperature 20° C and 30°C.

Based on selectivity diagrams shown in Fig. S-22 the following conclusions can be drawn :

i)As molecular weight of solute aromatics increases from Benzene to Toluene to Xylene,under otherwise identical conditions selectivity values increase.

Thus for example, at a constant temperature of 40° C and for a constant value of D2=0.4, when Benzene is changed to Toluene the values of D1 are 0.23 and 0.13 respectively.

ii)It is interesting to observe that at temperature 40 $^{\circ}$ C, different values of selectivity follow a single straight line /curve

The values of relative decrease in solubility of aromatics in extract phase and also aliphatic in extract phase remain practically constant when Benzene is changed to Toluene and Toluene is changed to Xylene.

iii) Partially similar trend is observed with respect to selectivity at 20 °C and 30 °C temperatures.

As expected the values of selectivity for Benzene for the systems under consideration are lowest.

(iii)System : B/T/X-H-80% Dmf – 20% W at three values of temperature with molecular weight of aromatics as a parameter:

(i) The data required for construction of distribution diagrams and selectivity diagrams has been reported in tables D-23 and S-23 respectively.

Accordingly distribution diagrams and selectivity diagrams have been plotted in Figs D-23 and S-23 respectively.

The following are the important conclusions based on distribution diagrams:

(i) For different systems under consideration at 20°C and 30°C temperatures, distribution diagrams follow normal trend i.e. as Benzene is replaced by Toluene and Toluene is replaced by Xylene, extraction capacity of solute (aromatics) decreases. Consequently, selectivity of solvent under otherwise identical conditions is expected to increase.

Thus for example for temperature of 30° C and D2 =0.7, for Benzene and when Benzene is replaced by Toluene and Toluene further replaced by Xylene the corresponding values of D1 are 0.2, 0.13, and 0.07 respectively.

(ii) However an abnormal trend is observed with respect to aromatic effect for different systems under considerations at a constant value of temperature of 40°C under otherwise identical conditions. Extraction capacity of Benzene happens to be lowest and that of Toluene highest followed by in between trend for Xylene. The reasoning for this type of behaviour is not clear.

Based on selectivity diagram depicted in S-23 following conclusions can be drawn:-

i)At 20°C temperature, for different systems under considerations selectivity diagrams follow two close straight lines. Hence, there is no appreciable effect of replacing aromatics on selectivity values.



Fig D-23 Distribution diagrams for system: B/T/X-H-80%Dmf+20%W at different temperatures with Aromatic effect as a parameter.



Fig S -23 Selectivity diagrams for system: B/T/X-80%Dmf+20%W at different temperatures with molecular weight of Aromatics as a parameter.

ii)For different systems under consideration at temperatures 30°C and 40°C all selectivity diagrams follow normal trend for systems containing solute Benzene/Xylene. However for systems containing Toluene selectivity values are highest. The reason for this is behaviour not clear.

iii)For all other observations excluding above sighted for systems containing Toluene, normal trend is observed i.e. as molecular weight increases, selectivity of solvent increases.

5.3.7 Effect of Molecular weight of aromatics on extraction capacity and selectivity of solvent Dmso : -

(i) System : B/T/X-H-100% Dmso – 0% W at three values of temperature with molecular weight of aromatics as a parameter :

Based on data reported in Table D-24 and S-24, distribution diagrams and selectivity diagrams have been drawn in Figs.D-24 and S-24.

Following are the conclusions based on distribution diagrams Fig. D-24:-

(i)Under otherwise identical conditions extraction capacity of solvent Dmso decreases when solute aromatics are replaced in a sequence B->T->X. Thus for example at anti solvent concentration value of 0%W and temperature of 30°C for a fixed value of D2 = 0.4, the values of D1 are 0.3, 0.2 and 0.04 for Benzene and when Benzene is changed to Toluene and Toluene is changed to Xylene respectively.,

(ii) Thus with respect to extraction capacity, system follow normal trend.

Based on the Figs. S-24 following are the conclusions with respect to selectivity diagrams :

(i)Different systems under different sets of conditions follow normal trend with respect to selectivity except the system containing solute Xylene at temperature 20° C.



Fig D -24 Distribution diagrams for system: B/T/X-H-100%Dmso+0%W at different different temperatures with molecular weight of aromatics as a parameter.





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As Benzene is replaced by Toluene and Toluene is replaced by Xylene, the values of selectivity increase.

(ii)For the system X-H-100% Dmso - 0%Wat 20°C. the values of selectivity happen to be the lowest which should have been otherwise. This may be considered as exception to normal trend.

(ii)System : B/T/X - H - 90% Dmso - 10 %W at three values of temperature with molecular weight of aromatics as a parameter:

Based on data reported in Tables D-25 and S-25, distribution diagrams and selectivity diagrams under different sets of conditions have been plotted in Fig. D-25 and S-25 respectively.

The followings are the conclusions from distribution diagrams depicted in Fig, D-25:

For the different system under consideration under different sets of operating conditions, all the system follow normal trend with respect to extraction capacity. i.e. as molecular weight of aromatic increases, corresponding values of extraction capacity do decrease.

Based on Fig. S-25 where in selectivity diagram have been plotted under different sets of condition, following are the important conclusions:-.

(i)Effect of aromatics being replaced in a sequence Benzene to Toluene, selectivity values remain practically the same. This can be explained as under : -

The values of relative increase in solubility of aromatic (Benzene / Toluene) in extract phase and corresponding values of solubility of hexane in extract phase remain practically identical. Hence selectivity value are expected to have no change.

(ii)Values of selectivity for solvent Dmso in presence of Xylene at temperature 20°C and 30°C under otherwise different sets of operating conditions are the lowest in



Fig - D -25 Distribution Diagrams for system: B/T/X-H-90%Dmso+10%W at different temperatures with molecular weight of aromatics as a parameter.

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comparison to systems containing aromatics – Benzene and Toluene wherein solvent under consideration is Dmso. This may be considered as exception.

(iii)System : B/T/X - H - 80% Dmso - 20 %W at three values of temperature with molecular weight of aromatics as a parameter:

Based on data reported in Table D-26 and S-26, distribution diagrams and selectivity diagrams have been constructed and depicted in Figs. D-26 and S-26 respectively.

Following are the conclusion based on the Fig. D-26 which indicates distribution diagrams.:-

Effect of aromatics under constant conditions for fixed water concentration and fixed temperature appears to be marginal and it follows normal trend.

Based on selectivity diagrams depicted in Fig. S-26 following are the conclusion.

(i)Effect of aromatic being replaced in a sequence Benzene to Toluene, selectivity values remain practically the same.

It is expected that the values of relative increase in solubility of aromatics (Benzene replaced by Toluene) in the extract phase and the corresponding values of solubility of hexanein extract phase remain practically comparable. Hence selectivity values remain practically constant for all the systems under consideration except solute containing Xylene.

(ii)Values of selectivity for solvent Dmso in presence of aromatics Xylene at temperatures 20°C, 30°C and 40°C under otherwise different sets of operating conditions are the lowest in comparison to the other systems containing aromatics-Benzene and Toluene where in solvent under consideration is Dmso. This may be considered as an exception.



Fig D -26 Distribution diagrams for system: B/T/X-H-80%Dmso+20%W at different different temperatures with molecular weight of aromatics as a parameter.



Fig S-26, Selectivity diagrams for system: B-T-X-90%Dmso+20%W at different temperatures with molecular weight of aromatics as a parameter.

5.3.8 Effect of molecular weight of aliphatics on extraction capacity and selectivity of solvent Dmf.

(A) Effect of molecular weight of aliphatics on distribution capacity values of solvent Dmf.

(i) System : B- H / Hept / Oct-100%Dmf-0%W at three values of temperature with molecular weight of aliphatics as a parameter :

For the System B-H/Hept/Oct-Dmf -W at fixed value of anti solvent concentration of 0% W, the values of aromatics in extract phase (D1) have been presented against aromatic fraction in raffinate phase (D2) in fig D27 at three temperatures 20°C, 30°C, and 40°C with molecular weight. of aliphatic as a parameter.

As molecular weight of aliphatics increases, the values of aromatics-Benzene in extract phase are expected to decrease as non solute-Hexane is replaced by Heptane and Heptane is subsequently replaced by Octane. Thus for example, for a constant value of D2 = 0.10 at constant temperature 20°Cvalues of D1 for systems containing Hexane, Heptane and Octane are 0.14,0.10 and 0.075 respectively. Further for the systems under consideration at constant temperature of 30 °C. for a constant value of D2=0.10 the values of D1 for systems containing Hexane, Heptane and Octane are 0.20, 0.14 and 0.08 respectively.

However, at constant temperature of 40°C the normal behavior is not observed and the values of Benzene in extract phase for system containing Heptane are highest than the system containing Hexane and Octane. Further the values of Benzene in extract phase for the systems containing Hexane and Octane are comparable. The reason for such an abnormal behavior is not clear.

Thus for example, at 40°C for the three systems under consideration for a fixed value of D2=0.1, the values of D1 for system containing Heptane are highest being 0.22 and for systems containing Hexane and Octane have single value of 0.14.





(ii) System : B- H / Hept / Oct-.90% Dmf-10% W at three values of temperature with molecular weight of aliphatic as a parameter :

Based on fig D-28 wherein water concentration has been altered from 0%W in previous case to 10%W in the present case, the following are the important conclusions:-

1) When temperature is of the order of 20°C, the values of aromatics – Benzene in extract phase practically remain the same when Molecular weight is increased from component Hexane to Heptane and further to Octane.

Probably, the values of solubility of Benzene in extract phase do not get altered much (in decreasing order). As a result values of D1 for fixed value of D2 remain practically constant for all the three systems containing aliphatics-Hexane, Heptane and Octane.

2) At 30°C, the values of Benzene in extract phase are lowest for system containing Hexane and for all the systems containing non -solute- Heptane and Octane values of D1 are comparable.

Thus for example, at 30° C for a constant values of D2=0.5, values of D1, for systems containing non solute-Heptane and Octane is 0.32 only i.e. comparable and for system containing non -solute- Hexane the value of D1 is lowest being 0.23.

3) At temperature 40°C, the values of D1 for constant value of D2 are highest for system containing Octane and comparable for systems containing Hexane and Heptane. The reason for such an abnormal trend is not clear.





(iii) System : B-H-80%Dmf- 20%W at three values of temperature with molecular weight of aliphatic as a parameter:

Based on values of D1 plotted against D2 in Fig D-29, following are important conclusions:-

(1)At temperatures- 20°Cand 30°Cfor all systems when aliphatic is replaced from Hexane to Heptane and subsequently to Octane, distribution diagrams follow a single straight line / curve.

(2)For system involving aliphatics Hexane, Heptane and Octane at temperature 40°C follow again abnormal trend wherein values of distribution coefficients for Octane are highest followed by Heptane and followed by a least value for Hexane.

Thus for example, at 40°C for systems consisting of Octane, Heptane and Hexane, the corresponding values of D1 at constant value of D2=0.3, are 0.12,0.05 and 0.002 respectively.

(B) Effect of molecular weight. of aliphatic on Selectivity values of Solvent Dmf:

(1) From Fig. S-27 which depicts selectivity values for system B-H/Hept/oct-100%Dmf-0%W, at three temperatures 20°C,30°Cand 40°C. the values of selectivity for all three temperatures are highest for system containing Octane and lowest for systems containing Hexane and Heptane.

Probably, when Hexane is changed to Heptane relative decrease in solubility of Hexane and Heptane in extract phase appears to be the same. As a result selectivity values are comparable for these systems containing Hexane and Heptane.

(2) From Fig S-28 wherein values of selectivity have been plotted for system Benzene-H/Hept/Oct -90% Dmf -10%W at different temperatures, normal trend is


Fig D-29, Distribution diagrams for system: B-H/Hep/Oct-Dmf+20%W at different temperatures with molecular weight of aliphatics as a parameter.



Fig. S-27 Selectivity diagrams for system: B/H/Hep-Oct-100%Dmf+0%W at different temperatures with molecular weight of aliphatics as a parameter.

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Fig S-28 Selectivity diagrams for system: B-H-Hep-Oct-90%Dmf+10%W at different temperatures with Aliphatic effect as parameters.

observed at all the three temperatures i.e. Selectivity values are highest for system involving Octane and lowest for system involving Hexane.

(3) From selectivity diagram drawn in Fig. S-29 wherein anti solvent concentration has been altered to 20% W, following conclusions can be drawn:-

At 20°C.selectivity values remain practically the same when aliphatics have been replaced by a sequence: - from Hexane via Heptane to Octane.

At temperature of 30°C, the values of selectivity are comparable for systems consisting of Heptane and Octane and the values of selectivity are lowest for system consisting of Hexane.

At temperature 40°C various values of selectivity depicted in selectivity diagrams follow the normal trend i.e. selectivity values are highest for system containing non-solute Octane and selectivity values are lowest for system containing non-solute Hexane.

Thus for example, for a constant value of S2 of 0.4 at 40°C, the values of S1 for systems containing non solute Octane, Heptane and Hexane are 0.98, 0.55 and 0.48 respectively.

5.3.9 Effect of molecular weight of aliphatic on extraction capacity and selectivity of solvent Dmso:

(A) Effect of molecular weight of aliphatics on distribution capacity values of solvent Dmso:-

(i) System: B-H/Hept/Oct-100% Dmso-0%W at three values of temperature with molecular weight of aliphatics as a parameter:

From the Fig. D-30 wherein distribution diagrams have been plotted for three temperatures under consideration, the following conclusions can be drawn:-



Fig S -29 Selectivity diagrams for system: BH/Hep/Oct-80%Dmf+20%W at different temperatures with molecular weight of aliphatics as a parameter.





solvent consisting of 90% Dmso + 10% W is observed in this case for all the three temperatures.

Extraction capacity of solvent Dmso for the systems consisting of Heptane is highest than that for the systems consisting of Hexane and Octane which should have been other wise under normal trend conditions.

Thus for example when Hexane is replaced by Heptane at conditions of 20% Water and constant value of D2 = 0.4, the values of D1 are 0.0025 and 0.16 at temperature 30°C and are 0.003 and 0.18 at 40°C respectively.

However as expected, under otherwise identical conditions for all the system consisting of aliphatic Octane, the values of extraction capacity are lowest.

(B) Effect of molecular weightof aliphatics on selectivity values for solvent Dmso

(1) From Fig. S-30 wherein selectivity diagrams have been depicted under different sets of conditions for solvent consisting of 100% Dmso + 0% water, the following conclusions can be drawn:-

Selectivity values at temperatures 20°C and 30°C under different sets of conditions remain practically the same indicating that effect of increase in molecular weight of aliphatics on the values of selectivity appear to be practically nill for all the systems consisting of solvent 100% Dmso and 0% water.

At temperature of the order of 40°C, the values of selectivity for system consisting of aliphatics Octane are highest. This trend is normal as expected.

(2)Selectivity diagrams are depicted in Fig. S-31 for different systems consisting of solvent 90% Dmso + 10% W. The values of selectivity at temperature 30°C and 40°C follow a similar trend as already observed for previous systems consisting of 100% Dmso and 0% W i.e. the values of selectivity remain practically unaltered.



Fig. S-30 Selectivity diagrams for system: B-H/Hep/Oct-100%Dmso+0%W at different temperatures with molecular weight of aliphatics as a parameter.

Extraction capacity of extracting Benzene for solvent Dmso also decreases as aliphatic Hexane is replaced by Heptane and further Heptane is replaced by Octane.

It is interesting to observe this nature for all the nine system variations under consideration.

Thus for example, for fixed temperature of 20° C and for fixed value of D2 = 0.3 the values of D1 for system involving Hexane, Heptane and Octance are 0.23, 0.17 and 0.02 respectively.

At temperatures 30°C and 40°C, similar observations can be made.

(ii) System: B-H/Hept/Oct-90% Dmso-10% W at three valuesof temperature with molecular weight of aliphatics as a parameter:

Distribution diagrams under different sets of conditions plotted in Fig. D.31 can be analysed as under:

(1) At 20°C and 10% W normal trend i.e."with an increase in molecular weight of aliphatic extraction capacity of solvent decreases" is observed.

(2) However at temperatures 30°C and 40°C extraction capacity of solvent Dmso for systems consisting of aliphatic Hexane are hightest than that for systems consisting of Heptane/Octane. This may be considered as abnormal trend.

(iii) System: B-H/Hept/Oct-80% Dmso-20% W at three values of temperature with molecular weight of aliphatic as a parameter:

Distribution diagrams for system B-H/Hept/Oct-80% Dmso+ 20% W at different temperature have been depicted in Fig.D-32. Critical analysis of various distribution curves indicates that the same abnormal trend which was observed for









Relative increase in the value of solubility of Benzene in extract phase and non solute -Hexane/Hept/ Oct in extract phase remains practically the same. As a result, the values of selectivity at temperatures under consideration i.e. 20°C and 40°C follow a single straight line.

However, at temperature 30°C normal trend is observed i.e. as molecular weight of aliphatics increases under otherwise identical conditions, the values of selectivity do increase. Thus for example, for a constant value of S2 = 0.5 for the system consisting of aliphatic Hexane, Heptane and Octane, the corresponding values of S1 are 0.94, 0.98 and 1.0 respectively. Thus, range of selectivity values is highest for the case under consideration.

(3) Selectivity diagrams for different systems consisting of solvent 80% Dmso and 20% water under conditions of three temperature namely 20°C, 30°C and 40°C are depicted in Fig. S-32.

It is interesting to observe that values of selectivity for a fixed value of temperature for all three temperatures under consideration follow a single straight line under different sets of conditions. Thus the values of selectivity for solute Benzene do not get alter when aliphatic are replaced in the following order i.e. Hexane is replaced by Heptane and Heptane is replaced by Octane.

It is expected that the relative decrease in solubility of Benzene in extract phase and that of non-solute Hexane/Heptane/Octane in extract phase practically remain the same. As a result the values of selectivity are expected to remain same.









5.4.0 DISTRIBUTION COEFFICIENTS FOR SOLVENTS-DMF AND DMSO

5.4.1 Effect of different parameters on the values of distribution coefficient for solvent Dmf/Dmso :

The distribution coefficient values of (m) obtained for the systems B/T/X - H/Hep/Oct-100%/90%/80%Dmf/Dmso - 0%/10%/20%W at different temperatures reported in Tables-31 and 32 have been critically analysed and effect of different parameters – anti solvent concentration, temperature, molecular weight. of aromatics and aliphatics have been critically evaluated.

(1)Effect of anti solvent concentration of water:

Referring to Tables-31 and 32 wherein the values of 'm' have been reported, the following conclusions can be drawn :-

(1)The values of distribution coefficient decreases with an increase in concentration of anti solvent water. Thus for example, in the case of first system: Benzene-Hexane- Dmf-W; with an increase in the concentration of anti solvent water from 0 % W to 20 % W at 30 °C, the values of distribution coefficient (m) decrease from 1.25 to 0.25 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration of water, the solubility of Benzene in solvent –(Dmf+W) decreases and hence the value of distribution coefficient (m). consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 % W for other two temperatures 20°C and 40 °C.

(2) The values of distribution coefficients decrease with an increase in anti solvent concentration of water, also, in the case of second system :Toluene-Hexane-Dmf-W .With an increase in the concentration of water from 0 % W to 10% up to 20 % W at 30 °C, the values of distribution coefficient (m) decrease from 1.1 to 0.557 and up to 0.25 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent

Sr.No.	System	Dist	Values	
	- · ·	20 °C	30 °C	40 °C
1	B-H-100%Dmf+0%W	1.250	1.270	1.530
2	B-H-90%Dmf+10%W	0.333	0.333	0.75
3	B-H-80%Dmf+20%W	0.187	0.250	. 0.083
4	T-H-100%Dmf+0%W	1.013	1.100	1.500
5	T-H-90%Dmf+10%W	0.165	0.557	0.560
6	T-H-80%Dmf+20%W	0.166	0.250	0.440
7	X-H-100%Dmf+0%W	1.050	1.200	-
8	X-H-90%Dmf+10%W	0.175	0.300	0.370
9	X-H-80%Dmf+20%W	0.067	0.088	0.133
10	B-Hep-100%Dmf+0%W	0.650	0.980	1.250
11	B-Hep-90%Dmf+10%W	0.504	0.610	0.709
12	B-Hep-80%Dmf+20%W	-	0.290	0.310
13	B-Oct-100%Dmf+0%W	0.750	0.900	1.150
14	B-Oct-90%Dmf+10%W	0.500	0.600	1.000
15	B-Oct-80%Dmf+20%W	0.200	0.200	0.375

Table-31Values of Distribution coefficients for systemB/T/X-H/Hep/Oct-Dmf-W at different sets of conditions

Sr.No.	B/T/X-H/Hep/Oct System	-Dmso-W at different sets of conditions Distribution coefficients Values			
		20 °C	30 °C	40 °C	
1	B-H-100%Dmso+0%W	0.750	0.800	0.815	
2	B-H-90%Dmso+10%W	0.350	0.350	0.400	
3	B-H-80%Dmso+20%W	0.050	0.050	0.100	
. 4	T-H-100%Dmso+0%W	0.500	0.600	0.833	
5	T-H-90%Dmso+10%W	0.163	0.163	0.288	
6	T-H-80%Dmso+20%W	0.025	0.025	0.101	
7	X-H-100%Dmso+0%W	0.020	0.210	0.600	
8	X-H-90%Dmso+10%W	0.01	0.025	0.300	
9	X-H-80%Dmso+20%W	0.005	0.008	0.100	
10	B-Hep-100%Dmso+0%W	0.550	0.575	0.650	
11	B-Hep-90%Dmso+10%W	0.300	0.400	0.525	
12	B-Hep-80%Dmso+20%W	0.175	0.250	0.400	
13	B-Oct-100%Dmso+0%W	0.400	0.450	0.500	
14	B-Oct-90%Dmso+10%W	0.250	0.300	0.350	
15	B-Oct-80%Dmso+20%W	0.045	0.110	0.150	
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Table 32Values of Distribution coefficients for systemT/X-H/Hep/Oct-Dmso-W at different sets of condition

concentration water, the solubility of Toluene in the solvent decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W 10%W and 20 % W for the temperatures 20°C and 40 °C Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 % W for the temperatures 20°C and 40 °C

(3)The values of distribution coefficient decrease with an increase in anti solvent concentration of water in the case of third system: Xylene-Hexane- Dmf-W .With an increase in the concentration of water from 0 % W to 10% and up to 20 % W at 30 °C, the values of distribution coefficient m decrease from 1.2 to 0.3 and up to 0.088 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of Xylene in the solvent decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures . 20° C and $40 ^{\circ}$ C

(4)The values of distribution coefficient decrease with an increase in anti solvent concentration of water in the case of fourth system: Benzene-Heptane- Dmf-W ,with an increase in the concentration of water from 0 % W to 10% and up to 20 % W at $30 °^{\rm C}$ the values of distribution coefficient m decrease from 0.98 to 0.61 and up to 0.29 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of Benzene in solvent in presence of aliphatic Heptane also decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 % W for the temperatures . 20°C and 40 °C

(5)The values of distribution coefficient decreases with an increase in concentration of anti solvent water Thus for example in the case of system :Benzene-Octane-Dmf-W. With an increase in the concentration of water from 0 % W to 10% and up to 20 % W at 30 °C, the values of distribution coefficient m decrease from 0.9 to 0.6 and up to 0.2 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent

concentration water, the solubility of Benzene in the solvent in presence of aliphatic Octane also decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%, 10% and 20% for the temperatures 20 °C and 40 °C.

(6)The values of distribution coefficient decrease with an increase in concentration of anti solvent water. Thus for example in the case of sixth system :Benzene-Hexane- Dmso-W at 30 °C, with an increase in the concentration of water from 0 % to 10% and up to 20 % the values of distribution coefficient (m) decrease from 0.800 to 0.350 and up to 0.050 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of aromatics in the solvent decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures $20^{\circ}C$ and $40^{\circ}C$

(7) The values of distribution coefficient decreases with an increase in anti solvent concentration of water also in the case of seventh system :Toluene-Hexane-Dmso-W .With an increase in the concentration of water from 0 % to 10% and up to 20 % at 30 °C the values of distribution coefficient (m) decrease from 0.6 to 0.163 and up to 0.025 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration of water, the solubility of Toluene in the solvent decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures . $20^{\circ}C$ and $40^{\circ}C$

(8)The values of distribution coefficient decreases with an increase in anti solvent concentration of anti solvent water in the case of eighth system :Xylene-Hexane-Dmso-W .With an increase in the concentration of water from 0 % to 10% and up to 20 % at 30 $^{\circ C}$ the values of distribution coefficient (m) decrease from 0.21to 0.025 and up to 0.008 respectively.

Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of Xylene, in the solvent decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures $20^{\circ}C$ and $40^{\circ}C$

(9)The values of distribution coefficient decreases with an increase in anti solvent concentration of water in the case of ninth system :Benzene-Heptane- Dmso-W. With an increase in the concentration of water from 0 % to 10% and up to 20 % at $30 \,^{\circ C}$ the values of distribution coefficient m decrease from 0.575 to 0.400 and up to 0.250 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of Benzene in the solvent in the presence of aliphatic Heptane also decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures 20°C and 40 °C

(10) The values of distribution coefficient decreases with an increase in anti solvent concentration of anti solvent water in the case of tenth system :Benzene-Octane-Dmso-W With an increase in the concentration of water from 0 % to 10% and up to 20 % at 30 $^{\circ C}$ the values of distribution coefficient (m)decrease from 0.45 to 0.3 and up to 0.11 respectively. Hence addition of water appears to have substantial effect on the values of (m). As pointed out elsewhere with an increase in anti solvent concentration water, the solubility of Benzene in the solvent in presence of aliphatic Octane also decreases and hence the values of (m) consequently decreases under otherwise identical conditions. Similar trend is observed for other anti solvent concentrations namely 0%W, 10%W and 20 %W for the temperatures 20°C and 40 °C

(II)Effect of Temperature :

Referring to data reported in Tables -31 and 32 where in values of distribution coefficient have been reported the following conclusions can be drawn.

and up

(1) With an increase in temperature from 20 °C to 30 °C to 40 °C the values of distribution coefficient increase.

In general, this conclusion can be drawn for all the systems involving Benzene / Tofuene/Xylene – Hexane / Heptane/ Octane – Dmf + w under different sets of conditions.

(2) However, effect of temperature in the temperature range 20 °C to 30 °C appears to be relatively less than the temperature range 30 °C to 40 °C.

Thus for example, for system Benzene-Hexane- 100 %Dmf + 0 % W, when temperature is increased form 20 °C to 30 °C the value of distribution coefficient increases very marginally from 1.25 to 1.27. However for the same system. when temperature is increased from 30 °C to 40 °C, the volume of distribution coefficient increases from 1.27 to 1.53. Similar observation can be made for system T-H-100 % Dmf + 0% W where in when temperature is increased from 20 °C to 30 °C and up to 40 °C, the values of distribution coefficient increase from 1.01 to 1.1 and up to 1.5 respectively.

(3) For system Xylene – H – 80 % Dmf + 20 % W, effect of temperature appears to be stringent where in when temperature is increased from 20 °C to 40 °C, the value of distribution coefficient increases from 0.067 to .133. Thus as could be seen effect of temperature- just for 10 °C rise in temperature, distribution coefficient value gets doubled which can be considered as exception. The other exceptions being for wherein system. T-H-90 % Dmf + 10 % W and alsoT-H-80%Dmf+20 %W, the values distribution coefficient increase by a factor of 3. The values of m increase from 0.16 to 0.44 - 0.56.

(4) Excluding above observation for all the other systems under consideration having different sets of conditions effect of temperature on the value of distribution coefficient appears to be marginal in temperature range 20 °C to 30 °C and relatively more in the temperature range 30 °C to 40 °C.

(5) Effects of anti solvent concentration on the values of m has been already discussed in detail which appears to be more stringent in companion to temperature effect.

Hence the value of distribution coefficient appear to be a strong function of anti solvent concentration and a weak function of temperature this conclusions are likely to be very helpful while developing generalized correlation for the values of Hands constant k.

(6) For different systems involving solvent Dmso, effect of temperature on the values of distribution coefficients follow similar trend which was observed in the case of different systems involving solvent Dmf. Effect of temperature in the temperature range 20 °C to 30 °C is marginal and effects of temperature in the temperature range 30 °C to 40 °C appear to be relatively more.

(7) Thus for example for system, T-H-100 % Dmso + 0 % W, with an increase in temperature from 20 °C to 30 °C and up to 40 °C the values of distribution coefficients increase from 0.5 to 0.6 and up to 0.833. Similar observation can be made for the system B-H-100% Dmso + 0 % W ,where in when temperature is increased from 20 °C to 30 °C and up to 40 °C values of distribution coefficients increase from 0.55 to 0.575 and up to 0.65 respectively.

(8) For different systems containing 80%Dmso+20 % W as anti solvent, effect of temperature when temperature is increased from 20 °C to 40 °C appears to be substantially higher. The values of distribution coefficient increase by a factor of 3 to 4. Thus for example, for system B-H-80 % Dmso + 20 % W when temperature is increased from 20 °C to 40 °C, the value of m increase from 0.05 to 0.1. For systems T-H-80 % Dmso + 20 % W, the value of m increase by a factor of 4 from 0.025 to 0.1 when temperature is increased form 20 °C to 40 °C. This observation can be considered as exception.

(9) Excluding above exceptions, the normal trend for effect of temperature on the values of m appear to be as under.

When temperature is increased from 20 °C to 30 °C effect of temperature is marginal and when temperature is increased from 30 °C to 40 °C its effect on the values of m appear to be relatively more.

(10) For different systems involving second solvent which has been used in this investigation i.e. Dmso also follow same trends like first solvent Dmf and this trend is as under.

Effect of anti solvent concentration on the values of m appears to be very stringent in comparison to effect of temperature on the value of m.

(III) Effect of molecular weight of aromatics:

Referring to the same Tables -31 to 32 where in values of m have been reported for solvents Dmf and Dmso respectively the following conclusions can be drawn.

(1) When in a particular system Benzene is replaced by Toluene and Toluene is replaced by Xylene under otherwise identical conditions, the values of distribution coefficient (m) decrease with an increase in molecular weight of aromatics. Thus for example for solvent Dmf at 20 °C and anti solvent concentration being 20 %, the values of 'm' for systems consisting of Benzene, Toluene and Xylene are 0.187, 0.166 and 0.067 respectively. The corresponding values of 'm' for systems consisting of Benzene, Toluene and Xylene and 0.005 respectively.

In general ,similar trend is observed for other systems involving solvents Dmf and Dmso.

(2) Some exception to the above normal trend are listed below:-

(i) For system, consisting of solvent Dmf at temperature 30 °C and anti solvent concentration of 10 % W, the value of m for systems consisting of Benzene, Toluene

and Xylene are 0.33, 0.55 and 0.3 respectively. Thus the value of 'm ' for system consisting of Toluene is highest.

(ii) Further at temperature of 40 C and anti solvent contraction of the order of 20 % W the value of 'm' for different systems consisting of Benzene, Toluene and Xylene for solvent Dmf are 0.083, 0.44 and 0.133 respectively. Thus the value of 'm' for system consisting of Toluene appears to be highest.

(iii) For solvent Dmso, at temperature 40 °C and anti solvent concentration of 20 % W ,the values of 'm' for systems consisting of Benzene, Toluene and Xylene appear to remain practically a constant value being 0.1 for all the three cases.

(iv) For system consisting of solvent Dmso for anti solvent concentration of 10 %W and 40 °C values of 'm' for systems involving Toluene and Xylene also remain constant in the range of 0.29 to 0.3 as if no effect of molecular weight.

(v) Thus the values of distribution coefficient for systems involving aromatics Toluene appear to be higher than for the system involving aromatics- Benzene and Xylene.

(IV) Effect of molecular weight of Aliphatics:

Referring to same Tables -31 and 32 where in value of m have been reported for solvent Dmf and dmso respectively. One can observe following important conclusions.

(1) When in a particular system Hexane is replaced by Heptane and Heptane is replaced by Octane, under otherwise identical conditions the values of distribution coefficients decrease with an increase in molecular weight of aliphatics. Thus for example for solvent Dmf at temperature 30 °C and anti solvent concentration of 0 % W, the value of 'm' for systems consisting of Hexane, Heptane and Octane are 1.2, .98 and 0.9 respectively. Further in the case of solvent Dmso also at temperature 30 °C and anti solvent concentration of 0 % W, the value of for system consisting of Hexane , Heptane and Octane are 0.80, 0.575 and 0.45 respectively. Thus in general, similar trend is observed for other systems involving solvents Dmf and Dmso.

(2) For the case under consideration wherein effect of molecular weight of aliphatic is being considered, there are also some exceptions. Some of these exceptions are listed below:-

(i) For system consisting of solvent Dmf at temperature 20 °C and anti solvent concentration 10 % W, the values of 'm' for different systems consisting of Hexane, Heptanes and Octane for solvent Dmf are 0.333, 0.504 and 0.500 respectively.

(ii) Further at temperature 30 °C and anti solvent concentration of 10 % W, the values of 'm' for different systems consisting of Hexane, Heptanes and Octane for solvent Dmf 0.33, 0.61 and 0.60 respectively.

(iii) For system consisting of solvent Dmso at temperature 40 $^{\circ}$ C and anti solvent concentration of 10 % W, the values of 'm' for systems consisting of Hexane, Heptane and Octane are 0.400, 0.525 and 0.35 respectively.

(iv) Further at temperature 20 °C and anti solvent concentration of 20 % W and solvent being Dmso ,the value of 'm' for different systems consisting of Hexane , Heptanes and Octane are 0.05, 0.175 and 0.045 respectively.

(v) Thus the values of distribution coefficient for systems involving aliphatic Heptane under different sets of conditions appear to be higher than for the systems involving aliphatics – Hexane and Octane.

5.5.0 CORRELATING QUATERNARY LIQUID-LIQUID PHASE EQUILIBRIUM DATA

An attempt has been made in this investigation to correlate quaternary liquidliquid phase equilibrium data in terms of equivalent ternary equilibrium data by means of modified Hand's plots. ⁽¹³⁶⁾

5.5.1 Liquid-liquid Equilibrium data and four Tie line data correlations:-

For testing consistency of liquid-liquid equilibrium data, the following different correlations are available in the literature.

- (i) Bachman correlation 134
- (ii) Hand's correlation 132
- (iii) Campbell correlation¹³³

(iv) Othmer and Tobias correlation ¹³⁵

1.	Bachman correlations is a plot of	a_1 Vs. a_1/b_2
2.	Hand's correlation is a plot of	H_1 Vs. H_2
3.	Campbell correlation is a plot of	C_1 Vs. C_2
4.	Othmer correlation is a plot of	O1 Vs. O2

Where notations are as under:-

$a_1 = X(_{DE} + _{WE,)}$	b ₂ =solute fraction
$O = 1 - a_1 / a_1$	$O_2 = 1 - b_2 / b_2$
$H_1 = \log X_{AE} / (X_{SE} + X_{WE}),$	H ₂ =logX _{AR} /X _{A'R}
A=Aromatics,	S=Solvent,
W=Water,	A'=Co-solvent
$C_1 = X_{PE}$	$C_2 = X_{PP}$

The liquid-liquid equilibrium data obtained in this investigation can be correlated by this correlation and its consistency can be checked.

5.5.2 Checking consistency of Tie line data:

Initially, consistency of the data has been tested for two systems namely:

B-Hex-Dmf-W and B-Hex-Dmso-W at 30°C by using all above correlations .The parameters required for obtaining these plots are reported in Tables- I and - II and are plotted in Figures I and II.

Following Generalised observations can be made from these figures under consideration.:-

{1). All correlation results in a straight line plot with water concentration as a parameter involving three straight lines for each correlation.

(2) Deviation from straight line plots for different straight lines appear to be least in case of Hand's correlation.

The value of slopes and intercepts for Campbell correlation, Othmer Tobias correlation and Bachman Correlation do not follow a fixed trend. For example, lines in case of Campbell correlation cross each other. Further various line in Bachman correlation also crossed each other. In case of Othmer and Tobias correlation, different lines for systems involving solvent Dmf are with a steep slope and that involving for the system for the solvent Dmso is having values of slope very less As a result some lines are practically parallel to X-axis.

(3) It is interesting to observe that with anti solvent concentration of water as a parameter, three parallel lines with distinct intercepts are obtained only for Hand's plots

Parameters required for four Correlations under consideration for the system B-H-Dmf + W at 30° C

Table-I

	Camp	Dell	Uthmer a	nd Tobia's	Batch	man		Hand's	
	Correl	ation	Corr	elation	Correl	ation		Correlation	•
%Dmf+%W	C	3	01	03	al	a1/b1	H	H2	
	0.0500	0.0150	0.3072	0.0811	0.7650	0.8270	-1.1840	-1.6650	
• .	0.0800	0.0420	0.4184	0.1628	0.7050	0.8198	-9.4500	-1.2810	
100+0	0.1000	0.0800	0.5385	0.2500	0.6500	0.8125	-0.8120	-1.0520	
	0.0420	0.0150	0.3072	0.2658	0.7650	0.9684	-1.2600	-1.6400	•
	0.0220	0.0100	0.3333	0.1696	0.7500	0.8772	-1.5320	-1.9310	
	0.0600	0.0400	0.3605	0.6139	0.7350	1.1862	-1.0880	-1.1610	
	0.0500	0.2650	0.1765	0.4493	0.8500	1.2319	ł		
90+10	0.1400	0.4670	0.4925	1.0408	0'6700	1.3673	, 1	3	
• •	0.2400	0.6970	0.6694	2.6630	0.5990	2.1941	-0.8350	-0.4150	
	0.0270	0.1350	0.1038	0.1765	09060	1.0659	-0.6500	-0.2000	
	0.4520	0.7530	1.2883	3.4643	0.4370	1.9509	-0.5480	-0.0190	
	0.0300	0.1700	0.0444	0.2821	0.9575	1.2276	-0.3000	-0.2000	
			,				-0.1000	0.4350	, .
80+20	0.0775	0.3900	0.0959	0.7699	0.9125	1.6150			•
	0.0875	0.4300	0.1050	0.8692	0.9050	1.6916	-1.5080	-0.6630	
-	0.2050	0.7100	0.2658	2.5088	0.7900	2.7719	-1:0750	-0.1730	
	0.1462	0.5700	0.1783	1.3529	0.8487	1.9969	-0.5850	0.3960	
	ı	•	ı	ı	•	•.	-0.7630	0.1270	
			-				* •	•	
Foot note :	C1=X _{BE}	C2=X _{BR}		$O2=(1-b_2)/b_2$	2a1=X _{DE+WE}	H	C/ary/)	(A'R	
O1=(1-a,)/a,	a1=XDE+WE	$a1/b1 = X_{\text{DE+W}}$	E/ YHB	H1=loeXAE	V(XSE + XW)	E)			

	L-Dmso + W at 30° C	Hand's Correlation
· [for the system B-H	Batchman Correlation
Table-II	Correlations under consideration	Othmer and Tobia's Correlation
	Parameters required for four	Campbell Correlation

••

%Dmso+%W	CI	C	0	03	a1	a1/b1	HI	H2	
	0.0800	0.1500	0.1110	0.2190	0.9000	1.0970	-0.6400	-0.7500	Γ
	0.1570	0.2561	0.2580	0.3690	0.7950	1.0890	-0.0500	-0.4500	
100+0	0.2380	0.3710	0.3030	0.6550	0.6970	1.1530.	-0.4200	-0.2000	-
	0.3680	0.4470	0.8110	1.0830	0.5520	1.1500	-0.2900	-0.0200	
	0.4450	0.5040	1.5510	1.7770	0.3920	1.0880	-0.0500	-0.6400	
	0.0500	0.1650	0.0580	0.2190	0.9450	1.1520	ı	٠	•
	0.0875	0.3025	0.1050	0.4700	0.9050	1.3300	•		
90+10	0.1150	0.4050	0.1280	1.0720	0.8860	1.8360	-1.2830	-0.6960	• •
-	0.1500	0.5550	0.1900	1.3520	0.8400	1.9700	-1.0170	-0.3510	
	0.1750	0.6700	0.2270	2.2250	0.8150	2.6290	-0.8860	-0.0760	
	0.0080	0.2570	0600.0	0-3660	0.9910	1.3530	-0.7490	0.1140	
	0.0170	0.4650	0.0180	0.8790	0.9820	1.8450	-0.6690	0.3330	
_	t	н 1 1 1	•	•	, 1,	1	-0.9500	-0.2400	
80+20	0.0220	0.6720	0.0240	2.1250	0.9760	3.0500	-2.3950	-0.8010	
	0.0650	0.8450	0.0710	6.6920	0.9330	7.1760	-2.0960	-0.4540	
	1	1 	1		1	ł	-1.7690	-0.0580	
-	•	ı	1	1	I	1	-1.6570	0.3210	
	•	١	•	t .	ŧ	ı	-1.9150	-0.2390	
									1
Foot note :	C1=X _{BE}	C2=X _{BR}		$O2=(1-b_2)/b_2$	2al=X _{DE+WE}	H	2=logX _{AR} /X _{A'R}		
O1=(1-a ₁)/a ₁	al=XDE+WE	al/bl= X _{DE+W}	E/ XHR	H1=logXAE	/(XSE + XW	(E)			





in case of both systems under consideration. For remaining correlations, such Generalised observations are not feasible.

(4).Hence, it is expected that under different sets of operating conditions for the system B-H-Dmf-W and B-H-Dmso-W, a set of different parallel lines are likely to be obtained with distinct intercepts and single value of slope at a fixed temperature. Hence, for obtaining Generalised correlation to correlate liquid-liquid equilibrium data, Hand's plot- wherein quaternary systems have been converted to equivalent ternaries- appears to be more presentative and sound than remaining plots obtained for other correlations.

(5). Therefore consistency of liquid-liquid equilibrium data obtained in this investigation has been tested only by by modified Hand's correlation for remaining 28 systems under consideration under different sets of conditions.

5.5.3 Hand's correlation modified for quaternary liquid-liquid phase equilibrium data:-

Hence processing of liquid-liquid equilibrium data for the following five systems involving solvent Dmf and additional five systems involving solvent Dmso at three temperature 20° , 30° and 40° C along with variation in water concentration 0%, 10% and 20% as a parameter for both solvents has been performed.

For solvent Dmf

For solvent Dmso

(i)	B-H-Dmf-W
(ii)	T-H-Dmf-W
(iii)	X-H-Dmf-W
(iv)	B-Hep-Dmf-W
(v)	B-Oct-Dmf-W

vi)	B-H-Dmso-W
vii)	T-H-Dmso-W
viii)	X-H-Dmso-W
ix)	B-Hep-Dmso-W
x)	B-Oct-Dmso-W

5.5.4 Basis for Mathematical Modeling:

Though the systems under consideration are quaternary in nature, if one considers solvent as a dual solvent consisting of solvent + anti solvent, then all the systems under consideration can be reduced to ternary systems. Data can be represented in terms X_{BE} , X_{HE} , and X_{SE} for Extract phase and X_{BR} , X_{HR} & X_{SR} for raffinate phase for a fixed concentration of anti solvent.

It has been observed that the values of equilibrium compositions in Extract phase and raffinate phase could be correlated in the form of an equation of type given by: -

 $[(X_{AE}) / (X_{SE} + X_{WE})] = (k) [X_{AR} / X_{A'R}]^{n}$

Where,

 X_{AE} = wt. frac. of aromatic in extract. X_{SE} = wt. frac. of solvent in extract phase. X_{WE} = wt.frac. of water in extract phase. X_{AR} = wt. frac. of aromatic in raffinate. X_{AR} = wt. frac. of aliphatic in raffinate.

This equation can be considered as modified Hand's plots wherein quaternary liquid-liquid phase equilibrium data has been converted to equivalent ternary liquid-liquid phase equilibrium data.

Thus if one plots a graph of log[$X_{AR} / X_{A'R}$] Vs.Log [$X_{AE} / (X_{SE} + X_{WE})$] is expected to result in a straight line having intercept as log k and slope as n.

5.5.5 Correlating equilibrium properties in terms of straight line plots: -

All the values of liquid-liquid phase equilibrium data obtained in the present investigation has been plotted in terms of straight line plots in Figures (H-1) to (H-10) as per following details: -

Figure (H-1): Straight line plots for systems – B-H-Dmf-Water with temperature and anti solvent concentration as parameters.

Figure (H-2): Straight line plots for systems – T-H-Dmf-Water with temperature and anti solvent concentration as parameters.

Figure (H-3): Straight line plots for systems – X-H-Dmf-Water with temperature and anti solvent concentration as parameters.

Figure (H-4): Straight line plots for systems – B-Hep-Dmf-Water with temperature and anti solvent concentration as parameters.

Figure (H-5): Straight line plots for systems – B-Oct-Dmf-Water with temperature and anti solvent concentration as parameters.

Figure (H-6): Straight line plots for systems – B-H-Dmso-Water with temperature and anti solvent concentration as parameters.

Figure (H-7): Straight line plots for systems – T-H-Dmso-Water with temperature and anti solvent concentration as parameters.

Figure (H-8): Straight line plots for systems – X-H-Dmso-Water with temperature and anti solvent concentration as parameters.

		for sy	stem :B-H-D	mf-W		
Temp.	. 0%	6W	109	%W -	209	%W
	·H1	H2	H1	H2	H1	H2
··· · · · ·						
	•		· · · · ·		• • • • • •	
20 °C	-1.204	-1.568	-0.319	0.382	-1.551	-0.594
	-0.863	-1.171	-1.060	-0.474	-1.130	-0.093
	-0.746	-0.929	-0.432	0.245	-0.878	0.187
	-0.054	-0.804	-0.127	0.578	-0.380	0.783
	-0.351	-0.632	-0.513	0.075	-0.587	0.437
30 °C	-1.184	-1 665	-0.835	-0.415	-1 508	-0.663
	-9.450	-1.281	-0.650	-0.200	-1.075	-0.173
•	-0.812	-1.052	-0.548	-0.019	-1.017	-0.095
	-1.260	-1.640	-0.300	-0.200	-0.585	0.396
	-1.532	-1.931	-0.100	0.435	-0.763	0.127
	-1.088	-1.161	-			-
40 °C	-0.728	-1.229	-0.692	-0.573	-0.950	-0.326
	-0.493	-0.779	-0.413	-0.118	-1.337	0.035
	-0.454	-0.732	-0.157	0.298	-1.187	0.310
×	-0.625	-0.966	0.160	0.720	-1.650	-0.560
	-0.783	-1.041	0.019	0.486	*	

Tables .33Parameters H1 and H2 for Hand's plotsfor system :B-H-Dmf-W

Tables . 34Parameters H1 and H2 for Hand's plotsfor system :T-H-Dmf-W

Temp.	0%W		109	6W	20%W	
-	H1	H2	H1	H2	H1	H2
20 °C	-0.908	-0.970	-1.051	-0.024	-1.630	-0.404
	-0.605	-0.641	-1.073	0.120	-1.375	-0.060
	-0.331	-0.530	-0.944	0.257	-1.026	0.307
-	-0.485	-0.605	-1.170	-0.100	-0.949	0.645
	-0.730	-0.785	-0.829	0.300	-1.171	0.508
30 °C+	-1.356	-1.643	-1.050	-0.614	-1.086	-0.050
•	-0.954	-1.230	-0.812	-0.385	-0.946	0.022
	-0.724	-0.892	-0.725	-0.162	-0.903	0.235
	-0.623	-0.748	-0.450	0.155	-0.749	0.507
	-0.445	-0.533	-0.200	0.464	-0.818	0.359
40 °C	-0.706	-0.924	-0.770	0.153	-1.500	-0.491
	-0.806	-1.038	-0.321	0.461	-1.052	-0.040
	-1.090	-1.306	0.035	0.820	-0.468	0.507
	-0.973	-1.120	-0.882	-0.216	-1.269	-0.195
	-0.771	-0.979	-0.517	0.317	-0.709	0:248

		101 55	300m · 27-11-1		· · · · · · · · · · · · · · · · · · ·	
Temp.	0%	6W	109	%W	20%W	
-	H1	H2	H1	H2	H1	H2
		- -	•		, *	1 - A
			•	, ,	· · ·	· · ·
20 °C	-1.462	-1.685	-1.883	-1.022	-1.796	0.23
	-0.899	-0.994	-1.218	-0.209	-1.252	0.401
	-0.66	-0.691	-0.82	0.328	-1.471	0.082
-	-1.099	-1.228	-1.439	0.511	-1.364	0.235
•	-0.763	-0.888	-0.98	0.058	-1.611	-0.073
•	•		• •			
30 °C	-0.878	-1.277	-1.249	-0.542	-1.903	-0.516
	-0.728	-0.927	-1.003	-0.23	-1.508	-0.178
	-0.557	-0.698	-0.678	0.176	-1.297	0.112
-	-0.657	-0.834	-0.6	0.272	-1.211	0.282
	-0.616	-0.745	-0.824	-0.18	-0.81	0.649
40 °C	-1.23	-1.48	-0.631	0.297	-1.354	-0.342
	-1.08	-1.31	-1.237	-0.501	-1.166	-0.108
	-0.96	-1.17	-0.827	-0.117	-1.04	0.247
	-0.81	-1.0	-0.77	0.079	-1.09	0.075
	-0.650	-0.8	-0.67	0.123	-1.25	-0.013

	្រា	Fabl	es .3	5		
Parameters	H1	and	H2	for	Hand's	plots
for S	Syste	em :	X-F	I-D	mf-W	-

Tables . 36Parameters H1 and H2 for Hand's plotsfor system B-Hept-Dmf-W

		101 0,0				
Temp.	0%W		10%	6W	20%W	
-	H1	H2	H1	H2	H1	H2
·			0.00		0.600	0.050
20 °C	-1.612	-1.613	-0.764	-0.283	-0.650	0.350
	-1.423	-1.378	-0.942	-0.594	-0.950	0.100
	-1.170	-0.994	-0.427	0.126	-1.050	-0.090
-	-1.120	-1.160	-0.629	-0.031	-1.220	-0.190
	-1.233	-1.079	-0.528	0.055	-1.340	-0.370
30 °C	-0.754	-0.831	-0.730	-0.469	-0.741	0.102
	-1.137	-1.255	-0.533	-0.108	-1.213	-0.489
	-0.878	-0.971	-0.252	0.051	-0.863	-0.106
	-1.557	-1.959	-0.625	-0.278	-0.638	0.328
	-1.301	-1.498	-0.383	-0.033	-0.328	0.477
40 °C	-1.425	-1.653	-0.875	-0.643	-1.071	-0.176
	-1.176	-1.457	-0.453	-0.173	-0.513	0.307
	-0.920	-1.297	-0.147	0.159	-0.278	0.660
	-0.858	-1.212	-0.636	-0.377	-0.730	0.063
	-0.645	-1.084	-0.290	-0.002	-0.393	0.465

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		rarameters 1 for sy	stêm B-Oct-J	or Hand's plo Dmf-W	TS .	
Temp.	09	⁄oW	10	%W	209	%W
	H1	H2	H1	H2	H1	H2
						· ·
·		,	:			
. *			• •	· .		
- 、		• •				•
	,					
						۰. . :
20 °C	-1.357	-1.371	-0.820	-0.382	-1.009	-0.087
	-0.931	-0.937	-1.070	-0.582	-1.666	0.747
	-0.827	-0.640	-1.227	-0.682	-1.412	-0.471
	-0.581	-0.489	-0.904	-0.494	-0.784	0.261
	-0.510	-0.364	-0.693	-0.285	-0.544	0.494
	-0.404	-0.264	-	-	- .	• • • • • • •
	-					0
		*				5.
. ,		*				
30 °C	-0.771	-0.847	-1.062	-0.690	-1.111	-0.271
	-0.623	-0.749	-0.796	-0.449	-0.885	0.046
	-0.545	-0.555	-0.622	-0.269	-0.584	0.427
	-0.470	-0.445	-0.372	0.009	-0.985	-0.108
•	-0.399	-0.329	-0.274	0.137	-0.717	0.230
				•		1 de la
			•	·		2 19 18 - 1 1 19 18 - 1 1 19 19 19 19 19 19 19 19 19 19 19 19 19
		•.	· .	· · · · · ·		· · ·
• •	• .	-				
			- ,			4
40 °C	-0.918 [`]	-1.013	-0.880	0.888	-1.230	-0.860
	-0.851	-1.025	-0.650	-0.579	-1.130	-0.576
	-0.582	-0.746	-0.308	-0.314	-0.738	-0.309
	-0.581	-0.695	-0.086	-0.092	0.666	-0.217
	-0.360	-0.458	-0.074	0.097	-0.939	-0.430

 Tables .37

 Parameters H1 and H2 for Hand's plots

 for system B. Oct Def W

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· .		10133	Stelli D-II-DI			
Temp.	· 0%	W ·	109	%W	209	%W
	H1	H2	<u>H1</u>	<u>H2</u>	H1	H2
	3		, •		· .	
	•		3			
20 °C	-0.625	-0.459	-0.6	1.3	-1.698	-0.026
	-0.510	-0.298	-0.821	-255	-2	-0.48
,	-0.450	-0.130	-0.86	-0.0048	-1.283	-0.564
	-0.394	-0.062	-0.55	0.764	-1.161	0.949
	-0.315	40.042	-0.245	-0.28	н во с	-
	-0.490	-0.235	-	-	•	
30 °C	-0.64	-0.75	-1.283	-0.696	-2.395	-0.801
	-0.05	-0.45	-1.017	-0.351	-2.096	-0.454
	-0.42	-0.2	-0.886	-0.076	-1.769	-0.058
	-0.29	-0.02	-0.749	0.114	-1.657	0.321
·. · ·	-0.05	-0.64	-0.669	0.333	-1.915	-0.239
			-0.950	-0.240	-	-
40 °C	-0.53	-0.58	-0.922	-0.820	-1.87	0.770
	-0.45	-0.28	-0.670	-0.270	-1.638	-0.252
-4	-0.3	-0.17	-0.742	-0.129	-1.52	-0.011
	-0.13	-0.33	-0.820	-0.748	-2.184	-1.104
	-0.62	-0.8	-0.490	-0.149	-1.736	-0.465

Table.38
Parameters H1 and H2 for Hand's plots
formation D U Drago W

Table. 39 . Parameters H1 and H2 for Hand's plots for System : T-H-Dmso-W

Temp.	0%	6W .	109	6W	209	6W
-	H1	H2	H1	H2	H1 ,	H2
		0. 41 m		0.000		
20 °C	-0.801	-0.417	-1.088	0.271	-2.000	-0.382
	-0.447	0.170	-0.976	0.383	-1.698	0.287
	-0.360	0.333	-0.864	0.670	-1.650	0.379
	-0.631	-0.099	-1.278	0.044	-1.450	0.762
	-0.677	-0.248	-1.420	-0.195	-1.837	-0.039
	-0.526	0.025		-	·*	
30 °C	-0.682	-0.397 ·	-1.340	-0.508	-2.092	-0.514
	-0.906	-0.849	-1.275	-0.267	-1.823	-0.089
	-0.490	-0.018	-1.136	-0.107	-1.698	0.314
	-0.850	-0.700	-0.700	0.745	-1.400	0.748
	-0.749	-0.489	-0.818	0.474	-1.952	-0.284
	-0.630	-0.300		-	-1.734	0.119
40 °C	-0.510	-0.405	-0.963	-0.101	-1.571	-0.498
	-0.440	2.262	-0.780	0.238	-1.346	-0.054
	-0.318	-0.046	-0.563	0.799	-1.179	0.280
	-0.240	0.070	-0.853	0.074	-0.940	0.714
	-0.422	-0.338	-0.662	0.584	-1.423	-0.264
	-0.370	-0.150			· · ·	

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. 1.1.

0%	6W	109	%W	20	%W
H1	H2	H1	H2	H1	H2
·	· ·	÷			
-1.760	-0.124	-2.740	-0.089	-3.067	0.005
-1.681	0.100	-2.693	0.206	2.880	0.293
-1.371	0.437	-2.650	0.246	-2.694	0.626
-1.600	0.190	-2.517	0.471	-2.518	1.040
-1.500	0.390	-2.392	0.739	-2.900	-0.271
-1.565	0.293	- .	-	-	••• .
-1.019	-0.193	-2.088	0.014	-2.819	-0.301
-0.900	0.222	-1.991	0.029	-2.596	0.188
-0.861	0.313	-1.813	0.424	-2.450	0.53
-1.130	-0.300	-1.704	0.64	-2.690	-0.052
-0.979	-0.018	-2.179	-0.286	-2.510	0.348
-0.915	-0.600	-1.756	-1.255	-1.836	-1.108
-0.835	-0.501	-1.586	-1.003	-1.732	-0.903
-0.770	-0.350	-1.377	-0.623	-1.625	-0.648
-0.693	-0.234	-1.663	-1.113	-1.784	-0.996
-0.617	-0.045	-1.470	-0.838	-1.677	-762.000
-0.640	-0.120	-		. ••	
	0% H1 -1.760 -1.681 -1.371 -1.600 -1.500 -1.565 -1.019 -0.900 -0.861 -1.130 -0.979 -0.915 -0.835 -0.770 -0.693 -0.617 -0.640	0%W H1 H2 -1.760 -0.124 -1.681 0.100 -1.371 0.437 -1.600 0.190 -1.500 0.390 -1.565 0.293 -1.019 -0.193 -0.900 0.222 -0.861 0.313 -1.130 -0.300 -0.979 -0.018 -0.915 -0.600 -0.835 -0.501 -0.770 -0.350 -0.693 -0.234 -0.617 -0.045 -0.640 -0.120	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table.40 Parameters H1 and H2 for Hand's plots for system X-H-Dmso-W

Table. 41Parameters H1 and H2 for Hand's plotsfor system B-Hept-Dmso-W

		101 0901	viii is interpt i			000/ 337			
Temp.	0%	W	10%	6W	20%	6W			
	H1	H2	H1	H2	H1	H2			
9.2 2	* -								
20 °C	-0.850	-0.512	-1.380	-0.716	-1.646	-1.110			
	-0.700	-0.352	-1.180	-0.421	-1.379	-0.540			
-	-0.770	-0.440	-1.050	-0.195	-1.259	-0.361			
	-0.807	-0.097	-0.920	-0.019	-1.157	-0.170			
	-0.478	-0.024	-0.800	-0.219	-1.090	-0.050			
	· •	· •	-0.700	-0.373	-1.205	-0.217			
		•							
30 °C	-0.778	-0.391	-1.100	0.651	-1.580	-1.146			
•	-0.670	-0.320	-0.906	-0.298	-1.300	-0.654			
	-0.616	-0.209	-0.716	-0.104	-1.121	-0.396			
	-0.544	-0.090	-0.598	-0.218	-0.905	-0.054			
	-0.380	0.110	-0.450	0.366	-0.727	0.270			
	-0.307	0.195	-	-		-			
40 °C	-751.000	-0.548	-1.220	-1.070	-1.150	0.824			
	-0.629	-0.329	-0.998	-0.685	-1.271	-1.046			
	-0.450	-0.056	-0.638	-0.143	-1.050	-0.613			
	-0.301	0.210	-0.350	0.339	-0.745	-0.173			
	-0.390	0.060	-0.483	0.090	-0.567	0.150			
	-0.680	-0.420	-	-	-0.650	-0.011			

		for syste	em B-Oct-	Dmso-W		
Temp.	0%	6W	. 109	%W	209	%W
	H1	H2	H1	H2	H1	H2
				· .	• .	
		×				,
		•				
20 °C	-1.991	-0.626	-1.278	-0.004	-1.362	0.508
	-1.535	-0.379	-1.031	0.163	-1.950	0.126
· ·	-1.187	-0.135	-0.688	0.316	-1.538	0.395
	-1.080	-0.107	-0.280	0.595	-1.233	0.640
	-1.800	-0.520	-1.139	0.124	-1.704	0.255
	-1.400	-0.290		-	-	-
						[
30 °C	-1.501	-0.339	-1.689	-0.415	-1.880	-0.117
		-0.214	-0.885	0.040	-1.509	0.091
u .	-1.307	-0.328	-0.367	0.308	-1.320	0.254
	-0.920	-0.072	-0.175	0.430	-1.031	0.400
	-0.700	0.061	-0.576	0.172	-1.657	-0.013
	-1.720	-0.507	-	-	. .	-
			· ·			ŀ
			- -			
					,	
40 °C	-1.240	0.000	-1.760	-0.646	-1.670	-0.134
	-0.641	-0.098	-0.610	0.126	-1.400	0.075
	-0.194	0.270	-1.200	0.228	-0.950	0.396
	_1 498	-0.608	-1 341	_0 414	-1 120	0.270
	-1.470	-0.000	-0.816	-0.048	· 1 · 1 ú	0.210
·	-1.077	-0.525	-0.010	-0.040	-	
	-0.010	-0.240		**	**	-

Table . 42Parameters H1 and H2 for Hand's plotsfor system B-Oct-Dmso-W







Hand's plot for System : T-H-Dmf-Water with Temperature and anti solvent concentration as parameter Fig H -2



Hand's plot for System : X-H-Dmf-Water with Temperature and anti solvent concentration as parameter

Fig H -3



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Fig H -4



Hand's plot for System : B-Oct-Dmf-Water with Temperature and anti solvent concentration as parameter

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Hand's plot for System : T-H-Dmso-Water with Temperature and anti solvent concentration as parameter ▲ 10%W ,30 0C ▲ 10%W ,40 0C □ 20%W ,20 0C ■ 20%W ,30 0C 0%W ,30 0C0%W ,40 0C ■ 20%W ,40 0C ▲ 10%W,20 0C o 0%W ,20 0C 2.5 2 1.5 T-H-Dmso-W H2 -2.5 -0.5 7 -1.5 Fig H -7 ΙH



.

Hand's plot for System : X-H-Dmso-Water with Temperature and anti solvent concentration as parameter









Figure (H-9): Straight line plots for systems-B-Hep-Dmso-Water with temperature and anti solvent concentration as parameters.

Figure (H-10): Straight line plots for systems-B-Oct-Dmso-Water with temperature and anti solvent concentration as parameters.

Data processing Tables -33 to42 containing values of H1 and H2 under different sets of conditions have been utilized while constructing all the above straight lines plots.

It is interesting to note that all the experimental data obtained in the present investigation could be correlated satisfactorily in terms of straight lines plots. The values of 'n' from slope of straight line and the values of 'k' from the corresponding intercept obtained for these lines under different sets of conditions have been tabulated in Tables 43 and 44 for two solvents under consideration namely –Dmf and Dmso.

All the values of 'k' and 'n' obtained under different sets of conditions for the two solvents under considerations namely – Dmf and Dmso can be utilized conveniently while developing a generalized correlation for correlating 'k' data in terms of variables-(i)Temperature of phase equilibrium data , (ii) Anti solvent concentration of water in solvent , (iii) Molecular weight of aromatics and (iv) Molecular weight of aliphatics.

5.6.0 VALUES OF 'k' AND 'n' BASED ON HAND'S PLOTS

The values of 'k' and 'n' for the systems: Benzene-Hexane-Dmf +W and Benzene-Hexane-Dmso +W at different anti solvent (water) concentrations at 20°C, 30°C, and 40°C are reported in Table-43 and Table-44 respectively

5.6.1 Discussion for values of 'k' and 'n' for systems consisting of B/T/X-H/Hep/Oct-Dmf-W:-

(i)Effect of temperature and anti solvent concentration on the values of 'n'

As could be seen from Table-45, effect of temperature on the values of 'n' appears to be practically negligible. Also effect of anti solvent concentration on the value of 'n' appears to be practically negligible . Values of 'n' appear to be practically the same in the range of 0.82 to 0.89 for the case of solvent Dmf +W under different sets of conditions.

Table 43 Values of 'k' and 'n' for system

Aliphatics + Aromatics + Dmf under different sets of conditions using solvent Dmf

•••

	-		•		-		. s	· ·	•		t		•	•	•		•	· ·			
ņ	n		0.8300	0.8230			0.8460	0.8290	0.8420		0.8400	0.8473	0.8430	•••	0.8440	0.8500	0.8470		0.8720	0.8710	0.8660
40	k		1.5840	0.4160	I		1.1220	0.3090	0.0950		0.9440	0.1620	0.0850		1.4450	0.4780	0.1540		1.1480	0.8120	0.3310
, C	u ,		0.8800	0.8850	0.8910		0.8060	0:7960	0.8000		0.8010	0.8280	0.8330		0.8250	0.8200	0.8030		0.8630	0.8660	0.8530
30	- k r -		1.5130	0.3160	0.1140		1.0230	0.2690	0.0830		0.9770	0.1510	0.0390		0.9330	0.4460	0.1410		0.8910	0.4160	0.1120
ں ت	- U		0.8450	0.8580	0.8490		0.8400	0.8310	0.8370		0.8190	0.8290	0.8160		0.8420	0.8310	0.8470	•	0.8600	0.8530	0.8650
20	. k	-	1.3480	0.2340	0.0890		0.8310	0.0830	0.0450	•	0.8120	0.0810	0.0250		0.7760	0.2750	0.1000		0.6450	0.2710	0.0970
W%	1	•	0	10	20	· , ' :	0	10	20		0	10	20	• •	0	10	20		0	10	20
System				B - H - Dmf +W				T - H - Dmf +W			-	X - H - Dmf + W				B - Hept - Dmf + W	•	· · · · · · · · · · · · · · · · · · ·		B - Oct - Dmf +W	
							ſ												-		

System	www.	20.C	arin Janin	30.C		is using so 40.C	ivent JJmso	
		K	U	ĸ	đ	Å	, d ,	
	0	0.4260	0.5280	0.5240	0.5000	0.7490	0.4800	•
B - H - Dmso +W	10	0.1120	0.5960	0.2290	0.5200	0.2750	0.4530	
i	20	1	I .	0.0190	0.5380	0.0290	0.4650	
•	0	0.2810	0.5380	0.3230	0.5000	0.5000	0.5000	
T - H - Dmso +W	10	0.0560	0.5380	0.0810	0.5010	0.1230	0.4870	
	20	0.0148	0.5400	0.0150	0.4770	0.0450	0.5000	
	0	0.0190	0.5000	0.0900	0.5080	0.2630	0.5600	
X - H - Dmso +W	10	0.0010	0.5570	0.0040	0.5120	0.0950	0.5390	
ł	20	0.0005	0.5120	0.0020	0.5000	0.0540	0.5400	
							2 1	
	0	0.3090	0.6280	0.3460	0.6310	0.3710	0.5960	
B - Hept - Dmso +V	10	0.1180	0.6400	0.2080	0.6260	0.2810	0.6250	
	20	0.0910	0.6500	0.1310	0.6200	0.2230	0.6210	
······································	. 0	0.1140	0.5630	0.1410	0.6600	0.2750	0.5520	
B - Oct - Dmso +W	10	0.0530	0.6720	0.1120	0.8330	0.1620	0.5160	
	20	0.0070	0.5160	0.0210	0.5710			

Table 44

/alues of 'k' and 'n' for sys

under differe	nt sets of co	ndition using solve	nt Dmf	. ·
		n	n	n .
System	<u>% w</u>	20°C	30°C	40°C
· · · · · · · · · · · · · · · · · · ·	0	0.8450	0.8800	0.8300
B - H - Dmf + w	10	0.8580	-	0.8230
	20.	0.8490	0.8910	-
<u>'</u>	0	0.8400	0.8060	0.8460
T - H - Dmf + w	10	0.8310	0.7960	0.8290
	20	0.8370	0.8000	0.8420
	-	0.0100	0.0010	0.8400
	0	0.8190	0.8010	0.8400
X - H - Dmf + w	. 10	0.8290	0.8280	0.8473
	20	0.8160	0.8330	0.8430
	,n`	0.8420	0.8250	0.8440
D Hant Durf + 11	10	0.0420	0.8200	0.8500
B - Hept - Dim + w	20	0.8470	0.8030	0 8470
· · · ·	20	0.0470	0.0050	
	0	0.8600	0.8630	0.8720
B - Oct - Dmf + w	10	0.8530	0.8660	0.8710
	20	0.8650	0.8530	0.8660
	% w	k	k	k
	0	1,3480	1.5130	1.5840
B-H-Dmf+w	10	0.2340	0.3160	0.4160
	20	0.0890	0.1140	·
				·
	0	0.8310	1.0230	1.1220
T - H - Dmf + w	10	0.0830	0.2690	0.3090
· · · ·	20	0.0450	0.0830	0.0950
•	•	•		
	0	0.8120	0.9770	0.9440
X - H - Dmf + w	10	0.0810	0.1510	0.1620
	20	0.0250	0.0390	0.0850
		0.0000	0.0220	1 4450
· · · · ·	0	0.7760	0.9330	0.4250
B - Hept - Dmf + w	10	0.2750	0.4460	0.4230
	20	0.1000	0.1410	0.1540
,	0	0.6450	0.8910	1,4800
D Oat Dmf+11	10	0.2710	0.4160	0.8120
	20	0.2710	0.1120	0.3310
· · ·	20	0.0270	V.1120	0.5510
			والمراجع والمحاد والمحاد والمحاد والمحاد والمحاد والمحاد	

	Lanic-45
	Values of 'n,' 'k' for different systems
nder d	ifferent sets of condition using solvent Dmf

(ii) Effect of temperature and anti solvent concentration on the value of 'k'

For System B-H-Dmf-W

As could be seen from Table-46 with an increase in temperature from 20 °C to 30 °C, value of 'k' increases. With further increase in temperature from 30 °C to 40 °C the value of 'k' increases, however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table 46 wherein the values of 'k' for system B-H-Dmf-W lie in the range of .09 to 1.58. With an increase in temperature from 20°C to 30 °C, the value of 'k' increases from 1.35 to 1.513 for 0%water, from 0.23 to 0.32 for 10 % water and from 0.09 to 0.11 for 20 % water.

Further as could be seen from Table-47 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W, the values of 'k' decrease substantially from 1.35 to 0.09.

Similar Conclusions can be drawn for other temperatures 30 °C and 40 °C and effect of increase in antisolvent concentration appears to be more stringent than the effect of increase in temperature.

For System T-H-Dmf-W:

As could be seen from Table-46 with an increase in temperature from 20 °C to 30 °C, value of 'k' increases marginally. With further increase in temperature from 30 °C to 40 °C, the value of 'k' increases however relatively more than prevous temperature range of 20 °C 30 °C. This generalized conclusion is observed practically for all the values of 'k' reported in Table 46 wherein the values of 'k' for system T-H-Dmf-W lie in the range of 0.045 to 1.12 With an increase in temperature from 20 °C to 40 °C the value of 'k' increases from 0.83 to 1.12 for 0% water, from 0.083 to 0.309 for 10 % water and from 0.045 to 0.095 for 20 % water.

Further as could be seen from Table-47 at constant temperature 20 °C for system- T-H-Dmf-W with an increase in antisolvent concentration from 0%W to 20%W, the value of 'k' decreases substantially from 0.83 to 0.045.

Similar conclusions can be drawn for other temperatures 30 °C and 40 °C and effect of increase in antisolvent concentration appears to be more stringent than the effect of increase in temperature.

Table-46Values of 'k' for different systemsAnti solvent effect under different sets of condition using solvent Dmf

												·			_
20% W k	0.0890	0.1140		0.0450	0.0830	0.0950	0.0250	0.0390	0.0850	0.1000	0.1410	0.1540	0.0970	0.1120	0.3310
10% W k	.0.2340	0.3160	0.4160	0.0830	0.2690	0.3090	0.0810	0.1510	0.1620	0.2750	0.4460	0.4780	0.2710	0.4160	0.8120
0% W k	1.3480	1.5130	1.5840	0.8310	1.0230	1.1220	0.8120	0.9770	0.9440	0.7760	0.9330	1.4450	0.6450	0.8910	1.1480
Temp 0C	20	30	40	50	30	40	20	30	40	50	30	40	50	30	40
System	B-H-Dmf+w	-		T H - Dmf + w			X.H.Dmf+w			B - Hept - Dmf + w	· · · · · · · · · · · · · · · · · · ·	i	B - Oct - Dmf + w		

Temp el	V ffect und	⁷ alues of 'k' for er different set	different system s of condition using	solvent Dmf	
System	м %	20°C k	30.C ·	40 C k	
•	0	1.3480	1.5130	1.5840	
B-H-Dmf+w	10	0.2340	0.3160	0.4160	
	20	0.0890	0.1140	1	
	0	0.8310	1.0230	1.1220	
T - H - Dmf + w	10	0.0830	0.2690	0.3090	
	20	0.0450	0.0830	0.0950	
	0	0.8120	0.9770	0.9440	. .
X - H - Dmf + w	10	0.0810	0.1510	0.1620	
	20	0.0250	0.0390	0.0850	
	0	0.7760	0.9330	1.4450	
B - Hept - Dmf + w	10	0.2750	0.4460	0.4780	
	20	0.1000	0.1410	0.1540	
4 }	0	0.6450	0.8910	1.1480	
B - Oct - Dmf + w	10	0.2710	0.4160	0.8120	
	20	0.0970	0.1120	0.3310	

Table47

For system X-H-Dmf-W:

As could be seen from the same Table-46 with an increase in temperature from 20 °C to 30 °C value of 'k' increases. With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table 46 where in the values of 'k' for system X-H-Dmf-W lie in the range of 0.025 to 0.944 .With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.81 to 0.944 for 0%water, 0.081 to 0.16 for 10 % water and from 0.025 to 0.085 for 20 % water.

Further as could be seen from Table- 47 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W, the values of 'k' decrease substantially from 0.81 to 0.025

Similar Conclusions can be drawn for other temperatures 30 °C and 40 °C and effect of increase in anti solvent concentration appears to be more stringent than the effect of increase in temperature.

For system B-Hep-Dmf-W:

As could be seen from Table-46 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table 46 where in the values of 'k' for system B-Hep-Dmf-W lie in the range of 0.1 to 1.44. With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.77 to 1.44 for 0% water, 0.27 to 0.478 for 10 % water and from 0.10 to 0.15 for 20 % water.

Further as could be seen from Table- 47 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W the values of 'k' decrease substantially from 0.77 to 0.10

Similar Conclusion can be drawn for other temperatures 30 °C and 40 °C and effect of increase in anti solvent concentration appears to be more stringent than the effect of increase in temperature.

For system B-Oct-Dmf-W:

As could be seen from Table-46 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table 46 where in the values of 'k' for system B-Oct-Dmf-W lie in the range of .097 to 1.148 With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.64 to 1.148 for 0%water, 0.27 to 0.81 for 10 % water and from 0.097 to 0.331 for 20 % water.

Further as could be seen from Table- 47 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W the values of 'k' decrease substantially from 0.64 to 0.097

(iii) Effect of molecular weight of Aromatics on the values of 'k' :-

For system B/T/X-H-Dmf-W:

As could be seen from Table-48 with an increase in molecular weight of aromatics i.e. Benzene is replaced by Toluene replaced by Xylene the value of 'k' decreases under conditions of constant temperature and constant value of anti solvent concentration. For all values of constant anti solvent concentration however, replacing Benzene by Toluene value of 'k' decreases substantially, however replacing Toluene by Xylene value of 'k' decreases marginally. Thus for example, at temperature 20 °C with anti solvent concentration of 20 % by wt. when Benzene is replaced by Toluene and then by Xylene , value of 'k' decreases from 0.09 to 0.045 and then to 0.025 respectively.

% W	Temp	B - H - Dmf + W	T - H - Dmf + W	X - H - Dmf + W
		k	k	k
	20.°C	1.3480	0.8310	0.8120
. 0	30.℃	1.5130	1.0230	0.9770
	40.°C	1.5840	1.1220	0.9440
	20.°C	0.2340	0.0830	0.0810
10%	30.°C	0.3160	0.2690	0.1510
, <u>,</u>	40.°C	0.4160	0.3090	0.1620
	20.°C	0.0890	0.0450	0.0250
20%	30.°C	0.1140	0.0830	0.0390
	40.°C	- 	0.0950	0.0850
		<i>.</i>	Table-49	

 Table 48

 Effect of Molecular Weight of Aromatic at constant temperature.

Effect of Molecular Weight of Aliphatic at constant temperature.

Тетр	% W	B - H - Dmf + W k	B - Hep - Dmf + W k	B - Oct - Dmf + W k
``	0	1.3480	0.7760	0.6450
20.°C	10	0.2340	0.2750	0.2740
	20	0.0890	0.1000	0.0970
· .	0	1.5130	0.9330	0.8910
30.°C	10	0.3160	0.4460	0.4160
	20	0.1140	0.1410	0.1120
	0	1.5840	1.4450	1.1480
40.°C	10	0.4160	0.4780	0.8120
	• 20	*	0.1540	0.3310

(iv) Effect of molecular weight of Aliphatics on the values of 'k':-

For system B-H/Hep/Oct-Dmf-W

As could be seen from Table-49 for many systems with an increase in molecular weight of aliphatic i.e. Hexane is replaced by Heptane replaced by Octane the value of 'k' decreases under conditions of constant temperature and constant value of anti solvent concentration. For all values of constant anti solvent concentration however, replacing Hexane by Heptane value of 'k' decreases substantially, however replacing Heptane by Octane value of 'k' decreases marginally. Thus for example, at temperature 20 °C with anti solvent concentration of 0 % by wt. when Hexane is replaced by Heptane and then by Octane , value of 'k' decreases from 1.34 to 0.776 and then to 0.645 respectively.

However, for some systems normal trend is not followed These cases can be considered as exception to normal trend. Thus for example, as an exception for the fixed value of water concentration 10% and 20% at 20 °C there appears to be practically no effect of increase in molecular weight of aliphatics on the value of 'k'.

5.6.2 Discussion for values of 'k' and 'n' for systems consisting of B/T/X-H/Hep/Oct-Dms0-W:-

(i)Effect of temperature and anti solvent concentration on the values of 'n':-

The values of 'n' for different systems consisting of aliphatic+aromatics-Dmso+water are reported in Table-50. Similar conclusions as drawn for solvent Dmf can be drawn for solvent Dmso also under different sets of conditions where in values of 'n' remain in the range of 0.5 to 0.63 for most of the cases. With an increase in temperature value of 'n' appears to decrease slightly.

under differe	nt sets of con	ndition using solvent	Dmso	
System	% w	20°C	30°C	40°C
		n	n	n
	0	0.5280	0.5000	0.4800
B - H - Dmso + w	10	0.5960	0.5200	0.4530
· · ·	20	-	0.5380	0.4650
	0	0.5380	0.5000	0.5000
T - H - Dmso + w	10	0.5380	0.5010	0.4870
	20	0.5400	0.4770	0.5000
	0	0 5000	0 5080	0 5600
X - H - Dmso + w	10	0.5570	0.5120	0.5390
	20	0.5120	0.5000	0.5400
	0 '	0.6280	0.6310	0.5960
B - Hept - Dmso + w	10	0.6400	0.6260	0.6250
	20	0.6500	0.6200	0.6210
	0	0.5630	0.6600	0.5520
B - Oct - Dmso + w	10	0.6720	0.8330	0.5160
	20	0.5160	0.5710	_
	% w	k	k	k
	0	0.4260	0.5240	0.7490
B - H - Dmso + w	10	0.1120	0.2290	0.2750
	20	-	0.0190	0.0290
	•	0.0010	0.0000	0.5000
	0	0.2810	0.3230	0.5000
I - H - Dmso + w	10	0.0560	0.0810	0.1230
	20	0.0140	0.0150	0.0450
	0	0.0190	0.0900	0.2630
X - H - Dmso + w	10	0.0010	0.0040	0.0950
	20	0.0005	0.0020	0.0540
4	0	0.3090	0.3460	0.3710
B - Hept - Dmso + w	10	0.1180	0.2080	0.2810
	20	0.0910	0.1310	0.2230
	0	0.1140	0.1410	0.2750
B - Oct - Dmso + w	10	0.0530	0.1120	0.1620
	20	0.0070	0.0210	- -
·				

Table-50 Values of 'n,' 'k' for different system ler different sets of condition using solvent Dms

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(ii) Effect of temperature and anti solvent concentration on the value of 'k':-

For system B-H-Dmso-W:

As could be seen from Table–51 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table-51 where in the values of 'k' for system B-H-Dmso-W lie in the range of 0.02 to 0.74. With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.4260 to 0.7490 for 0% water, 0.1070 to 0.2750 for 10 % water and with an increase in temperature from 30 °C to 40 °C, the value of 'k' increases from 0.0290 for 20 % water,

Further as could be seen from Table- 52 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 10%W the values of 'k' decrease substantially from 0.4260 to 0.1120.

Similar Conclusion can be drawn for other temperatures 30 °C and 40 °C and effect of increase in anti solvent concentration appears to be more stringent than the effect of increase in temperature.

For system T-H-Dmso-W :

As could be seen from Table-51 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table-51 where in the values of 'k' for system T-H-Dmso-W lie in the range of .018 to 0.5 With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.28 to 0.5 for 0% water, 0.056 to 0.123 for 10 % water and from 0.014 to 0.045 for 20 % water.

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Values of 'k' for different systems Anti solvent effect under different sets of condition using solvent Dmso

System	Temp	0% W	10% W	20% W
	20	×	k	k
B - H - Dmso + w	20	0.4260	0.1120	• •
	30	0.5240	0.2290	0.0190
•	40	0.7490	0.2750	0.0290
•				
T - H - Dmso + w	20	0.2810	0.0560	0.0140
	30	0.3230	0.0810	0.0150
	40	0.5000	0.1230	0.0450
X - H - Dmso + w	20	0.0190	0.0010	0.0005
ł	30	0.0900	0.0040	0.0020
	40	0.2630	0.0950	0.0540
B - Hept - Dmso + w	20	0605.0	0.1180	0.0910
	30	0.3460	0.2080	0.1310
	40	0.3710	0.2810	0.2230
B - Oct - Dmso + w	20	0.1140	0.0530	0.0070
	30	0.1410	0.1120	0.0210
	40	0.2750	0.1620	

Further as could be seen from Table-52 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W, values of 'k'. decrease substantially from 0.28 to 0.014.

For system X-H-Dmso-W:

As could be seen from Table-51 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table-51 where in the values of 'k' for system X-H-Dmso-W lie in the range of .0005 to 0.263 With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.019 to 0.263 for 0%water, 0.001 to 0.095 for 10 % water and from 0.0005 to 0.054 for 20 % water.

Further as could be seen from Table- 52 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W, the values of 'k' decrease substantially from 0.019 to 0.0005.

For system B-Hep-Dmso-W:

As could be seen from Table-51 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table-51 where in the values of 'k' for system B-Hep-Dmso-W lie in the range of 0.1 to 0.4. With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.309 to 0.371 for 0% water, 0.118 to 0.28 for 10 % water and from 0.091 to 0.223 for 20 % water .

Further as could be seen from Table- 52 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W the values of 'k' decrease substantially from 0.309 to 0.091

Table52 Values of 'k' for different system

0.2750 0.2630 0.3710 0.2810 0.7490 0.5000 0.0450 0.0950 0.2230 0.1620 0.2750 0.0290 0.1230 0.0054 40.C Temp effect under different sets of condition using solvent Dmso Ч 0.1410 0.1310 0.0900 0.0040 0.0020 0.1120 0.0210 0.3460 0.2080 0.0190 0.3230 0.0810 0.0150 0.2290 0.5240 30.C 4 0.0560 0.0190 0.0010 0.0005 0.1140 0.0530 0.0140 0.3090 0.1180 0.0910 0.0070 0.4260 0.1070 0.2810 20.C , 2 M.% <u></u> 2010 20 10 0 20 10 20.10 3 0 10 0 0 0 B - Hept - Dmso + w B - Oct - Dmso + w X - H - Dmso + w T - H - Dmso + wB - H - Dmso + w System

For system B-Oct-Dmso-W:

As could be seen from Table–51 with an increase in temperature from 20 °C to 30 °C the value of 'k' increases .With further increase in temperature from 30 °C to 40 °C the value of 'k' increases however marginally. This generalized conclusion is observed practically for all the values of 'k' reported in Table-51 where in the values of 'k' for system B-Oct-Dmso-W lie in the range of 0.007 to 0.275 .With an increase in temperature from 20 °C to 40 °C, the value of 'k' increases from 0.114 to 0.275 for 0%water, 0.053 to 0.162 for 10 % water and from 0.007 to 0.021(at 30 °C) for 20 % water

Further as could be seen from Table-52 at constant temperature 20 °C with an increase in anti solvent concentration from 0%W to 20%W the values of 'k' decrease substantially from 0.114 to 0.007.

(iii) Effect of molecular weight of Aromatics on the values of 'k' :-

For system B/T/X-H-Dmso-W

As could be seen from Table-53 with an increase in molecular weight of aromatics i.e. Benzene is replaced by Toluene replaced by Xylene the value of 'k' decreases under conditions of constant temperature and constant value of anti solvent concentration. For all values of constant anti solvent concentration however, replacing Benzene by Toluene value of 'k' decreases marginally, however replacing Toluene by Xylene value of 'k' decreases substantially. Thus for example, at temperature 30 °C with anti solvent concentration of 20 % by wt. when Benzene is replaced by Toluene and then by Xylene, value of 'k' decreases from 0.019 to 0.015 and then to 0.002 respectively.

(iv) Effect of molecular weight of Aliphatics on the values of 'k': For system B-H/Hep/Oct-Dmso-W

As could be seen from Table-54 with an increase in molecular weight of Aliphatic i.e. Hexane is replaced by Heptane and Heptane is replaced by Octane, the value of 'k' decreases under conditions of constant temperature and constant value of anti solvent concentration. For all values of constant anti solvent concentration however, replacing Heptane by Octane value of 'k' decreases substantially, However replacing Hexane by Heptane, the value of 'k' decreases marginally. Thus for example, at temperature 20 °C with anti solvent concentration of 0 % by wt. when Hexane is replaced by Heptane and then by Octane , value of 'k' decreases from 0.426 to 0.309 and then to 0.114 respectively.

However, for a couple of systems, the above normal trend is not observed and these cases can be considered as exception to normal trend. Thus for example, as an exception for the fixed value of water concentration 10%W at 40 °C and 20%Wat 30 °C, the values of 'k' appear to be highest for system containing aliphatic –Heptane.

5.7.0DEVELOPMENT OF GENERALIZED CORRELATIONS

(I) Modified Hand's Correlation:

For correlating ternary liquid - liquid phase equilibrium data for liquid - liquid extraction of aromatics, Hand's correlation¹³² can be written as

$$\left[\frac{\mathbf{X}_{\text{BR}}}{\mathbf{X}_{\text{HR}}}\right] = \mathbf{k} \left[\frac{\mathbf{X}_{\text{BE}}}{\mathbf{X}_{\text{SE}}}\right]^{n}$$

Wherein symbols-B, H and S are for solute, non-solute and solvent respectively. Further, symbols k & n are constants of Hand's equations and 'X'stand for composition of Extract (E) or Raffinate (R).

For quaternary liquid & liquid phase equilibrium data for extraction of aromatics which consists of four component-s, aromatic + aliphatic + solvent + antisolvent, if anti-solvent concentration is zero then quaternary system as such gets

ffect of M	constant Temp.			
Temp	% W	B - H - Dmso + W	T - H - Dmso + W	X - H - Dmso + W
	ik K	k	k	. k
,	0	0.4260	0 2810	0.0190
20.°C	10	0.1120	0.0560	0.0010
•	20	-	0.0180	0.0005
	0	0.5240	0.3230	0.0900
30.°C	10	0.2290	0.0810	0.0040
	20	0.0190	0.0150	0.0020
	0	0.7490	0.5000	0.2630
40.°C	10	0.2750	0.1230	0.0950
	20	0.0290	0.0450	0.0540

Table 54

% W -	Temp	B - H - Dmso + W	B - Hept - Dmso + W	B - Oct - Dmso + W
	0 °C:	k ta	k	k
	20.°C	0.4260	0.3090	0.1140
0	30.°C	0.5240	0.3460	0.1410
	40.°C	0.7490	0.3710	0.2750
19. 19	20.°C	0.1070	0.1180	0.0530
10%	30.°C	0.2290	0.2080	0.1120
	40.°C∙	0.2750	0.2810	0.1620
	20.°C	-	0.0910	0.0070
20%	30.°C	0.0190	0.1310	0.0210
	40.°C	0.0290	0.2230	-

reduced to ternary. Hence above Hand's correlation can be applied for quaternary system also.

Further, if one analyses quaternary systems critically, it is observed that solvent and anti-solvent utilized in this investigation are completely miscible in all proportions. Hence by introducing the concept of mixed solvent which constitutes as if a single solvent for a fixed value of anti-solvent concentration, the quaternary system under consideration can be reduced to "Equivalent Ternary System".

Thus quaternary system consisting of four component-s:- Aromatics- (B / T / X)+ Aliphatics (H/H'/O) + Solvents (Dmf / Dmso) + Anti solvent (W) reduces to an equivalent ternary system consisting of three components : Aromatics (B/T/X) + Aliphatics (H/H'/O)+Mixed Solvent (Dmf + W)/(Dmso+W) wherein mixed solvent at a time will have fixed value of anti-solvent concentration like 10% W, 20% W etc.

Thus for Equivalent Ternary System, the above mentioned Hand's equation is thus applicable and can be written as under:

$$\left[\frac{\mathbf{X}_{\mathrm{BR}}}{\mathbf{X}_{\mathrm{HR}}}\right] = \mathbf{k} \left[\frac{\mathbf{X}_{\mathrm{BE}}}{\mathbf{X}^*_{\mathrm{SE}}}\right]^{\mathbf{n}}$$

Wherein $X^*Se = (XDE + XWE)$ for a fixed anti-solvent concentration value.

Thus for a fixed value of anti solvent concentration, given quaternary system can be considered as Equivalent Ternary System and a plot of

$$\log\left[\frac{X_{BR}}{X_{HR}}\right] \text{ Vs. } \log\left[\frac{X_{BE}}{X_{DE} + X_{WE}}\right]$$

results in a straight line, having intercept being log' k' and slope being 'n'.

Based on various approaches available in the literature proposed by Moulton & Chang¹³, Dhabe & Puranik⁴³ and Bansod & Puranik⁴⁴, the above modified correlation / equation has been proposed which could be conveniently utilized to correlate quaternary liquid - liquid Phase equilibrium data.

Thus, for different systems involving [B / T / X] - [H / H' / O] - (Dmf+W) with three variation of temperatures - 20^o C, 30^o C and 40^o C and three variation in anti

solvent concentration - 0% W, 10% W and 20% W totally 45 equivalent ternaries can be obtained for liquid - liquid phase equilibrium data for mixed solvent (Dmf + W)

Also for different systems involving [B / T / X] - [H / H' / O] - (Dmso+W) with three variation of temperatures - 20° C, 30° C and 40° C and three variation in anti solvent concentration - 0% W, 10% W and 20% W totally 45 equivalent ternaries can be obtained for liquid - liquid phase equilibrium data for mixed solvent (Dmso + W)

(II) Analysis of Straight Line Nature Obtained for Modified Hand's Plot:

It has been already discussed that all the plots based on modified Hand's Equation under consideration are straight line plots for both the mixed solvents - (Dmf+W) and (Dmso + W). For different anti solvent concentration values at a fixed value of temperature - T, parallel lines are obtained practically for all the systems under considerations. Further for different temperature values at a fixed value of anti solvent concentration, parallel lines are obtained practically for all the systems. For both mixed solvents (Dmf+W) & (Dmso + W), a set of 45 straight lines can be grouped in to five categories as under:

(i) Totally nine systems consisting of B - H - (Dmf / Dmso) + W at three different temperatures and three different anti-solvent concentration values.

(ii) Totally nine systems consisting of T - H - (Dmf / Dmso) + W at three different temperatures and three different anti-solvent concentration values.

(iii) Totally nine systems consisting of X - H - (Dmf / Dmso) + W at three different temperatures and three different anti-solvent concentration values.

(iv) Totally nine systems consisting of B - Hept - (Dmf / Dmso) + W at three different temperatures and three different anti-solvent concentration values.

(v) Totally nine systems consisting of B - Oct - (Dmf / Dmso) + W at three different temperatures and three different anti-solvent concentration values.

Thus totally 45 straight lines and corresponding 45 values of constant 'k' for first mixed solvent - (Dmf+W) have been obtained in this investigation. Further, totally 45 straight lines and corresponding 45 values of constant 'k' for second mixed solvent - (Dmso+W) have been obtained in this investigation.

UNIQUE FEATURE

OF

THIS INVESTIGATION

Oza-Puranik (O-P)

GENERALIZED CORRELATION
Based on critical analysis of "k" & "n" already discussed in detail under subheading - 5.6.0 : Values of "k" & "n", the important conclusions which have been already drawn, are summarized below :

(i) The values of "n" for different forty five systems under consideration for mixed solvent (Dmf+W) remain practically constant in the range of 0.85 to 0.87. Also the values of "n" for different forty five system under consideration for mixed solvent (Dmso+W) remain practically constant in the range of 0.55 to 0.60.

(ii) The value of "k" appears to be a very strong function of antisolvent concentration. As anti-solvent concentration increases, the value of "k" decreases and decrease in the value of "k" with an increase in anti-solvent concentration is substantial.

(iii) The values of "k" appear to be a weak function of temperature (T). As temperature increases, the value of "k" also increases; however marginally.

(iv) With an increase in molecular weight of aromatics under otherwise identical conditions the value of "k" decreases.

From the above discussion, it is crystal clear that Hand's constant - "k" in modified Hand's plot, is expected to be a function of four important parameters. These parameters have been introduced in terms of dimensionless group - in order to make correlation to be developed, more generalized in nature.

'k'=f(temperature, anti-solvent concentration, molecular weight of aromatics, molecular weight of aliphatics.)

$$k' = f\left(\left[\frac{T_1}{T_0}\right]^0, \left[\frac{S+W}{S}\right]^p; \left[\frac{M_1}{C_1}\right]^q, \left[\frac{M_2}{C_2}\right]^r\right)$$

This can be looked up as the basis for the "Proposed New Model".

5.7.1 New Model Proposed for Estimating "k":-

The following generalized correlation is proposed in terms of four important dimensionless groups, each group – having an index.

$$\log' k' = \log \left[\frac{T_1}{T_0}\right]^0 + \log \left[\frac{S+W}{S}\right]^p + \log \left[\frac{M_1}{C_1}\right]^q + \log \left[\frac{M_2}{C_2}\right]^r$$

Where in

k = Hand's constant in modified Hand's eqn. for quaternary system.

 $T_1 = Temperature,$

 $T_0 = 273 \ ^0K$

S = Solvent concentration.

W = anti-solvent concentration

M1 = molecular weight of aromatics - solute to be extracted.

M2 = molecular weight of aliphatics - non-solute component-

C1 = molecular weight of Benzene

C2 = molecular weight of Hexane

The above generalized proposed correlation in this investigation has been labeled as Oza - Puranik correlation (O - P Correlation)

NRTL method has been also utilized later on to correlate quaternary liquid liquid phase equilibrium data obtained in this investigation. NRTL method involves a set of 12 constants in terms of

A (1, 2), 2A (1, 3), A (1, 4); A (2, 1), A (2, 3), A (2, 4), A (3, 1), A (3, 2), A (3, 4), A (4, 1), A (4, 2), A (4, 3).

The values of twelve constants are required to be obtained for a particular component- solute, non-solute, solvent and anti solvent. Thus for mixed solvent either (Dmf+W) or (Dmso+W) is likely to involve totally 60 constants minimum.

In comparison to NRTL method, Oza-Puranik (O - P) Correlation proposed in this investigation appear to involve a set of four constants only i.e. o, p, q & r.

Thus these new approaches proposed in this investigation appear to be relatively simple and it can be utilized conveniently to correlate and also to predict quaternary liquid - liquid phase equilibrium data.

5.7.2 Obtaining Values of 'o' & 'p' in Oza - Puranik (O - P) Correlation for Mixed Solvent (Dmf + W):-

The set of values of "k" obtained under different sets of a conditions reported in Table- 43 for different systems consisting of B/T/X - H/H/O - Dmf + W have been utilized to prepare basic Data Table and relevant Data Processing Table for the development of generalized O - P correlation. Accordingly Basic Data Table- 55 has been prepared. Further using values of different parameters listed in Table-55 and different values of index 'o' & 'p' derived Table- 56 has been prepared which lists values of log' k' and the corresponding the values of A1, 2, 3... etc.

Based on this Derived Table-56, different Plots of log' k' Vs. log A have been depicted in Figs. GC-1 to GC-30. All the data in this Derived Table has been divided under three categories as under:

(i) Data processing for "k" values for systems - B / T / X - H - Dmf + W under three temperatures - 20° C, 30° C, 40° C and anti-solvent concentration 0%W, 10% W & 20% W.

(ii) Data processing for "k" values for systems - B - Hept- Dmf + W under three temperatures - 20° C, 30° C, 40° C and anti-solvent concentration 0%W, 10% W & 20% W.

(iii) Data processing for "k" values for systems - B - Oct - Dmf + W under three temperatures - 20° C, 30° C, 40° C and anti-solvent concentration 0%W, 10% W & 20% W.

Accordingly various GC-plots of log 'k' Vs. log'A' have been presented in Figs. GC-1 to GC--18 for category – (i), in Figs. GC-19 to GC-24 for category – (ii) and in Figs. GC-25 to GC-30 for category – (iii).

Critical Observations and Remarks w.r.t.Plots-GC-1to GC-30:

(1) In Fig.GC-1 to GC-18 which depicts "k" data for different systems - B / T / X - H - Dmf + W plotted as log (k) Vs. log (A), the values of index 'p' has been varied from (-2.5) to (-3.25) while plotting data of log(A). For value of P=(-3.0), the scattering of points

 Table -55

 Basic Data required for Development of Generalised Correlation for solvent Dmf

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	Sr. No.	oystem	 .	S %	%	S/(M+S)	¥	log k	log T'	(W+S) gc	/ logMI	logM2	logM1/C1	logM2/C2
		Fq	r Aromatics	<u>е</u>			•	Ĩ.	=(T+273)	1273			C1=78	C2=86
		B-H-100%Dmf+0%W.	20°C	100.00	0.0	1.00	1.348	0.129	0.03	0.00	1.89	1.93	0.00	00.0
	7	B-H-90%Dmf+10%W.	20°C	90.00	10.0	1.11	0.234	-0.63	0.03	0.05	1.89	1.93	0.00	0.0
	ς.	B-H-80%Dmf+20%W.	20°C	80.00	20.0	1.25	0.089	-1.05	0.03	0.10	1.89	1.93	0.00	00.0
	4	B-H-100%Dmf+0%W.	30°C	100.00	0.0	1.00	1.513	0.18	0.05	0.00	1.89	1.93	0.00	0.00
	S	B-H-90%Dmf+10%W.	30°C	90.00	10.0	1.11	0.316	-0.50	0.05	0.05	1.89	1.93	0.00	0.00
	9	B-H-80%Dmf+20%W.	30°C	80.00	20.0	1.25	0.114	-0.94	0.05	0.10	1.89	1.93	0.00	0.00
•	7	B-H-100%Dmf+0%W.	40°C	100.00	0.0	1.00	1.584	0.20	0.06	0.00	1.89	1.93	000	000
	∞	B-H-90%Dmf+10%W.	40°C	90.00	10.0	1.11	0.416	-0.38	0.06	0.05	1.89	1.93	000	000
	6	B-H-80%Dmf+20%W.	40°C	80.00	20.0	1.25		4	0.06	0.10	1.89	1.93	0.00	000
	•	Fo	or Aromatics	-1	• •									
	10	T-H-100%Dmf+0%W.	20°C	100.00	0.0	1.00	0.831	-0.08	0.03	0.00	1.98	1.93	0.07	ÛÛ Û
	11	T-H-90%Dmf+10%W.	20°C	00.0 0	10.0	1.11	0.083	-1.08	0.03	0.05	1.98	1 93	0.07	
	12	T-H-80%Dmf+20%W.	20°C	80.00	20.0	1.25	0.045	-1.34	0.03	0.10	1.98	1.93	0.07	000
	13	T-H-100%Dmf+0%W.	30°C	100.00	0.0	1.00	1.023	0.01	0.05	0.00	1.98	1.93	0.07	
•	14	T-H-90%Dmf+10%W.	30°C	90.00	10.0	1.11	0.264	-0.57	0.05	0.05	1.98	1.93	0.07	000
	15	T-H-80%Dmf+20%W.	30°C	80.00	20.0	1.25	0.083	-1.08	0.05	0.10	1.98	1.93	0.07	00.0
•	16	T-H-100%Dmf+0%W.	40°C	100.00	0.0	1.00	1.122	0.05	0.06	0.00	1.98	1.93	0.07	0.00
	12	T-H-90%Dmf+10%W.	40°C	90.00	10.0	1.11	0.309	-0.51	0.06	0.05	1.98	1.93	0.07	0.00
	18	T-H-80%Dmf+20%W .	40°C	80.00	20.0	1.25	0.095	-1.02	0.06	0.10	1.98	1.93	0.07	00.0
		Fo	or Aromatics	X-		۰ ^۰						-)
	19	X-H-100%Dmf+0%W	- 20°C	100.00	0.0	1.00	0.812	-0.09	0.03	0.00	2.03	1.93	0.13	0.00
	20	X-H-90%Dmf+10%W.	20°C	90.00	10.0	1.11	0.081	-1.09	0.03	0.05	2.03	1.93	0.13	0.00
	21	X-H-80%Dmf+20%W.	20°C	80.00	20.0	1.25	0.025	-1.60	0.03	0.10	2.03	1.93	0.13	00.0
•	52	X-H-100%Dmf+0%W.	30°C	100.00	0.0	1.00	0.977	-0.01	0.05	0.00	2.03	1.93	0.13	00.0
•	23	X-H-90%Dmf+10%W.	30°C	90.00	10.0	1.11	0.151	-0.82	0.05	0.05	2.03	1.93	0.13	0.00
	24	X-H-80%Dmf+20%W .	30°C	80.00	20.0	1.25	0.039	-1.40	0.05	0.10	2.03	1.93	0.13	0.00
	25	X-H-100%Dmf+0%W.	40°C	100.00	0.0	1.00	0.944	0.03	0.06	0.00	2.03	1.93	0.13	0.00
	26	X-H-90%Dmf+10%W.	40°C	90.00	10.0	1.11	0.162	-0.79	0.06	0.05	2.03	1.93	0.13	0.00
	27	X-H-80%Dmf+20%W.	40°C,	80.00	20.0	1.25	0.085	-1.07	0.06	0.10	2.03	1.93	0.13	0.00
4	A1,2,31	ogT'+log (S+W/S)p	- -		•	-								

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X1,2,3---=

logT+log(S+W/S)p+log(M1/78)q+log(M2/86)r

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Table55 (continued)

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	ſ	Basic Data 1	required	for Deve	lopment of G	Feneralised C	orrelation	for solv	ent Dmf		•		
Sr. No.	System	E.	s%	₩%	S/(M+S)	*	log k	log T'	/(M+S) Bc	logM1	logM2	logM1/C1	logM2/C2
	·	For - H'			•					· ·	,))
28	B-Hep-100%Dmf+0%W .	20°C	100.00	0.0	1.00	0.776	-0.11	0.03	0.00	1.89	2.00	0.00	0.07
29	B-Hep-90%Dmf+10%W.	20°C	00.00	10.0	1.11	0.275	-0.56	0.03	0.05	1.89	2.00	0.00	0.07
30	B-Hep-80%Dmf+20%W .	20°C	80.00	20.0	1.25	0.100	-1.00	0.03	0.10	1.89	2.00	0.00	0.07
31	B-Hep-100%Dmf+0%W.	30°C	100.00	0.0	1.00	0.933	-0.03	0.05	0.00	1.89	2.00	0000	0.07
32	B-Hep-90%Dmf+10%W.	30°C	90.00	10.01	1.11	0.446	-0.55	0.05	0.05	1.89	2.00	0.00	0.07
33	B-Hep-80%Dmf+20%W .	30°C	80.00	20.0	1.25	0.141	-0.85	0.05	0.10	1.89	2.00	0.00	0.07
34	B-Hep-100%Dmf+0%W.	40°C	100.00	0.0	1.00	1.445	-0.30	0.06	0.00	1.89	2.00	0.00	0.07
35	B-Hep-90%Dmf+10%W.	. 40°C	90.00	10.0	1.11	0.425	-0.32	0.06	0.05	1.89	2.00	0.00	0.07
36	B-Hep-80%Dmf+20%W.	40°C	80.00	20.0	1.25	0.154	-0.82	0.06	0.10	1.89	2.00	0.00	0.07
		For - Oct			•						•		>>>
37	B-Oct-100%Dmf+0%W.	20°C	100.00	0.0	1.00	0.645	-0.19	0.03	0.00	1.89	2.06	000	010
38	B-Oct-90%Dmf+10%W.	20°C	90.00	10.0	1.11	0.271	-0.56	0.03	0.05	1.89	2.06	0.00	0 12
39	B-Oct-80%Dmf+20%W.	20°C	80.00	20.0	1.25	0.097	-1.01	0.03	0.10	1.89	2.06	000	012
40	B-Oct-100%Dmf+0%W.	30°C	100.00	0.0	1.00	0.891	-0.05	0.05	0.00	1.89	2.06	000	0 12
41	B-Oct-90%Dmf+10%W.	30°C	90.00	10.0	1.11	0.416	-0.38	0.05	0.05	1.89	2.06		012
42	B-Oct-80%Dmf+20%W.	30°C	80.00	20.0	1.25	0.112	-0.95	0.05	0.10	1.89	2.06	000	0 12
43	B-Oct-100%Dmf+0%W.	40°C	100.00	0.0	1.00	1.480	0.06	0.06	0.00	1.89	2.06	000	<u>c10</u>
44	B-Oct-90%Dmf+10%W.	40°C	90.00	10.0	1.11	0.812	-0.09	0.06	0.05	1.89	2.06	0000	0.15
45	B-Oct-80%Dmf+20%W.	40°C	80.00	20.0	1.25	0.331	-0.48	0.06	0.10	1.89	2.06	0.00	0.12
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'oot note : A1,2,3-- logT+log (S+W/S)p X1,2,3---=

logT+log(S+W/S)p+log(M1/78)q+log(M2/86)r

	A6	P=-3.25	0.03	-0.12	-0.28	0.05	-0.10	-0.27	0.06	-0.09	-0.25	P=-3.25	0.03	-0.12	-0.28	0.05	-0.10	-0.27	0.06	-0.09	-0.25	P=-3.25	0.03	-0.12	-0.28	0.05	-0.10	-0.27	0.06	-0.09	-0.25	
	A5	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	
	A4	P=-2.75	0.03	-0.09	0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	P=-2.75	0.03	-0.09	0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	P=-2.75	0.03	-0.09	-0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	
ent Dmf	A3	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.24	0.06	-0.08	-0.23	
on for solv	A2	P=-2.75	0.03	-0.09	-0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	P=-2.75	0.03	-0.09	-0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	P=-2.75	0.03	-0.09	-0.23	0.05	-0.08	-0.22	0.06	-0.06	-0.21	d[S)
Correlati	AI	P=-2.5	0.03	-0.08	-0.21	0.05	-0.07	-0.20	0.06	-0.05	-0.18	P=-2.5	0.03	-0.08	-0.20	0.05	-0.07	-0.15	0.06	-0.05	-0.18	P=-2.5	0.03	-0.08	-0.21	0.05	-0.07	-0.20	0.06	-0.05	-0.18	'+log[(S+W)
eneralised	log k		0.129	-0.630	-1.050	0.180	-0.500	-0.940	0.200	-0.380	1		-0.080	-1.080	-1.340	0.010	-0.570	-1.080	0.050	-0.510	-1.020		-0.090	-1.090	-1.600	-0.010	-0.820	-1.400	0.03	-0.790	-1.070	Tgol
ble for Go	k		1.348	0.234	0.089	1.513	0.316	0.114	1.584	0.416	ı		0.831	0.083	0.045	1.023	0.264	0.083	1.122	0.309	0.095		0.812	0.081	0.025	0.98	0.151	0.039	0.944	0.162	0.085	A1,2,3=
cessing Ta	W%	- B	0	10	20	0	10	20	0	10	20	Ľ,	0	10	20	0	10	20	0	10	20	×	0	10	50	0	10	20	0	10	20	Foot note :
Data Pro(L	Aromatics	20	20	20	30	30	30	40	40	40	Aromatics	20	20	20	30	30	30	40	40	40	Aromatics	20	20	50	30	30	30	40	40	40	
	Sr. No.	For /	pund	7	ŝ	4	S	; 0	7	8	6	For A	10	11	12	13	14	. 15	16	17	18	For /	19	50	21	53	23	24	25	26	27	

Table 56

		Dat	a Process	ing Table	for Gener	alised Co	rrelation fo	r solvent]	Dmf	
Sr. No.	т	M%	k	log k	A1	A2	A3	A4	A5	9
-	For - H'				P=-0.5	P=-0.75	P=.1	P=-0.75	P=-1	P=-1.25
28	20	0	0.776	-0.11	0.03	0,03	0.03	0.03	0.03	0.03
29	20	10	0.275	-0.56	0.01	0.00	-0.02	0.00	-0.02	-0.03
30	20	20	0.100	-1.00	-0.02	-0.04	-0.07	-0.04	-0.07	-0.09
31	30	0	0.933	-0.03	0.05	0.05	0.05	0.05	0.05	0.05
32	30	10	0.446	-0.55	0.02	0.01	0.00	0.01	0.00	-0.01
.33	30	20	0.141	-0.85	0.00	-0.03	-0.05	-0.03	-0.05	-0.08
34	40	0	0.445	0.16	0.06	0.06	0.06	0.06	0.06	0.06
35	40	10	0.425	-0.32	0.04	0.03	0.01	0.03	0.01	0.00
36	40	20	0.154	-0.82	0.01	-0.01	-0.04	-0.01	-0.04	-0.06
-	For - Oct				P=-0.25	P=-0.5	P=-0.75	P=-0.5	P=-0.75	P=-1
37	20	0	0.645	-0.19	0.03	0.03	0.03	0.03	0.03	0.03
38	20	10	0.271	-0.56	0.02	0.01	0.00	0.01	0.00	-0.02
39	20	20	0.097	-1.01	0.01	-0.02	-0.04	-0.02	-0.04	-0.07
40	30	0	0.891	-0.05	0.05	0.05	0.05	0.05	0.05	0.05
41	30	10	0.416	-0.38	0.03	0.02	0.01	0.02	0.01	0.00
42	30	20	0.112	-0.95	0.02	0.00	-0.03	0.00	-0.03	-0.05
43	40	0	1.480	0.06	0.06	0.06	0.06	0.06	0.06	0.06
44	40	10	0.812	-0.09	0.05	0.04	0.03	0.04	0.03	0.01
45	40	20	0.331	-0.48	0.04	0.01	-0.01	0.01	-0.01	-0.04
1	- 1 - 1	t, t		,		1 .			÷	
× .		Foot note :	A1,2,3=	log1	["+log[(S+W	/Slp				

Table 56



for the development of Generalised correlation For systems B-H-Dmf-W



For systems T- H-Dmf-W









For systems T-H-Dmf-W







Fig.GC-21 Plots of log k Vs, log T'+log[(S+W)/S]⁻¹. for the development of Generalised correlation For system B-Hep-Dmf-W



For system B-Hep-Dmf-W





















along the straight line is the least in case of 27 systems under consideration. Hence the value of index 'p' of (-3) appears to be optimum value in generalized O - P correlation for systems involving solutes B/T/X.

(2) In figs. GC-19 to GC-24 which depicts 'k' data for different systems. B - Hep - Dmf + W plotted as log' k' Vs. log A. The value of index 'p' has been varied from (-0.5) to (-1.25). While plotting data of "A", the scattering of data points in the plot of GC-19 is highest when value of index 'p' is (-0.5). As value of index 'p' gets increased futher from (-0.5) to higher absolute values, the scattering of points gets reduced and the value of index 'p' gets increased further, a stage is reached when scattering of points again starts increasing but on the lower side of straight line. Thus only in Fig.GC-21 or GC-23 in comparison to all other remaining figures the scattering of points w. r. t. proposed generalized correlation line appears to be least wherein value of index 'p' is (-1) amongst the range varied from (-0.5) to (-1.25). Hence, the value of index 'p' of -1 appears to be the optimum value in the proposed generalized "O-P" correlation.

Though the best fit is obtained for index 'p' having value of (-1) to maintain uniformity in the value of index 'p' for aliphatics H/H'/O, the selected value of index 'p' is (-0.75) only.

(3) In figs. GC-25 to GC-30 which depicts 'k' data for different systems. B - Oct - Dmf + W plotted as log' k' Vs. log A, the value of index 'p' has been varied from (-0.25) to (-1.0). While plotting data of "A", the scattering of data points in the plot of GC-25 is highest value of index 'p' is (-0.25). As value of index 'p' gets increased further from (-0.25) to higher values, the scattering of points gets reduced and the value of index 'p' gets increased further, a stage is reached when scattering of points again starts increasing but on the lower side of straight line. Thus only in Figer 29 in comparison to all other remaining figures the scattering of points w.r.t. proposed generalized correlation line appears to be least wherein value of index 'p' is (-0.75) among the range varied from (-0.25) to (-1.0). Hence, the value of index 'p' of -0.75 appears to be the optimum value in the generalized O - P correlation.

(4) It is interesting to observe that index of Temperature Term labeled as 'o' has an optimum value of (+1) for all "k" data values obtained for mixed solvent - (Dmf+W). The index of anti-solvent concentration term labeled as 'p' has optimum

value of (-3) for system involving B - T - X along with Hexane system: and (-0.75) for systems involving Heptane and Octane along with Benzene.

5.7.3 Obtaining Values Of 'o' & 'p' in Oza - Puranik (O - P) Correlation for Mixed Solvent (Dmso + W):-

The performance of second mixed solvent- Dmso+W has been also investigated and the value of 'k' have been obtain under different sets of conditions for different systems consisting of B/T/X-H/H'/O- Dmso +W and the relevant values are reported in Table- 44. Using Table- 44 as the basis, basic data required for development of generalized correlation for mixed solvent- Dmso+W for ploting of different plots is reported in Table- 58.

Accordingly data processing Table for the development of generalized correlation for mixed solvent- Dmso+W has been prepared and the corresponding values of log' k' Vs. log A using different values of index 'o' & 'p' are reported in Table- 59.

Based on this Derived Table- 59, different plots of log k Vs log A have been depicted in Figs GC-31 to GC-60. The relevant data has been divided in four categories as under.

(i) Data processing for 'k' values for system involving B/T-H-Dmso+W under different sets of conditions.

(ii) Data processing for 'k' values for system involving X-H- Dmso +W under different sets of conditions.

(iii) Data processing for 'k' values for system involving B-Hep- Dmso +W under different sets of conditions.

(iv) Data processing for 'k' values for system involving B-Oct- Dmso +W under different sets of conditions.

Accordingly, various generalized correlations plots of log k Vs log A have been presented in Figs. GC--31 to GC-42 for category (i), in Figs GC-43 to GC-48 for

Table -58

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-	Basic	: Dati	a req	luire	I for Develo	pment of	Generalise	ed Correlati	ion for solvent Dms	20			
Sr. No	. System	T°C	3%	N% S	<pre>S/(M+S) /</pre>	k	log k	log T'	N/S/(W+S) Sol	logM1	logM2	logM1/C1	logM2/C
	For A	roma	tics -	В				T'=(T+273)	//273			C1=78	C2=86
*****	B-H-100%Dmso+0%W	20	100	0	1.00	0.426	-0.371	0.03	0,00	1.89	1.93	0.00	0,00
64	B-H-90%Dmso+10%W	20	90	10	1.11	-0.112	-0.950	0.03	0.05	1.89	1.93	0.00	0.00
ر	B-H-80%Dmso+20%W	20	80	30	1.25	ŀ	1	ł	, 1	١	ı	,	
4	B-H-100%Dmso+0%W	30	100	0	1.00	0.524	-0.281	. 0.05	0.00	1.89	1.93	0.00	0.00
S	B-H-90%Dmso+10%W	30	90	10	1.11	0.229	-0.640	0.05	0.05	1.89	1.93	0.00	0.00
9	B-H-80%Dmso+20%W	30	80	20	1.25	0.019	-1.721	0.05	0.10	1.89	1.93	0.00	0.00
-	B-H-100%Dmso+0%W	40	100	0	1.00	0.749	-0.126	0.06	0.00	1.89	1.93	0.00	0.00
~	B-H-90%Dmso+10%W	40	90	10	1.11	0.275	-0.561	0.06	0.05	1.89	1.93	0.00	0.00
6	B-H-80%Dmso+20%W	40	80	50	1.25	0.029	-1.538	0.06	0.10	1.89	1.93	0.00	0.00
	For A	roma	tics -	Ŀ,					•				
10	T-H-100%Dmso+0%W	20	100	0	1.00	0.281	-0.551	0.03	0.00	1.98	1.93	0.07	0.00
11	T-H-90%Dmso+10%W	20	90	10	1.11	0.056	-1.252	0.03	0.05	1.98	1.93	0.07	0.00
12	T-H-80%Dmso+20%W	20	80	20	1.25	0.014	-1.854	0.03	0.10	1.98	1.93	0.07	0.00
13	T-H-100%Dmso+0%W	30	100	0	1.00	0.323	-0.491	0.05	0.00	1.98	1.93	0.07	0.00
14	T-H-90%Dmso+10%W	30	90	10	1.11	0.081	-1.092	0.05	0.05	1.98	1.93	0.07	0.00
15	T-H-80%Dmso+20%W	30	80	20	1.25	0.016	-1.796	0.05	0.10	1.98	1.93	0.07	0.00
16	T-H-100%Dmso+0%W	40	10	0	1.00	0.500	-0.301	0.06	0.00	1.98	1.93	0.07	0.00
17	T-H-90%Dmso+10%W	40	90	10	1.11	0.123	-0.910	0.06	0.05	1.98	1.93	0.07	0.00
18	T-H-80%Dmso+20%W	40	80	20	1.25	0.045	-1.347	0.06	0.10	1.98	1.93	0.07	0.00
	For A	roma	tics -	×						•	I • •		
19	X-H-100%Dmso+0%W	20	100	0	1.00	0.019	-1.721	0.03	0.00	2.03	1.93	0.13	0.00
20	X-H-90%Dmso+10%W	20	90	10	1.11	0.002	-2.750	0.03	0.05	2.03	1.93	0.13	0.00
21	X-H-80%Dmso+20%W	20	80	50	1.25	0.001	-3.000	0.03	0.10	2.03	1.93	0.13	0.00
22	X-H-100%Dmso+0%W	30	100	0	1.00	0.090	-1.046	0.05	0.00	2.03	1.93	0.13	00.0
23	X-H-90%Dmso+10%W	30	8	10	1.11	0.004	-2.398	0.05	0.05	2.03	1.93	0.13	0.00
24	X-H-80%Dmso+20%W	30	80	5	1.25	0.002	-2.70	0.05	0.10	2:03	1.93	0.13	0.00
25	X-H-100%Dmso+0%W	40	100	0	1.00	0.263	-0.58	0.06	0.00	2.03	1.93	0.13	0.00
26.	X-H-90%Dmso+10%W	40	90	10	1.11	0.095	-1.022	0.06	0.05	2.03	1.93	0.13	0.00
27	X-H-80%Dmso+20%W	4	8	ន	1.25	0.054	-1.268	0.06	0.10	2.03	1.93	0.13	0.00

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 Table -58(continued)

 Basic Data required for Development of Generalised Correlation for solvent Dmso

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Sr. N	o. System	É	%S	W%	S/(M+S)	k	log k	log T'	log (S+W)/S	logM1	logM2	logM1/C1	logM2/C2
		<mark>ي</mark>					Ľ	=(T+273)/27.	3		,	C1=78	C2=86
	ц	or -]	Ē	•		-						•	
28	B-Hep-100%Dmso+0%W	20	100	0	1.00	0.309	-0.51	0.03	0.00	1.89	2.00	0.00	0.07
29	B-Hep-90%Dmso+10%W	20	90	10	1.11	0.118	-0.925	0.03	0.05	1.89	2.00	0.00	0.07
30	B-Hep-80%Dmso+20%W	20	-80	-20	-1.25	60.0	-1.041	0.03	0.10	1.89	2.00	0.00	0.07
				-			• _			Ŀ			
31	B-Hep-100%Dmso+0%W	30	100	0	1.00	0.346	-0.461	0.05	0.00	1.89	2.00	0.00	0.07
32	B-Hep-90%Dmso+10%W	30	90	10	1.11	0.208	-0.682	0.05	0.05	1.89	2.00	0.00	0.07
33	B-Hep-80%Dmso+20%W	30	80	20	1.25	0.131	-0.883	0.05	0.10	1.89	2.00	0.00	0:07
, ,	D II	Ċ,	001	¢									• ,
	D-riep-100%DmS0+0%W	1	100	>	1.00	1/2.0	-0.431	0.06	0.00	1.89	2.00	0.00	0.07
35	B-Hep-90%Dmso+10%W	40	8	10	1.11	0.281	-0.551	0.06	0.05	1.89	2.00	0.00	0.07
36	B-Hep-80%Dmso+20%W	40	80	20	1:25	0.223	-0.652	0.06	0.10	1.89	2.00	0.00	0.07
	Fc	or -C	Sct		-		•				-		
37	B-Oct-100%Dmso+0%W	20	100	0	1.00	0.114	-0.943	0.03	0.00	1.89	2.06	000	0.12
38	B-Oct-90%Dmso+10%W	20	8	10	1.11	0.053	-1.276	0.03	0.05	1.89	2.06	0.00	0.12
39	B-Oct-80%Dmso+20%W	20	80	20	1.25	0.007	-2.155	0.03	0.10	1.89	2.06	0.00	0.12
	•				•		•	•	-			-	
40	B-Oct-100%Dmso+0%W	30	100	0	1.00	0.141	-0.851	0.05	00.0	1.89	2.06	0.00	0.12
41	B-Oct-90%Dmso+10%W	30	90	10	1.11	0.112	-0.951	0.05	0.05	1.89	2.06	0.00	0.12
42	B-Oct-80%Dmso+20%W	30	80	20	1.25	0.021	-1.678	0.05	0.10	1.89	2.06	0.00	0.12
· .				. (1			•	×			
43	B-Oct-100%Dmso+0%W	40	100	0	1.00	0,275	-0.561	0.06	0.00	1.89	2.06	00.0	0.12
44	B-Oct-90%Dmso+10%W	40	8	10	1.11	0.162	-0.790	0.06	0:02	1.89	2.06	0.00	0.12
45	B-Oct-80%Dmso+20%W	40	80	20	1.25	'ı	ı		0.10	1.89	2.06	0.00	0.12

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			\mathbf{A}_{6}	P=-3.25	0.03	-0.12	1	0.05	-0.10	-0.27	0.06	-0.09	-0.26	P=-3.25	0.03	-0.12	-0.28	0.05	-0.10	-0.27	0.06	-0.09	-0.26	P=1.25	0.03	-0.03	-0.09	0.05	-0.01	-0.08	0.06	0.00	-0:06	
			A_5	P≕-3.	0.03	-0.11	ł	0.05	-0.09	-0.25	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.25	0.06	-0.08	-0.23	P=-1	0.03	-0.02	-0.07	0.05	0.00	-0.05	0.06	0.01	-0.04	
•		ent. Dmso	· A4	P=-2.75	0.03	-0.10	. •	0.05	-0.08	-0.22	0.06	-0.07	0.21	P=-2.75	0.03	-0.10	-0.24	0.05	-0.08	-0.22	0.06	-0.07	-0.21	P=-0.75	0.03	0.00	-0.04	0.05	0.01	-0.03	0.06	0.02	-0.01	logT+log[(S+W)/S] ^p
	65	n for solv	A3	P=-3	0.03	-0.11	,	0.05	-0.09	-0.25	0.06	-0.08	-0.23	P=-3	0.03	-0.11	-0.26	0.05	-0.09	-0.25	0.06	-0.08	-0.23	P=0.;	0.03	0.00	-0.04	0.05	0.01	-0.03	0.06	0.02	-0.01	A _{1,2,3=}
	Table -	Correlatic	\mathbf{A}_2	P=-2.75	0.03	-0.10	1	0.05	-0.08	-0.22	0.06	-0.07	-0.21	P=-2.75	0.03	-0.10	-0.24	0.05	-0.08	-0.22	0.06	-0.07	-0.21	P=0.5	0.03	0.01	-0.02	0.05	0.02	0.00	0.06	0.04	0.01	-
		ble for Generalised	A1	P=-2.5	0.03	-0.08	3	0.05	-0.07	-0.20	0.06	-0.06	-0.18	P=-2.5	0.03	-0.08	-0.21	0.05	-0.07	-0.20	0.06	-0.06	-0.18	P=0.33	0.03	0.01	0.00	0.05	0.03	0.01	0.06	0.04	0.03	Foot note :
		Processing Tal	log k		-0.371	-0.950		-0.281	-0.640	-1.721	-0.126	-0.561	-1.538	·	-0.551	-1.252	-1.854	-0.491	-1.092	-1.796	-0.301	-0.910	-1.347		-1.721	-2.750	-3.000	-1.046	-2.398	-2.70	-0.58	-1.022	-1.268	•
	1	Data	4		0.426	-0.112	."	0.524	0.229	0.019	0.749	0.275	0.029		0.281	0.056	0.014	0.323	0.081	0.016	0.500	0.123	0.045		0.019	0.002	0.001	0.090	0.004	0.002	0.263	0.095	0.054	
			T°C %W	- Aromatics - B	20 0	20 10	20 20	30 0	30 10	30 20	40 0	40 10	40 20	r Aromatics - T	20 0	20 10	20 20	30 0	30 10	30 20	40 0	40 10	40 20	Aromatics - X	20 0	20 10	20 20	30 0	30 10	30 20	40 0	40 10	40 20	· · · ·
		:	Sr. No.	For	y	2	M	4	S	Q	7	8	6	For	10	11	12	13	14	15	16	17	. 18	For	19	20	21	22	23	24	25	26	27	· .
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•				Â	ata Proces.	sing Table	e for Genera	Table -59(co lised Correlati	ntinued) ion for solvent	t Dmso		
	Sr. No.	Ţ	M%	k	log k		A1	A2	A ₃	A4	Ås	A
		ပ္ရ									,	,
	•	For -	Ħ				P=-0.5	P=-0.75	P= . 1	P=-1.25	P=-1.5	p=-1.75
	28	20	0	0.309	-0.51		0.03	0.03	0.03	0.03	0.03	0.03
	29	20	10	0.118	-0.925		0.01	0.00	-0.0-	20.02		50.0
	30	20	20	0.09	-1.041		-0.02	-0.04	-0.07	-0.09	-0.12	-0.0-
	31	30	0	0.346	-0.461		0.05	0.05	0.05	0.05	0.05	0.05
	32	30	10	0.208	-0.682		0.02	0.01	0.00	-0.01	-0.02	-0.04
	33	30	20	0.131	-0.883		0.00	-0.03	-0.05	-0.08	-0.10	-0.12
				••				•				
	34	40	0	0.371	-0.431	•	0.06	0.06	0.06	0.06	0.06	0.06
- -	35	40	10	0.281	-0.551		0.04	0.02	0.01	00.0	-0.01	000-
	36	40	20	0.223	-0.652		0.01	-0.01	-0.04	-0.06	00 0-	-0.11
		For -(Oct	v		•	P=-0.5	P=_0.75	P=_1	D=_1 25	D= 1 5	D- 1 75
	37	20	0	0.114	-0.943		0.03	0.03	0.03	0.02		C/-11
	38	20	10	0.053	-1.276		0.01	000		c0.0	50'0	0.03
	30	ЭО	20	0.007	2155		1010	20.0	*0.0-	CO'O-	-0.04	c0.0-
))	ì	2	10000			70.0-	-0.04	10.0-	-0.09	-0.12	-0,14
	40	30	0	0.141	-0.851		0.05	0.05	0.05	0.05	0.05	0.05
	41	30	10	0.112	-0.951		0.02	0.01	0.00	-0.01	-0.07	000-
	42	30	20	0.021	-1.678	,	0.00	-0.03	-0.05	-0.08	-0.10	-0.12
•	•							v				,
	43	40	0	0.275	-0.561	· •	0.06	0.06	0.06	0.06	0.06	0.06
	44	40	10	0.162	-0.790		0.04	0.02	0.01	0.00	-0.01	-0.02
	45	4	50 20		1		•		ł	•		
		, ; .						Foot note :	A1,2,3=	logT+log[(S+W)/S] ^p		

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For systems B-H-Dmso-W



For systems B-H-Dmso-W





For systems T-H-Dmso-W



Fig.GC-45 Plots of log k Vs, log T'+log[(S+W)/S]^{-0.75} for the development of Generalised correlation For systems X-H-Dmso-W







for the development of Generalised correlation For system B-Hep-Dmso-W



For system B-Hep-Dmso-W









On similar lines, the plots of log' k' Vs. log A for systems involving component- Heptane are shown in Figs GC-49 to GC-54 wherein value of index' p' has been varied from (-0.5 to -1.75).

As could be observed from Figs GC-49 and GC-54, the scattering of points is highest in these two Figures. The scattering of data points in the proposed generalized correlation straight line is the least in Fig. GC-51. Hence the value of 'p' =(-1) appears to be best fit wherein practically all points are on proposed generalized correlation straight line . However to keep uniformity in the value of index "p" for aliphatics-H/H'/O in generalized correlation, the value of index 'p' of (-0.75) has been selected.

(v) The relevant data of log' k' Vs. log A for systems involving component – Octane wherein value of index 'p' has been varied from (-0.5) to (-1.75), has been plotted in Figs. GC-55 to GC-60

Critical observations of all the Figures from figs GC-55 to GC-60 indicate that the scattering of data points in Fig.GC-55 having index 'p' value of (-0.5) as well as Fig.GC-60 having 'p' of value (-1.75) is highest.

Only in Fig.GC-56 wherein value of index 'p' is (-0.75), the scattering of data points along the proposed generalized correlation line is the least. Hence it can be considered as optimum value of index 'p' for systems involving aliphatic component-Octane. This value of index 'p' of (-0.75), matches with the value for systems involving aliphatic component-Heptane.

(vi) It is interesting to observe that index of Temperature Term labeled as 'o' has an optimum value of (+1) for all "k" data values obtained for mixed solvent - (Dmso+W).

The index of Anti-solvent Concentration Term has been labeled as 'p'. The value of index "p" of (-3) is for all systems involving aromatic component:-

Benzene & Toluene. However, the value of index involving aromatic component-Xylene is (0.333).

The value of index 'p' for all systems involving aliphatic components- Hexane, Heptane and Octane is (-0.75). category (ii), in Figs. GC-49 to GC-54 for category (iii) and in Figs. GC-55 to GC-60 for category (iv)

Critical Observations and Remarks w.r.t. Plots GC-31 to GC-60:

(i) In Figs GC-31 to GC-42, the index value of 'p' has been varied from (-2.5) to (-3.25) and data for different systems-B/T-H-Dmso+W has been plotted.

The scattering of data points of 'k' along generalized correlations straight line appears to be highest in Figs. GC-31 and GC--36. Further in Fig. GC-33 scattering of points along the generalized correlation straight line for system involving Benzene happens to be least for value of index of 'p' = (-3).

Hence values of index 'p' of the order of (-3) appears to be the optimum value.

For systems involving aromatic component- Toluene, similar observations can be made from Figs. GC-37 to GC-42 and value of index 'p' of the order of (-3.25) appears to be optimum value, as could be seen from Figs. GC-42.

However to keep uniformity in the value of index 'p'for aromatics for both the solvents, the value of 'p' = (-3) has been selected as the optimum value of systems involving aromatic component-Toluene.

(ii) For systems involving aromatic component- -Xylene, the value of log k Vs log A have been plotted in Figs GC-43 to GC-48 wherein value of index 'p' has been varied from (-0.333) to (-1.25). The critical observation of all these Figures indicates that the optimum value of index 'p' for systems involving aromatic component- Xylene (-0.333) as could be seen from Fig GC-37 wherein the scattering of data points is the least w. r. t. generalized correlation straight line.

Thus for systems consisting of aromatic component-s- Benzene and Toluene, the values of index 'p' appears to be (-3). However for system consisting of aromatic component- Xylene the value of 'p' has to be (-0.333). This can be considered as important exception for the value of index for systems consisting of aromatic component- Xylene. Excluding these nine systems, for all the remaining 81 systems, the value of index 'p' for aromatics -B/T/X for both mixed solvents -(Dmf+W) as well as -(Dmso+W) is (-3) only.

5.7.4 Obtaining Values of 'q' & 'r' in Oza - Puranik (O - P) Correlation for Mixed Solvent (Dmf + W):-

Oza-Puranik correlation can be written as

$$\log' k' = \log \left[\frac{T_1}{T_0}\right]^0 + \log \left[\frac{S+W}{S}\right]^p + \log \left[\frac{M_1}{C_1}\right]^q + \log \left[\frac{M_2}{C_2}\right]^r$$

In this correlation the term

$$\log\left[\frac{T_1}{T_0}\right]^{o} + \log\left[\frac{S+W}{S}\right]^{p}$$

has been labeled as 'A' and the given equation can be written as

log' k' = A + log
$$\left[\frac{M_1}{C_1}\right]^q$$
 + log $\left[\frac{M_2}{C_2}\right]^r$ = log X

Thus various values of 'A' already reported previous Table-56 could be utilized further to obtain values of 'X' wherein index of molecular weight of aromatic term and molecular weight of aliphatic term namely 'q' & 'r' needs to be finalized. While obtaining 'X' term for different index value of 'q', index of '0' & 'p' for "Temperature Effect Term" & "Anti solvent effect Term" respectively which have been already finalized in previous section-(5.7.2), have been utilized. The optimized values of index 'o' & 'p' are as under:

For "Temperature Effect Term" values of index 'o' is (+1). For "Anti solvent effect Term", the values of index 'p' is (-3) for component B-T-X and (-0.75) for component H' & O.

Using above mentioned values of 'o' and 'p', data processing Table- 57 (A) has been prepared for B-T-X systems. Further data processing Table-57((B) has been prepared for systems involving aliphatic- Heptane and data processing Table-57(C) has been prepared for systems involving aliphatic -Octane.

Using the values of 'X' and 'k' reported in Table- 57(A), Table- 57(B) & Table-57(C), various plots of log' k' Vs. logX have been depicted in figures. GC-. 61 to GC-.
			-		-																-			-	**	_						Y
	. X 5	P=-3q=-1	0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229		-0.042	-0.177	-0.330	-0.027	-0.162	-0.315	-0.013	-0.148	-0.301		-0.103	-0.238	-0.391	-0.088	-0.223	-0.376	-0.074	-0.209	-0.362	
	X4	P=-3q=-0.75	-0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229		-0.024	-0.159	-0.312	-0.009	-0.144	-0.297	0.005	-0.130	-0.283		-0.070	-0.205	-0.358	-0.055	-0.190	-0.343	-0.041	-0.176	-0.329	
	£3	· P=-3q=-0.5	0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229		-0.006	-0.141	-0.294	0.009	-0.126	-0.279	0.023	-0.112	-0.265		-0.037	-0.172	-0.325	-0.022	-0.157	-0.310	-0.008	-0.143	-0.296	
	X-2	P=-3q=-0.333	0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229		0.006	-0.129	-0.282	0.021	-0.114	-0.267	0.035	-0.100	-0.253		-0.014	-0.149	-0.302	0.001	-0.134	-0.287	0.015	-0.120	-0.273	•
	XI	P=-3q=-0.25	0.030	-0.105	-0.258	0.045	060.0-	-0.243	0.059	-0.076	-0.229	- - -	0.012	-0.123	-0.276	0.027	-0.108	-0.261	0.041	-0.094	-0.247	•	-0.003	-0.138	-0.291	0.012	-0.123	-0.276	0.026	-0.109	-0.262	
C.F	0X	P=-3,q=0	0:030	0.045	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229		0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0.076	-0.229	•	0.030	-0.105	-0.258	0.045	-0.090	-0.243	0.059	-0:076	-0.229	
	IOJIIIO	: CI=78	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072		0.133	0.133	0.133	0.133	0.133	0.133	0.133	0.133	0.133	8) ⁴ +log(M2/86)
1 (0 I WD/0	10g (5+W/S		0000	. 0.045	0.096	0.000	0.045	0.096	0.000	0.045	0.096		0.000	0.045	0.096	0.000	0.045	0.096	0.000	0.045	0.096	•	0.000	0.045	0.096	0.000	0.045	0.096	0.000	0.045	0.096	/S] ^p +log(M1/78
1001	log K		0.129	-0.630	-1.050	0.180	-0.500	-0.940	0.200	-0.380			-0.080	-1.080	-1.340	0.010	-0.570	-1.080	0.050	-0.510	-1.020		-0.090	-1.090	-1.600	-0.010	-0.820	-1.400	0.025	-0.790	-1.070	log[(S+W)
-	×		1.348	0.234	0.089	1.513	0.316	0.114	1.584	0.416			0.831	0.083	0.045	1.023	0.264	0.083	1.122	0.309	0.095		0.812	0.081	0.025	0.977	0.151	0.039	0.944	0.162	0.085	= logT'+
111.70	70 W	cs - B	0	10	20	0	10	20	0	10	20	cs - T	0	01	8	0	10	20	0	10	20	X - SS	0	10	20	0	10	20	0	01	8	(1,2,3-
C ₀ L		romati	50	20	20	30	90	30	40	40	40	romati	20	20	20	30	30	30	40	40	40	omati	20	50	20	30	30	30	40	40	4	
C. N.	01.10	For A		64	ώ	4	ŝ	9	7	×	6	For AI	10	11	12	13	14	15	16	17	18	For A ₁	19	50	51	22	53	24	22	26	27	Foot not
							'																									

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 Table-57(A)

 Data Processing Table for Generalised Correlation for solvent Dmf for parameter - (X) for Aromatics

 Table 57 (B)

 Data Processing Table for Generalised Correlation for solvent Dmf for parameter - (X) for Aliphatics Heptane.

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X 6	P=-0.75	q=0	Г — 3	-0.167	-0.200	-0.239	-0.152	-0.185	-0.224	-0.138	-0.171	-0.210	
X5	P=-0.75	d=0	r=-2.5	-0.134	-0.168	-0.206	-0.119	-0.153	-0.191	-0.105	-0.139	-0.177	•
X4	P=-0.75	q=0	F-2.25	-0.117	-0.151	-0.189	-0.102	-0.136	-0,174	-0,088	-0.122	-0.160	• •
° EX	P=-0.75	р Б	1 - -7	-0.101	-0.135	-0.173	-0.086	-0.120	-0.158	-0.072	-0.106	-0.144	eptions
X,	P=-0.75	0−р	<u>r-1.5</u>	-0.068	-0.102	-0.140	-0.053	-0.087	-0.125	-0.039	-0.073	-0.111	gary - exc
x	P=-0.75	0=0	1	-0.036	-0.069	-0.108	-0.021	-0.054	-0.093	-0.007	-0.040	-0.079	* Categ
X0=A2	P=-0.75	ось	L	- 0.030	-0.004	-0.042	0.045	0.011	-0.027	0.059	0.025	-0.013	•
logM2/C2	 			0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	
logM2				2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	(6) ¹
log (S+W)/S	73		-	- 0.00.0	0.045	0.096	0.000	0.045	0.096	0.000	0.045	0.096	78) ⁴ +log(M2/8
log T'	T+273)/2			0.030	0.030	0.030	0.045	0.045	0.045	0.059	0.059	0.059] ^{p+log(M1/}
log k	Ц. Ч			-0.110	-0.560	-1.000	-0.030	-0.550	-0.850	-0.500	-0.320	-0.820	g[(S+W)/S
		-'	•	0.776	0.275	0.100	0.933	0.446	0.141	0.445	0.425	0.154	logT+lo
S/(M+S)				1.00	1.11	1.25	1.00	1.11	1.25	1.00	1.1.1	1.25	•••• • • •
Μ%				0	10	20	0	10	20	0	10	50	
s%	5			100	90	80	100	06	. 08	100	60	80	K1,2,3=
т	or - H	ပ	1	20	20	20	30	30	30	40	40	40	
Sr. No.	Ц			28*	29	30	31*.	32	33	34	35	36	Foot not

Table 57 (C)

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Data Processing Table for Generalised Correlation for solvent Dmf for parameter - (X) for Aliphatics Octane. <

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	q=0 q=0	CZ.1-T I-T 1.24	.127 -0.158	.165 -0.196	.078 -0.109	0.112 -0.143	0.150 -0.181	0.064 -0.095	.098 -0.129	0.136 -0.167	
P=-0.75 P=	q=0	-0.062 -(-0.096 -(-0.134 -(-0.047 -(-0.081 -(-0.119 -(-0.033 -(-0.067	-0.105 -(
P=-0.75	q=0	-0.032	-0.065	-0.104	-0.017	-0.050	-0.089	-0.003	-0.036	-0.075	
P=-0.75	q=0	-0.011	-0.045	-0.083	0.004	-0.030	-0.068	0.018	-0.016	-0.054	
P=-0.75	q=0	c71	-0.035	-0.073	0.014	-0.020	-0.058	0.028	-0.006	-0.044	
P=-0.75	0=b	0.030	-0.004	-0.042	0.045	0.011	-0.027	0.059	0.025	-0.013	ptions
Inguter Ce		0.123	0.123	0.123	0.123	0.123	0.123	0.123	0.123	0.123	egory - excej
102014		2.058	2.058	2.058	2.058	2.058	2.058	2.058	2.058	2.058	* Cat
cifus ich Sm		0.000	0.045	0.096	0.000	0.045	960'0	0.000	0.045	0.096	;(M2/86) ^r
1 22		0:030	0.030	0.030	0.045	0.045	0.045	0.059	0.059	0.059	(1/78) ^{4+log}
4 490	x.	-0.190	-0.560	-1.010	-0.050	-0.380	-0.950	0.060	-0.090	-0.480	/S] ^p +log(N
4		0.645	0.271	0.097	0.891	0.416	0.112	1.480	0.812	0.331	/(M+S)]g(
		1.00	1.11	1.25	1.00	1.11	1.25	1.00	1.11	1.25	logT+lc
		0	10	20	0	10	20	0	10	20	
For - 00		100	90	80	100	06	80	100	06	80	X1,2,3=
		20	20	20	30	30	30	40	40	40	ote :
		37	. 38	39*	40	41	42*	43	44	45	Foot ne

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Fig.GC-61 Plots of log k Vs, X1 for the development of Generalised correlation for systems B/T/X-H-Dmf-W



Fig.GC-62 Plots of log k Vs, X2 for the development of Generalised correlation for systems B/T/X-H-Dmf-W



Fig.GC-63 Plots of log k Vs, X3for the development of Generalised correlation for systems B/T/X-H-Dmf-W



Fig.GC-64 Plots of log k Vs, X4 for the development of Generalised correlation for systems B/T/X-H-Dmf-W



Fig.GC-65 Plots of log k Vs, X5 for the development of Generalised correlation for systems B/T/X-H-Dmf-W



Fig.GC-66 Plots of log k Vs, X1 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W



Fig.GC-67 Plots of log k Vs, X2 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W







Fig.GC-69 Plots of log k Vs, X4 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W



Fig.GC-70 Plots of log k Vs, X5 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W



Fig.GC-71 Plots of log k Vs, X6 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W



Fig.GC-72 Plots of log k Vs, X1 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W and B-Oct-Dmf-W











Fig.GC-75 Plots of log k Vs, X4 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W and B-Oct-Dmf-W



Fig.GC-76 Plots of log k Vs, X5 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W and B-Oct-Dmf-W



Fig.GC-77 Plots of log k Vs, X6 for the development of Generalised correlation for systems B/T/X-H-Dmf-W and B-H'-Dmf-W and B-Oct-Dmf-W

77 for all the 45 values of 'k' obtained in this investigation for mixed solvent (Dmf+W) under different sets of conditions.

Critical Observations and Remarks w.r.t. Plots: Figs.GC-61to GC-77:

(i) Data processing Table- 57 (A) has been utilized while plotting different figures from GC-61 to GC-65.In Figs. GC-61 to GC-65 which depicts 'k' data for different systems: B/T/X-H-Dmf+W the values of index 'q' has been varied from (-2.5) to (-1) while plotting data of log' k' Vs. log (X). Scattering of points is highest on lower side of straight line in Fig-GC-61. As the index 'q' value gets altered from -0.25 to higher values, the scattering of points gets reduced.As the value of index 'p' gets increased further, a stage is reached when the scattering of points again starts increasing but on upper side of straight line. Thus, scattering of points is highest in two figures namely-Fig.GC-61 and Fig.GC-65. Thus only in Fig.GC-63, the scattering of points w.r.t. proposed generalized correlation line appears to be the least wherein the value of index 'q' of (-0.5) among the range varied from (-0.25) to (-1). Hence the value of index 'q' of (-0.5) appears to be optimum value in generalized O-P correlation.

(ii) Data processing Table- 57 (B) has been utilized while plotting different figures from GC-.66 to GC-.-71. In these figures wherein plots have been made for log' k' Vs. log'X' for different systems consisting of B-Hep-Dmf+W. The value of index 'r' has been varied from (-1) to (-3).

All the previous 27 data points with optimum value of index already decided have been plotted along with data points for the systems involving aliphatic Heptane. Scattering of data points is highest and on lower side of generalized correlation straight line in Fig.- 66 wherein the value of index of 'r' is (-1). As the value of index 'r' gets increased from (-1) to higher numerical value, the scattering of points along generalized correlation line starts decreasing. As the value of index 'r' increases further, a stage is reached such that the scattering of points again starts increasing. However, the scattering of points now starts increasing on the upper side of generalized correlation straight line.

Thus scattering of points is highest in two figures namely FigsGC-66 and GC-71 wherein the value of index 'r' are (-1) and (-3) respectively.

Thus only in Fig. GC-69, the scattering of points for the proposed generalized correlation line appears to be the least wherein value of index 'r' is (-2.25) among the range varied from (-1) to (-3). Hence the value of index 'r' in generalized correlation appears to be (-2.25). However, though the best fit is obtained for index of 'r' in the "Term Molecular Weight of Aliphatics" for a value of (-2.25), to maintain over all uniformity in the index value of 'r', the selected value of 'r' is (-2).

(iii) The data processing Table- 57 (c) has been utilized while plotting different Figs. GC-.70 to GC-.-77. In these Figs, data of log' k' and log'X' for systems involving B/T/X-H-Dmf+W and systems involving B-Hep-Dmf+W have been plotted along the data for systems involving B-O-Dmf+W. while finalizing value of 'r' for different systems involving B-O-Dmf+W. The already finalized values of index 'o', 'p', 'q' and 'r' for different systems involving- B/T/X+H/+Dmf+W. have been kept for proposed generalized correlation.

The range of index 'r' for Octane has been varied from (-0.25) to (-1.25).

All the previous 36 data points with optimum value of index already decided have been plotted along with data points for systems involving aliphatic Octane in Figures from GC-72 to GC-. -77.

As could be seen from Fig. GC-72, the scattering of data points is highest and on lower side of proposed generalized correlation straight line wherein index of 'r' for the term involving mol wt. of aliphatics is (-0.25)

As the value of index 'r' gets increased from (-0.25) to higher absolute values, the scattering of data points along generalized correlation line for systems involving aliphatic-Octane starts decreasing. As the value of index 'r' increased to a higher numerical value, a stage is reached such that the scattering of points along generalized correlation line again starts increasing. However, increase in scattering of points is on the upper side of generalized correlation straight line.

Thus as could be observed from Figs GC-72 to GC-77, scattering of points in two Figs Figs GC-72 and GC-77 is highest. In Fig. GC-72, the scattering of points is on lower side of proposed generalized correlation line and in Fig GC-77, the scattering happens to be on the upper side of the proposed generalize correlation line wherein the value of index 'r' are (-0.250) and (-01.25) respectively.

Thus in Fig.GC-74 the scattering of all the data points of 'k' is the least w.r.t. generalized correlation straight line and optimum value of index 'r' is expected to be (-0.5).

(iv) Thus the values of index 'r' for systems involving aliphatic-Heptane and systems involving aliphatic-Octane are (-2) and (-0.5) respectively. Since these two values of "r" differ considerably, the effect of increase in molecular weight of aliphatics when Hexane is replaced by Heptane and subsequently by Octane, the effect of increase in molecular weight happens to be most stringent for systems involving Heptane.

5.7.5 Obtaining Values of 'q' & 'r' in Oza - Puranik (O - P) Correlation for Mixed Solvent (Dmso + W):-

The correlation cited under sub-heading: (5.7.4) can also be utilized for mixed solvent Dmso + W. Thus the correlation utilized for fixing the values of 'q' and 'r' for mixed solvent Dmso +W is as under;

log' k' = A + log
$$\left[\frac{M_1}{C_1}\right]^q$$
 + log $\left[\frac{M_2}{C_2}\right]^r$ = log X

The values of (A) already reported in Table- 59 could be utilized conveniently to obtain the values of (X) by adding two terms namely: Ratio of molecular weight of aromatics having index 'q' and Ratio of molecular weight of aliphatics having index 'r' to the previously determined term (A).

The relevant values of 'X' along with values of 'k' for different systems involving mixed solvent- Dmso+W are reported in Table- 60 (A) wherein values of index 'o' and 'p' already finalized have been utilized and the values of index 'q' are varied in the range of (-0.25) to (-2).

Further data processing Table- 60 (B) has been prepared wherein aliphatic effect by replacing Hexane by Heptane has been considered and the values of index 'r' has been varied from (-0.75) to (-1.25). To study the effect of replacing aliphatic component- Heptane by Octane, data processing Table- 60(C) has been prepared wherein value of index 'r' has been altered from (-1) to (-1.5). Using values of 'X' and 'k' reported in Table-s- 60(A),60(B) & 60(C), various plots of log' k' Vs log[X] have

. Т°С	۸%		ata Pr lo	ocessin _{g k}	Ig Table I log T	for Genera og (S+W)/S	lised Cor logM1/C1	relation for logM2/C2	or solvent X0	Dmso for X1	parameter - X-2	(X) for Ard X3	matics X4	xs
					log T'				P3,q=0	P=-3q=-0.25	P-3q-0.333	P=-3q=-0.5	P-3q-0.75	P=-3q1
Ë	atics -	m m) L	T+273)/273		C1=78	C2=86						
20	0	0.42	26 -0	371	0.030	0.045	0.000	0	0:030	0.030	0.030	0.030	0.030	0:030
20	10	-0.1	12 -0.	.950	0:030	0.096	0.000	0	-0.107	-0.107	-0.107	-0.107	-0.107	-0.107
20	20	-		•	•	,		•	•	•	ı		•	¥
30	0	0.52	24 -0.	.281	0.045	0.045	0.000	0	0.045	0.045	0:045	0.045	0.045	0.045
30	10	0.2	29 -0.	.640	0.045	0.096	0.000	0	-0.092	-0.092	· -0.092	-0.092	-0.092	-0.092
30	50	0.0	19 -1.	.721	0.045	0.000	0.000	0	-0,246	-0.246	-0.246	-0.246	-0.246	-0.246
40	0	-2.0	49 -0	.126	0.059	0.045	0.000	.0	0.059	0.059	0.059	0.059	0.059	0.059
40	10	0.2	75 -0	.561	0.059	0.096	0.000	0	-0.078	-0.078	-0.078	-0.078	-0.078	-0.078
40	1 20	0.0	29 -1	.538	0.059	0.000	0.000	0	-0.232	-0.232	-0.232	-0.232	-0.232	-0.232
Lom	atics -	T							P=-3,q=0	P=-3q=-0.25	P-3q-0.333	P=-3q=-0.5	P=-3q=-0.75	P=-3q=-1
20	0	0.2	81 -0	1551	0.030	0.045	0.072	.0	0:030	0.012	0.006	-0.006	-0.024	-0.042
20) I(0.0	56 -1	.252	0.030	0.096	0.072	0	-0.107	-0.125	-0.131	-0.143	-0.161	-0.179
20	3(0.0 0	14 -1	.854	0.030	0.000	0.072	0	-0.261	-0.279	-0.285	-0.297	-0.314	-0.332
30	0	0.3	23 -0	.491	0.045	0.045	0.072	0	0.045	0.027	0.021	0.009	-0.009	-0.027
30	ž	0.0	I- 18	.092	0.045	0.096	0.072	0	-0.092	-0.110	-0.116	-0.128	-0.146	-0.164
ñ	й С	0.0	91	.796	0.045	0.000	0.072	0	-0.246	-0.264	-0.270	-0.282	-0.299	-0.317
4C	0	0.5	9 00	1301	0.059	0.045	0.072	0	0.059	0.041	0.035	0.023	0.005	-0.013
40	ž	0 0.1	23 -0	.910	0.059	0.096	0.072	0	-0.078	-0.096	-0.102	-0.114	-0.132	-0.150
4	2	0.0	145 -1	.347	0.059	0.000	0.072	0	-0.232	-0.250	-0.256	-0.268	-0.285	-0.303
LOID	atics - X								P=-0.333,q=0	P-0.333,q-0.5	P=-0.333,q=0.75	P=-0.333,q=-1	P=-0.333,q=1.5	P=-0.333,q=-2
ដ	0	0.0	61	.721	0.030	0.045	0.133	0	0.030	-0.037	-0.070	-0.103	-0.170	-0.236
3	≍ ~	0.0	022	.750	0.030	0.096	0.133	0	0.0148	-0.052	-0.085	-0.118	-0.185	-0.252
ž	ลั ด	0.0	0I -3	.000	0.030	0.000	0.133	0	-0.002	-0.069	-0.102	-0.135	-0.202	-0.269
З	0	0'0 (I- 06	.046	0.045	0.045	0.133	0	0.045	-0.022	-0.055	-0.088	-0.155	-0.221
Ř	ž	0 0.0	042	.398	0.045	0.096	0.133	0	0.030	-0.037	-0.070	-0.103	-0.170	-0.237
Ř	й 0	0.0	02 -2	669	0.045	0.000	0.133	0	0.013	-0.054	-0.087	-0.120	-0.187	-0.254
4	0	0.2	63 -0	.580	0.059	0.045	0.133	0	0.059	-0.008	-0.041	-0.074	-0.141	-0.207
¥	1	0.0	1- 561	.022	0.059	0.096	0.133	0	0.044	-0.023	-0.056	-0.089	-0.156	-0.223
¥	7	0.0	154 -1	.268	0.059	0.000	0.133	0	0.027	-0.040	-0.073	-0.106	-0.173	-0.240
	XI	2,3=	q	gT+log	3/(M+S)]	[] ^{p+log(M1}	/78) ^q +log	(M2/86) ^r		* Cat	egory - excel	otions		

Table-60(A)

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	Heptane
	a Processing Table for Generalised Correlation for solvent Dmso for parameter - (X) for Aliphatics He
	Da

— P=-0.75,r=-(P=-0.75,F=	P=0.75,r=	P=-0.75,r=	P=-0.75,r=	P=-0.75,r=	P=-0.75,r=	P=-0.75,r=	r - Hep P=-0.75,r=
0 <u>–</u> 6	q=0	d= 0	0=b	0=b	0=b	d= 0	d=b	d=b
0 -0.019	0.03	0.000 0.066 0.03	0.000 0.000 0.066 0.03	0.030 0.000 0.000 0.066 0.03	-0.510 0.030 0.000 0.000 0.066 0.03	0.309 -0.510 0.030 0.000 0.000 0.066 0.03	0 0.309 -0.510 0.030 0.000 0.000 0.066 0.03	20 0 0.309 -0.510 0.030 0.000 0.000 0.066 0.03
0.053 -0.053	-0.0	0.000 0.066 -0.00	0.046 0.000 0.066 -0.0	0.030 0.046 0.000 0.066 -0.00	-0.925 0.030 0.046 0.000 0.066 -0.0	0.118 -0.925 0.030 0.046 0.000 0.066 -0.0	10 0.118 -0.925 0.030 0.046 0.000 0.066 -0.0	20 10 0.118 -0.925 0.030 0.046 0.000 0.066 -0.0
43 -0.092	0.0	0.000 0.066 -0.0	0.097 0.000 0.066 -0.0	0.030 0.097 0.000 0.066 -0.0	-1.041 0.030 0.097 0.000 0.066 -0.0	0.091 -1.041 0.030 0.097 0.000 0.066 -0.0	20 0.091 -1.041 0.030 0.097 0.000 0.066 -0.0	20 20 0.091 -1.041 0.030 0.097 0.000 0.066 -0.0
45 -0.004	0.0	0.000 0.066 0.0	0.000 0.000 0.066 0.0	0.045 0.000 0.000 0.066 0.0	-0.461 0.045 0.000 0.000 0.066 0.0	0.346 -0.461 0.045 0.000 0.000 0.066 0.0	0 0.346 -0.461 0.045 0.000 0.000 0.066 0.0	30 0 0.346 -0.461 0.045 0.000 0.000 0.066 0.0
11 -0.038	0.0	0.000 0.066 0.0	0.046 0.000 0.066 0.0	0.045 0.046 0.000 0.066 0.0	-0.682 0.045 0.046 0.000 0.066 0.0	0.208 -0.682 0.045 0.046 0.000 0.066 0.0	10 0.208 -0.682 0.045 0.046 0.000 0.066 0.0	30 10 0.208 -0.682 0.045 0.046 0.000 0.066 0.0
0.077	-0.(0.000 0.066 -0.(0.097 0.000 0.066 -0.0	0.045 0.097 0.000 0.066 -0.0	-0.883 0.045 0.097 0.000 0.066 -0.0	0.131 -0.883 0.045 0.097 0.000 0.066 -0.0	20 0.131 -0.883 0.045 0.097 0.000 0.066 -0.0	30 20 0.131 -0.883 0.045 0.097 0.000 0.066 -0.0
59 0.010	0.0	0.000 0.066 0.0	0.000 0.000 0.066 0.0	0.059 0.000 0.000 0.066 0.0	-0.431 0.059 0.000 0.000 0.066 0.0	0.371 -0.431 0.059 0.000 0.000 0.066 0.0	0 0.371 -0.431 0.059 0.000 0.000 0.066 0.0	40 0 0.371 -0.431 0.059 0.000 0.000 0.066 0.0
25 -0.024	0.0	0.000 0.066 0.0	0.046 0.000 0.066 0.0	0.059 0.046 0.000 0.066 0.0	-0.551 0.059 0.046 0.000 0.066 0.0	0.281 -0.551 0.059 0.046 0.000 0.066 0.0	10 0.281 -0.551 0.059 0.046 0.000 0.066 0.0	40 10 0.281 -0.551 0.059 0.046 0.000 0.066 0.0
-0.063	-0.0	0.000 0.066 -0.0	0.097 0.000 0.066 -0.0	0.059 0.097 0.000 0.066 -0.0	-0.652 0.059 0.097 0.000 0.066 -0.(0.223 -0.652 0.059 0.097 0.000 0.066 -0.(20 0.223 -0.652 0.059 0.097 0.000 0.066 -0.0	40 20 0.223 -0.652 0.059 0.097 0.000 0.066 -0.0

 $X1,2,3 = \log T + \log[(S+W)/S]^{p} + \log(M1/78)^{q} + \log(M2/86)^{r}$

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Table-60(C)

Data Processing Table for Generalised Correlation for solvent Dmso for parameter - (X) for Aliphatics Octane

P=0.75,re-- P=0.75,re-1 P=0.75,re-1.25 P=0.75,re-1.5 P=0.75,re-1 =0.75,re-1.2P=0.75,re-1.5 X6 S X4 X X-2 XI Sr. No T^oC %W k log k log T og (S+W)/sogM1/C logM2/C2 X0 For - Oct

0=b	-0.155	-0.189	-0.228	0.000 -0.140	-0.174	-0.213	-0.126	-0.160	-0.199	
q=0	-0.124	-0.158	-0.197	0.000	-0.143	-0.182	-0.095	-0.129	-0.168	
q=0	-0.093	-0.128	-0.166	0.000	-0.113	-0.151	-0.064	-0.099	-0.137	-
q=0	-0.155	-0.189	-0.228	0.000	-0.174	-0.213	-0.126	-0.160	-0.199	
q=0	-0.124	-0.158	-0.197	-0.109	-0.143	-0.182	-0.095	-0.129	-0.168	
የ	-0.093	-0.128	-0.166	0.000-0.078	-0.113	-0.151	-0.064	-0.099	-0.137	
q=0	0.030	-0.004	-0.043	0.045	0.011	-0.028	0.059	0.025	-0.014	
	0.123	0.123	0.123	0.123	0.123	0.123	0.123	0.123	0.123	•
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	•
	0.000	0.046	0.097	0.000	0.046	0.097	0.000	0.046	0.097	-
-	0.03	0.03	0.03	0.045	0.045	0.045	0.059	0.059	0.059	-
	-0.943	-1.276	-2.155	-0.851	-0.951	-1.678	-0.561	-0.790		
	0.114	0.053	0.007	0.141	0.112	0.021	0.275	0.162		
*	0	10	20	0	10	20	0	10	8	
	20	20	20	30	30	30	40	40	40	
	37	38	39	40	41	42	43	44	45	
•	The second s			the second s						

Category - exceptions

logT+log[(S+W)/S]^p+log(M1/78)^q+log(M2/86)^r

X1,2,3=



Fig.GC-78 Plots of log k Vs, X1 for the development of Generalised correlation for systems B/T/-H-Dmso-W



Fig.GC-79 Plots of log k Vs, X2 for the development of Generalised correlation for systems B/T/-H-Dmso-W



Fig.GC-80 Plots of log k Vs, X3 for the development of Generalised correlation for systems B/T/-H-Dmso-W



Fig.GC-81 Plots of log k Vs, X4 for the development of Generalised correlation for systems B/T/-H-Dmso-W



Fig.GC-82 Plots of log k Vs, X5 for the development of Generalised correlation for systems B/T/-H-Dmso-W



Fig.GC-83 Plots of log k Vs, X1 for the development of Generalised correlation for systems B/T/X-H-Dmso-W



Fig.GC-84 Plots of log k Vs, X2 for the development of Generalised correlation for systems B/T/X-H-Dmso-W



Fig.GC-85 Plots of log k Vs, X3 for the development of Generalised correlation for systems B/T/X-H-Dmso-W



Fig.GC-86 Plots of log k Vs, X4 for the development of Generalised correlation for systems B/T/X-H-Dmso-W



Fig.GC-87 Plots of log k Vs, X5 for the development of Generalised correlation for systems B/T/X-H-Dmso-W











Fig.GC-90 Plots of log k Vs X2 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W



Fig.GC-91 Plots of log k Vs X4 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W







Fig.GC-93 Plots of log k Vs X6 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W



Fig.GC-94 Plots of log k Vs X1 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W and B-Oct-Dmso-W



Fig.GC-95 Plots of log k Vs X2 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W and B-Oct-Dmso-W



Fig.GC-96 Plots of log k Vs X3 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W and B-Oct-Dmso-W



Fig.GC-97 Plots of log k Vs X4 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-Wand B-Oct-Dmso-W



Fig.GC-98 Plots of log k Vs X5 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W and B-Oct-Dmso-W



Fig.GC-99 Plots of log k Vs X6 for the development of Generalised correlation for systems B/T/X-H-Dmso-W and B-Hep-Dmso-W and B-Oct-Dmso-W

been plotted in Figs GC-78 to GC-99 for all the 45 values of 'k' obtained in this investigation for mixed solvent- Dmso+W.

Critical observations and remarks w. r. t. plots: Figs GC-78 to GC-99:

(i) Data processing Table/s- 60(A) has been utilized while plotting different Figures from GC-79 to GC-82. In Figs GC-79 to GC-82 which depicts 'k' data for different systems B/T/H- Dmso+W, the values of index 'q' has been varied from (-0.25) to (-1) while plotting data of log X Vs log k, The scattering of data points w.r.t. generalized correlation straight line is highest in Fig GC-78 and GC-82 wherein values of 'q' utilized are (-0.25) and (-1) respectively.

Scattering of points w.r.t. the generalized correlation line appears to be the least in Fig GC-80 wherein power of 'q' utilized is (-0.5). Hence among the range of 'q' varied from (-0.5) to (-1) the optimum value of index 'q' appears to be (-0.5) for systems involving aromatic components-Benzene and Toluene.

tii) Since for data systems involving aromatic component- Xylene, the value of index 'p' is (-0.333), this data has been plotted in Figs. GC-83 to GC-87 wherein value of index 'q' has been altered from (-0.5) to (-2).

It is observed that scattering of points along the generalized correlation straight line is very high in two Figures- GC-83 and GC-87 wherein values of index 'q' happen to be (-0.5) and (-2) respectively.

Hence it is observed that only in Fig GC-85, the scattering of data points is least with reference to generalized correlation straight line. Here the value of index 'q' appears to be (-1) which gives best fit. Hence optimum values of index 'q' for systems involving aromatic component- Xylene appears to be (-1).

It may be noted that optimum value of index 'q' for systems involving aromatic components-Benzene & Toluene is (-0.5).

with The different values of log'X' and log' k' for aliphatic component- Heptane reported in Table- 60(B), have been plotted in Figs GC-88 to GC-93 wherein these Figs have been divided in two groups.

Group - 1: wherein values of index 'p' for Antisolvent concentration term has been kept as (-0.75) while finalizing value of "r"

Group - 2: wherein values of index 'p' for Antisolvent concentration term has been kept as (-1) while finalizing value of "r"

For these two groups-(1) and (2) the value of index 'q' has been varied from (-0.75) to (-1.25).

Observations for Group-1: Figs GC-89 to GC-90 : As could be seen from Fig GC-89 for Group-1, optimum value of index 'r' for system involving aliphatic component- Heptane happens to be (-1.25). In Fig GC-89, the scattering of points along generalized correlation straight line is the least. Hence the optimum value of index 'r' happens to be (-1.25). However to keep uniformity in different values of 'r', the value of index 'r' is selected as (-1)

Observations for Group-2: Figs GC-91 to GC-93 : As could be seen from Fig GC-91 for Group-2, optimum value of index 'r' for system involving component-Heptane happens to be (-0.75). Out of different Figures from GC-91 to GC-93, the scattering of points along generalized correlation straight line is the least in Fig GC-91. Hence optimum value of index 'r' for system having aliphatic component- Heptane is (-0.75) wherein optimum value of index 'p' of "Anti solvent Concentration Term" is (-1).

Thus for Group-1, optimum values of index 'p' and 'r' are (-0.75) & (-1) and optimum values of 'p' and 'r' for Group-2 are (-1) and (-0.75).

While plotting different graphs for systems involving aliphatic component-Octane and deciding optimum value of 'r' for systems involving Octane both the sets of Group-1 and Group-2 and corresponding sets of values of index 'p' and 'r' for component- Heptane have been utilized.

(iv) The different values of log X and log k for aliphatic component- Octane reported in Table - 60° have been plotted in Figures from GC - 94 to GC - 99 wherein these figures have been divided in two groups:

Figs. for Group - 1 are GC - 94 to GC - 96.

Figs. for Group - 2 are GC - 97 to GC - 99.

Discussion for Figures GC - 94 to GC - 96 for Group - 1:

While plotting data of log k Vs log X in these figures, data of log k of systems involving B / T / X - H / Hep - Dmso + W, the various values of index 'o', 'p', 'q' & 'r' already optimized have been utilized namely $p_{B, T} = (-3)$, $p_x = (-0.333)$, $p_{H} = (0.75)$, $q_{B,T,X} = (-1)$ and $r_{H} = (-1)$.

The value of index 'r' for systems involving component-Octane has been varied from (-1) to (-1.5).

The scattering of data points of 'k' w.r.t. proposed generalized correlation straight line appears to be least in Fig. GC - 94 in comparison to Figs. GC-95 and GC-96. Hence, optimum value of index 'r' for systems involving aliphatic component-Octane appears to be (-1).

Thus all the data of 'k' values can be correlated satisfactorily by 'O-P' generalized correlation as per plot shown in Fig. GC - 94.

Discussion for Figures- GC - 97 to GC - 99 for Group - 2:

While plotting data in this figs., the values of group -2 mentioned for systems involving Heptane i.e. $p_{H^{T}} = -1$ and $r_{H^{T}} = -0.75$ have been utilized. All the remaining values remain same as in group-1 i.e. $p_{B,T} = (-3)$, $p_{s} = (-0.333)$ and $q_{B,T,X} = (-1)$.

The values of index 'r' for systems involving component- Octane have been varied from (-1) to (-1.5).

The scattering of all the data points of 'k' from the proposed generalized 'O-P' correlation straight line appears to be least in Fig. GC - 97 in comparison to Figs. GC - 98 and GC - 99. Hence, the value of index 'r' for systems involving Octane is (-1) which can be called as optimum value of index 'r' for systems involving aliphatic component- Octane. Thus all the data of 'k' values can be correlated satisfactorily by Oza- Puranik (O-P) correlation as per plot of log k Vs. log X shown in fig. GC - 97.

(v) Comparison of Figs. GC - 94 and GC - 97:

Generalized correlation depicted in Figures- GC - 94 constituted six values of index 'p', 'q' & 'r' namely:

 $P_{BT} = -3,$ $P_{x} = -0.333$ $P_{H,0} = -0.75$ $q_{B,T} = -0.5$ $q_{x} = -1$ $r_{H'0} = -1$

Generalized correlation depicted in Fig. GC - 97 constitutes eight values of 'p', 'q' & 'r' namely

 $P_{B,T} = -3$, $P_x = -0.333$ $P_{H'} = -1$ & $P_o = -0.75$ $q_{B,T} = -0.5$ $q_x = -0.1$ $r_{H'} = -0.75$ & $r_o = -1$

Three values of index - 'p', 'q' & 'r' obtained in generalized correlation which has been proposed for mixed solvent-(Dmso + W) are common with the values obtained in generalized correlation proposed mixed solvent Dmf + W.

Hence to keep more uniformity in proposed Oza- Puranik (O-P) correlation, the plot shown in Fig. GC - 94 is selected for mixed solvent-(Dmso + W) in comparison to the plot shown in Fig. GC - 97.

5.7.6 Oza - Puranik (O-P) Correlation for

Quaternary Liquid - Liquid Phase Equilibilium Data :

The following generalized Oza-Puranik (O-P) correlation proposed in this investigation can be considered as one of the most important contribution of the present work.

$$\log k = \log \left[\frac{T}{T_0}\right]^0 + \log \left[\frac{S+W}{S}\right]^p + \log \left[\frac{M_1}{C_1}\right]^q + \log \left[\frac{M_2}{C_2}\right]^r$$

The above correlation constitutes four dimensionless groups as

$$\begin{bmatrix} T\\T_0 \end{bmatrix}, \begin{bmatrix} S+W\\S \end{bmatrix}, \begin{bmatrix} M_1\\C_1 \end{bmatrix}, \begin{bmatrix} M_2\\C_2 \end{bmatrix}$$

With index values o, p, q & r.

The terms in the denominator namely T₀, C₁ and C₂ are having values 273 °K, 78 (molecular weight of benzene) and 86 (molecular weight of hexane) respectively.
For quaternary systems - B/T/X - H/H'/O - Dmf + W:

Index values are as under:

$$p_{B,T,X} = -3, p_{H',0} = -0.75, q_{B,T,X} = -0.5, r_{H'} = -2 \& r_{0} = -0.5$$

For quaternary systems: B / T / X - H / H' / O - Dmso + W :

Index values are as under :

$p_{B,T,X} = -3,$	$p_{x} = -0.333$	&	р _{н, о} = -0.75
$q_{B,T} = -5,$	$q_{x} = -1$.	&	r _{H',0} = -1

5.7.7 Predicting Values of XBE, XSE & XBR, XHR :

Stepwise procedure mentioned by Dhabe and Puranik,⁽⁴³Bansod and Puranik ⁽⁷²⁾ can be followed to predict extract phase and raffinate phase composition, by trial and error approach.

(i)The values of temperature (T), antisolvent concentration (W) aromatic component to be extracted and aliphatic component in the feed with their composition in the feed should be fixed.

(ii)Hence using 'O-P' correlation, the value of 'k' can be predicted conveniently.

(iii)Once the value of 'k' is known for a fixed valued of feed composition, the ratio of E / R can be assumed.

Stepwise procedure mentioned by Dhabe and Puranik ⁴³has to be followed and a plot of

$$\log \left[\frac{X_{BR}}{X_{HR}}\right] \text{ Vs. } \log \left[\frac{X_{BE}}{X_{SE} + X_{WE}}\right]$$

can be constructed.

(v)Using trial and error approach, using material balance equations over all and individual for E & R phases in terms of F & S and the Hand's plot for the system under consideration, the step wise calculation procedure is repeated till the value of (E / R) assumed initially and (E / R) predicted by calculation match with each other.

S

(vi)Thus extract phase composition of solute and solvent i.e.($X_{BE} \& X_{DE}$), raffinate phase composition of solute and non-solute ($X_{BR} \& X_{DR}$) can be predicted.

5.8.0 CORRELATING QUATERNARY LIQUID-LIQUID PHASE EQUILIBRIUM DATA BY NRTL EQUATION.

Exhaustive work has been done by Kolha and Puranik⁷⁷ wherein different computer programs have been developed for correlating and predicting ternary as well as quaternary liquid-liquid phase equilibrium data inclusive of vapor-liquid equilibrium data.

These authors have used various novel approaches as under:

- (i) Correlating basic component binary vapor- liquid phase equilibrium data to correlate ternary vapor liquid equilibrium data.
- (ii) Correlating basic ternary equilibrium data to correlate quaternary liquid liquid phase equilibrium data.
- (iii) Using vapor liquid phase equilibrium data to predict liquid liquid phase equilibrium data.
- (iv) Using liquid liquid phase equilibrium data to predict vapor liquid phase equilibrium data.
- (v) Also using LEMF, NRTL, UNIVAC and UNIFAC models available in literature, various computer programmes have been prepared by these investigators.
- (vi) From these various programmes, different programs prepared for UNIFAC, UNIVAC and NRTL have been utilized to correlate exhaustive equilibrium liquid liquid Phase equilibrium data obtained for liquid.— liquid extraction of aromatics in this investigation.
- (vii) It has been observed that out of above mentioned three models NRTL model fits all the data obtained in present investigation most satisfactorily. Hence all the relevant details of computer programming have been mentioned in present thesis only for NRTL method.

This method has also been utilized successfully by Gandhi and Puranik¹⁶⁸.

Different systems classified into five categories for solvent involving Dmf and also five categories for solvent involving Dmso have been processed by computer programming and all the relevant details are mentioned in Appendix consisting of Tables-1.1 to 1.13 for solvent Dmf and Tables-2.1 to 2.15 for solvent Dmso.

While processing data by computer programming anti solvent concentration of water has been considered as a prime variable and temperature as secondary variable. Totally twelve NRTL constants have been involved for a fixed temperature for one system involving solute- (B / T / X), non-solute (H / Hept / Oct), solvent- (Dmf / Dmso) and antisolvent (W).

In this manner data for fourteen systems (actually $14 \ge 3 = 42$ systems if one takes into consideration anti solvent concentration as a variable) have been correlated for liquid. – liquid extraction of aromatics involving mixed solvent Dmf+W.

In similar manner data for fifteen systems (actually $15 \ge 3 = 45$ systems if one takes into consideration anti solvent concentration as a variable) have been correlated for liquid. – liquid extraction of aromatics involving mixed solvent Dmso+W.

5.8.1. NRTL Constant Values :

Based on exhaustive computer programming data reported in Appendix-IV, Summary Tables have been prepared for NRTL constants which also includes absolute mean deviation, optimum value of F and number of tie lines.

(i) NRTL constant values for Systems consisting of B/T/X-H/Hept/Oct-Dmf/W are reported in Tables 61 to 65 wherein classified Systems are as under :

- (1) Benzene (B) Hexane (H) Dmf Water (W)
- (2) Tolune (T) Hexane (H) Dmf Water (W)
- (3) Xylene'(X) Hexane(H) Dmf Water(W)
- (4) Benzene (B) Heptane (H') Dmf Water (W)
- (5) Benzene (B) Octane (Oct) Dmf Water (W)

At a glance one realizes that there can't be any specific trend regarding nature of constants for different systems involving mixed solvent- Dmf+W However, after critical analysis of data, it is observed that there exists a peculiar trend for all constants.

(ii) NRTL constant values for Systems consisting of B/T/X-H/Hept/Oct Dmso / W are reported in Tables 61 to 65 wherein systems are as under :

NRTL	20 °C	30 °C
A(1,2)	735.5074	586.2665
A (1,3)	662.2728	815.0587
A (1,4)	379.3250	658.4573
A (2, 1)	263.4166	317.7770
A (2, 3)	-1269.1480	-215.5683
A (2 ,4)	-37.2994	298.7109
A (3, 1)	707.7083	773.7364
A (3, 2)	-221.1540	-909.2023
A (3, 4)	426.6541	307.4060
A (4, 1)	82.0247	-267.9727
A (4,2)	585.6796	196.7304
A (4, 3)	794.1349	527.1005
ABSOLUTE MEAN DEVIATION (MOLE %) OPTIMUM VALUE OF F	1.54815 0.0515839	2.89683 0.0467786
No of Tie lines.	15.0	16.0

Table-61Value of Constants for NRTL equation for System B - H - Dmf - W

	·		
NRTL	20 °C	30 °C	40 °C
A (1, 2).	263.9734	433.7261	549.3115
A (1 , 3) .	373.1947	408.5995	529.5548
A (1,4).	273.1213	254.0914	-13.0831
A (2, 1).	465.8286	492.3210	271.4386
A (2,3).	-80.0822	-312.0891	53.3676
A (2,4).	602.0111	381.3229	161.2820
A (3 , 1) .	470.8522	933.8842	615.6130
A (3 , 2) .	10.4358	-567.8607	250.3456
A (3,4).	367.2550	451.3655	616.0107
A (4, 1).	-203.4787	293.5040	-257.9896
A (4,2).	582.3835	138.5687	392.7339
A (4,3).	520.9489	496.3878	464.8004
ABSOLUTE MEAN DEVIATION (MOLE %)	5.10046	1.87058*	3.09568*
OPTIMUM VALUE OF F 0.0841786	0.3641742	0.0863915	0.2254088
No of Tie lines.	9	15	15

Table-62Value of Constants for NRTL equation for System T - H - Dmf - W

NRTL	· .	20 °C	40 °C
A (1,2)=		982.6008	606.3065
A (1,3).		641.1958	448.0769
A (1,4).		-247.4561	56.8726
A (2,1).		47.1464	414.5657
A (2,3).		52.2038	-227.6839
A (2,4).		347.4907	228.2203
A (3,1).		661.2541	516.2860
A (3,2).		180.6193	104.3383
A (3,4).		657.9348	440.5740
A (4, 1).		106.1042	-595.2411
A (4,2).		660.4219	487.4023
A (4,3).	•	585.5577	397.7920
ABSOLUTE MEAN DEVIATIO	N (MOLE %)	2.98251	1.32106*
OPTIMUM VALUE OF F	0.0841786	0.1824451	0.0192564
No of Tie lines.		15	11

Table-63Value of Constants for NRTL equation for System X - H - Dmf - W

•			
NRTL	20 °C	30 °C	40 °C
A (1,2).	521.3718	727.8251	616.2385
A (1,3).	321.4382	856.1557	477.3983
A (1,4).	10.5100	387.7383	7.3420
A (2, 1).	346.1175	326.5732	333.4872
A (2,3).	-177.2816	5.7413	-673.4152
A (2 , 4) .	192.2867	590.2787	-438.6278
A (3,1).	485.9051	758.8549	422.4020
A (3,2).	-125.7842	680.7773	-1018.6990
A (3,4).	349.8169	627.6929	650.3218
A (4, 1).	-337.8912	505.6935	-243.1448
A (4 , 2) .	561.8356	501.4370	367.7644
A (4,3).	406.4340	641.1835	787.0422
ABSOLUTE MEAN DEVIATION (MOLE %)	. 2.94784	3.92413*	1.669075*
OPTIMUM VALUE OF F	0.0876058	0.3062868	0.0600729
No of Tie lines.	. 10	15	17

Table-64Value of Constants for NRTL equation for System B - Hep - Dmf - W

NRTL	20 °C	30 °C	40 °C
A (1,2).	1047.5770	1069.4170	715.9625
A (1,3).	-47.0931	637.5468	502.3986
A (1,4).	-613.8423	-396.0732	-24.2439
A (2, 1).	160.3802	933.0268	487.6512
A (2,3).	-1246.1990	23.4268	-182.7415
A (2,4).	-436.9845	-131.1132	126.6221
A (3, 1).	995.0690	681.0268	458.6049
A (3,2).	-821.1371	362.8768	-21.7067
A (3,4).	507.0612	815.9866	317.1026
A(4,1).	-427.5832	734.8904	-59.9024
A (4,2).	411.9515	667.5668	167.5441 ·
A (4,3).	352.9347	1036.5770	384.5162
ABSOLUTE MEAN DEVIATION (MOLE %)	1.66133	2.44740*	3.8940,5*
OPTIMUM VALUE OF F No of Tie lines .	0.0650122	0.1618726 15	0.2773978 15

Table - 65Value of Constants for NRTL equation for System B - Oct - Dmf - W

NIDIT	70.00	20.00	40.00
NRIL	20°C	30-0	40 °C
A(1,2)	1123.624	748.095	1082.717
	•		
A (1 ,3)	680.5751	452.095	629.737
A (1, 4)	319.7207	400.371	206.201
A (2, 1)	714.575	721.535	597.333
A (2, 3)	-214.425	-231.905	-316.412
A (2,4)	-67.425	153.754	-204.921
A (3, 1)	2110.575	1126.871	2087.281
A (3, 2)	-800.454	243.095	-1110.065
A (3,4)	646.575	1415.484	856.752
A (4, 1)	646.575	237.095	-149.419
A (4,2)	631.575	814.576	644.903
A (4, 3)	786.575	1206.095	768.841
ABSÓLUE MEAN DEVIATION[MÓLE%]	1.68877	1.54738*	0.8304
OPTIMUM VALUE OF F	0.0841786	0.0192064	0.0099850
No. of Tie lines.	15	16	. 14

Table-66Value of Constants for NRTL equation for System B - H - Dmso - W

		•	
NRTL A (1, 2)	20 °C 656.3872	30 °C 648.0947	40 °C 680.5551
A (1,3)	360.4989	352.0948	433.7349
A (1 , 4)	315.7503	300.3714	86.5692
A (2, 1)	681.9917	621.5348	704.2772
A (2,3)	-3240.4603	-131.9051	-189.4393
A (2,4)	102.2855	53.7541	64.5216
A (3 , 1)	858.1785	926.8710	953.3259
A (3 , 2)	151.4184	343.0949	280.2507
A (3 , 4)	1235.0480	1615.4840	1304.9020
A (4, 1)	145.6383	137.0949	553.2846
A (4,2)	790.6209	914.5758	741.4771
A (4,3)	1114.3650	1406.0950	1158.1130
ABSOLUTE MEAN DEVIATION(MOLE %)	1.54738	0.99164*	1.6944
OPTIMUM VALUE OF F	، 0.0458642	0.0192064	0.0492756
No of Tie lines.	16	16	15

Table-67Value of Constants for NRTL equation for System T - H - Dmso - W



Table-68Value of Constants for NRTL equation for System X - H - Dmso - W

NRTL	20 °C	30 °C	40 °C
A (1,2).	879.143	763.406	1045.488
A (1,3).	521.137	397.328	290.279
A (1,4).	189.969	346.916	341.288
A (2, 1).	790.301	790.757	780.690
A (2 , 3) .	169.900	381.138	288.868
A (2,4).	1026.869	923.500	819.018
A (3 , 1) .	845.431	967.104	891.483
A (3 , 2) =	140.2713	342.7327	199.7915
A (3 , 4) =	906.8153	1049.6560	962.4148
A (4 , 1) =	309.7488	486.8335	490.5774
A (4 , 2) =	358.2643	296.1371	107.8207
A (4 , 3) =	835.3828	725.6857	922.2023
ABSOLUTE MEAN DEVIATION (MOLE %)	0.83067	1.65215*	2.23821*
OPTIMUM VALUE OF F	0.0124217	0.0539820	0.1221319
No of Tie lines .	16	16	11

· ·			
NRTL	20 °C	30 °C	40 °C
A (1 , 2)	957.6147	698.7540	636.633700
A (1,3)	1050.9050	1087.7070	1183.902000
A (1 , 4)	26.0195	101.8724	374.678900
A (2, 1)	905.3219	919.1672	1010.458000
A (2,3)	-51.4001	202.8756	-105.097800
A (2 , 4)	-327.6503	-285.9129	-249.470200
A (3, 1)	997.4967	1015.3400	1111.902000
A (3 , 2)	-402.9991	469.2961	-361.095200
A (3 , 4)	1109.5120	1094.5900	1190.902000
A (4 , 1)	-258.2584	280.5459	-184.095200
A (4 , 2)	936.6920	1004.2680	1056.584000
A (4 , 3)	1050.8920	1180.1940	1276.902000
ABSOLUTE MEAN DEVIATION (MOLE %)	1.08454	1.09647*	1.7094
OPTIMUM VALUE OF F	0.0248281	0.0229795	0.0585277
No of Tie lines.	18	16	17

Table-69Value of Constants for NRTL equation for System B - Hep - Dmso - W

NRTL	20 °C	30 °C	40 °C
A (1,2).	1422.888	1488.058	1565.829
A (1,3).	721.702	877.024	955.301
A (1,4).	-261.488	-256.232	158.912
A (2, 1).	943.757	907.970	993.888
A (2,3).	-980.841	-927.106	-874.060
A (2,4).	-268.009	-417.592	-285.483
A (3,1).	-93.035	-62.309	40.522
A (3,2).	-634.937	-573.136	-505.921
A (3,4).	1244.617	1233.884	1307.964
A (4 , 1) .	-940.648	-891.741	-783.153
A (4 , 2) .	646.395	823.254	888.371
A (4,3).	783.753	766.868	906.026
ABSOLUTE MEAN DEVIATION (MOLE %)	1.12518	1.24104*	1.02741*
OPTIMUM VALUE OF F 0.0841786 No of Tie lines .	0.0388759 16	0.0422470 16	0.0250098 16

Table-70Value of Constants for NRTL equation for System B - Oct - Dmso - W

- (1) Benzene (B) Hexane (H) Dmso Water (W)
- (2) Tolune (T) Hexane (H) Dmso Water (W)
- (3) Xylene (X) Hexane (H) Dmso Water (W)
- (4) Benzene (B) Heptane (H') Dmso Water (W)
- (5) Benzene (B) Octane (Oct) Dmso Water (W)

At a glance one realizes that there can't be any specific trend regarding nature of constants for different systems involving mixed solvent- Dmso+W. However, after critical analysis of data, it is observed that there exists a peculiar trend for all constants.

5.8.2. NRTL Constant Values and Error Analysis :

(i)Values of NRTL constants for systems consisting of Benzene / Tolune / Xylene – Hexane – Dmf – Water at three different temperature 20° C, 30° C and 40° C are reported in Table - 71 which also indicates effect of molecular weight of aromatics on different values of constants.

Further values of NRTL constants for systems consisting of Benzene – Hexane / Heptane / Octane – Dmf – Water at three different temperatures 20° C, 30° C and 40° C are reported in Table- 72 which also indicates effect of molecular weight of aliphatics on different values of constants.

Each system consists of a set of twelve constants for a fixed value of temperature .Thus even effect of temperature on different values of constants can also be analyzed by preparing relevant Tables.

The critical analysis of data on NRTL constant values obtained for different systems consisting of mixed solvent – Dmf+W has been done in subsequent paragraphs else where.

(ii)Values of NRTL constants for systems consisting of Benzene / Tolune / Xylene – Hexane – Dmso – Water at three different temperature 20° C, 30° C and 40° C are reported in Table – 73 which also indicates effect of molecular weight of aromatics on different values of constants.

Further values of NRTL constants for systems consisting of Benzene – Hexane / Heptane / Octane – Dmso – Water at three different temperatures 20° C, 30° C and 40° C are reported in Table 74 which also indicates effect of molecular weight of aliphatics on different values of constants.

 Table-71

 Values of Constants for NRTL equation for System B/T/X - H - Dmf - W

			20 °C		•	30 °C			40 °C	
Sr.No.	NRTL	B	Ľ	X	A	H	X	Â	H	X
, ,	A(1,2)	735.5074	263.9734	982.6008	586.2665	433.7261		1	549.3115	606.3065
7	A(1,3)	662.2728	373.1947	641.1958	815.0587	408.5995	1	•	529.5548	448.0769
ŝ	A (1,4)	379.3250	273.1213	-247.4561	658.4573	254.0914	a -	н Т	-13.0831	56.8726
4	A(2,1)	263.4166	465.8286	47.1464	317.770	492.3210	8	1 ·	271.4386	414.5657
ŝ	A (2, 3)	-1269.1480	-80.0822	52.2038	-215.5683	-312.0891	•	' 1	53.3676	-227.6839
9	A(2,4)	-37.2994	602.0111	347.4907	298.7109	381.3229	ŧ	1 201	161.2820	228.2203
7	A (3, 1)	707.7083	470.8522	661.2541	773.7364	933.8842	1 1	L	615.6130	516.2860
∞	A (3, 2)	-221.1540	10.4358	180.6193	-909.2023	-567.8607		ł	250.3456	104.3383
6	A (3,4)	426.6541	367.2550	657.9348	307.4060	451.3655	ł	I	616.0107	440.5740
10	A (4,1)	82.0247	-203.4787	106.1042	-267.9727	293.5040	1	1	-257.9896	-595.2411
11	A (4,2)	585.6796	582.3835	660.4219	196.7304	138.5687	ı	4	392.7339	487.4023
13	A(4,3)	794.1349	520.9489	585.5577	527.1005	496.3878	1.	•	464.8004	397.7920
								*		

Values of Constants for NRTL equation for System B-H/Hep/Oct-Dmf-W Table-72

-182.7415 487.6512 458.6049 317.1026 502.3986 -24.2439 -21.7067 -59.9024 167.5441 384.5162 715.9625 126.6221 Oct -1018.6990 -673.4152 -438.6278 -243.1448 422.4020 477.3983 650.3218 367.7644 333.4872 787.0422 616.2385 7.3420 40 °C Hep H -131.1132 815.9866 637.5468 396.0732 933.0268 23.42679 681.0268 362.8768 734.8904 667.5668 1036.577 1069.417 Oct 758.8549 680.7773 501.4370 387.7383 326.5732 590.2787 627.6929 505.6935 641.1835 856.1557 5.7413 30 °C 727.8251 Hep 909.2023 -215.5683 -267.9727 298.7109 773.7364 815.0587 658.4573 317.7770 307.4060 196.7304 527.1005 586.2665 Η -1246.1990 436.9845 -427.5832 1047.5770 -613.8423 160.3802 507.0612 411.9515 995.0690 821.1371 352.9347 -47.0931 Oct -177.2816 -125.7842 -337.8912 192.2867 349.8169 321.4382 346.1175 561.8356 406.4340 521.3718 485.9051 10.5100 20 °C Hep -1269.1480263.4166 -221.1540 379.3250 -37.2994 585.6796 794.1349 662.2728 707.7083 426.6541 735.5074 82.0247 H A(2,1) A (2, 3) A(3,1) A(4,1) A(3,2) A(1,3) A(1,4) A(2,4) A (3, 4) A (4,2) A (4, 3) Sr.No. NRTL A(1,2) 10 Ï 2 9 Ś 6 5 ∞ 2 ŝ 4

 Table-73

 Values of Constants for NRTL equation for System B/T/X - H - Dmsn - W

			20 °C			30 °C			40 °C	
Sr.No.	NRTL	B	E-	X	æ	E-	X	B		X
	A(1,2)	1123.624	656.3872	879.1426	748.0947	648.0947	763.41	1083	680.5551	1045.4880
6	A(1,3)	680.5751	360.4989	521.1365	452.0948	352.0948	397.33	629.7	433.7349	290.2793
ຕ່	A (1,4)	319.7207	315.7503	189.9690	400.3714	300.3714	346.92	206.2	86.5692	341.2875
4	A (2, 1)	714.5751	681.9917	790.3014	721.5348	621.5348	790.76	597.3	704.2772	780.6902
ŝ	A (2, 3)	-214.4249	-3240.4603	169.8997	-231.9051	-131.9051	381.14	-316	-189.4393	288.8682
.9	A (2,4)	-67.4249	102.2855	1026.8690	153.7541	53.7541	923.5	-205	64.5216	819.0182
7	A(3,1)	2110.5750	858.1785	845.4309	1126.8710	926.8710	967.1	2087	953.3259	891.4832
∞	A (3,2)	-800.4540	151.4184	140.2713	243.0949	343.0949	342.73	-1110	280.2507	199.7915
6	A(3,4)	646.5751	1235.0480	906.8153	1415.4840	1615.4840	1049.7	856.8	1304.9020	962.4148
10	A(4,1)	646.5751	145.6383	309.7488	237.0949	137.0949	486.83	-149	553,2846	490.5774
	A (4,2)	631.5751	790.6209	358.2643	814.5758	914.5758	296.14	644.9	741.4771	107.8207
12	A (4,3)	786.5751	1114.3650	835.3828	1206.0950	1406.0950	725.69	768.8	1158.1130	922.2023

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 Table-74

 Values of Constants for NRTL equation for System B- H /Hep/Oct- Dmso - W

			20.02			30 °C			40 °C	
Sr.N	o. NRTL	H	Hep	Oct	Η	Hep	Oct	H	Hep	Oct
	A(1,2)	1123.624	957.6147	1422.8880	748.0947	698.7540	1488.058	1082.717	636.6337	1565.8290
7	A (1,3)	680.5751	1050.9050	721.7015	452.0948	1087.7070	877.0242	629.7367	1183.9020	955.3011
ε	A(1,4)	319.7207	26.0195	-261.4878	400.3714	101.8724	-256.2319	206.2008	374.6789	158.9116
4	A(2,1)	714.5751	905.3219	943.7567	721.5348	919.1672	907.9702	597.3326	1010.4580	993.8883
S	A (2,3)	-214.4249	-51.4001	-980.8409	-231.9051	202.8756	-927.1055	-316.4117	-105.0978	-874.0604
9	A (2,4)	-67.4249	-327.6503	-268.0087	153.7541	-285.9129	-417.5923	-204.9211	-249.4702	-285.4825
L	A (3, 1)	2110.5750	997.4967	-93.0354	1126.8710	1015.3400	-62.30892	2087.281	1111.9020	40.5224
~	A(3,2)	-800.4540	-402.9991	-634.9367	243.0949	469.2961	-573.1358	-1110.065	-361.0952	-505.9208
6	A (3,4)	646.5751	1109.5120	1244.6170	1415.4840	1094.5900	1233.884	856.7521	1190.9020	1307.9640
-10	A (4, 1)	646.5751	-258.2584	-940.6475	237.0949	280.5459	-891.7408	-149.4185	-184.0952	-783.1530
11	A (4,2)	631.5751	936.6920	646.3946	814.5758	1004.2680	823.2535	644.9026	1056.5840	888.3708
12	A (4,3)	786.5751	1050.8920	783.7527	1206.0950	1180.1940	766.8682	768.8411	1276.9020	906.0260
			\$							

. . .

Each system consists of a set of twelve constants for a fixed value of temperature .Thus even effect of temperature on different values of constants can also be analyzed by preparing relevant Tables.

The critical analysis of data on NRTL constant values obtained for different systems consisting of mixed solvent – Dmso+W has been done in subsequent paragraphs else where.

(iii)It appears that NRTL model fits the data on quaternary liquid. – liquid. phase equilibrium data for both the solvents satisfactorily. However, comparision of absolute mean deviation values for systems involving solvents Dmf and Dmso has been depicted in Table – 75. Interesting conclusion can be drawn from this table which has been also discussed separately.

5.8.3 Critical analysis of NRTL constants for different systems-B/T/X-H-Dmf-W:-

The various values of NRTL constants under different sets of conditions for solvent Dmf for different systems wherein Benzene has been replaced by Toluene and later on Toluene has been replaced by Xylene have been tabulated in Table-71

Component Hexane has been labeled as-1, Component Dmf has been labeled as-2, Component Water has been labeled as-3, andComponent Benzene/ Toluene / Xylene has been labeled as-4

Accordingly, twelve values of NRTL constants have been compared in Tables-71.

Based on critical analysis of NRTL constants following are the important observations/conclusion:-

(I) For Component Hexane (1) the three values of NRTL constants A(1,2), A(1,3) and A(1,4) follow a decreasing order for all systems consisting of Benzene, Toluene and Xylene as solute and also at all three temperatures 20° C, 30° C and 40° C.

The exceptions for the above observation being systems consisting of Toluene at 20°C and Benzene at 30°C wherein this order is not followed.

Thus for example for system B-H- Dmf -W at 20°C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical

conditions, , the values of constants A(1,2), A(1,3) and A(1,4) are 735.5, 662.2 and 379.3 respectively. Thus NRTL constants follow a decreasing trend.

Further, for example for system, X-H- Dmf -W at 20° C, for all the three antisolvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, , the values of constants A(1,2), A(1,3) and A(1,4) are 982.6, 641.2, and -247.4 respectively.

Thus, it is confirmed that NRTL constants for component Hexane (1) follow a decreasing trend.

(II) For Component Dmf (2), the values of NRTL constants namely A(2,1), A(2,3) and A(2,4) follow an interesting trend for all systems consisting of Benzene, Toluene and Xylene and also at all three temperatures i.e. middle constant A(2,3) is always having a lower value in comparison to constants A(2,1) and A(2,4). There is only one exception to the above conclusion for the system consisting of Xylene at temperature 20° C

Thus for example, for system T-H- Dmf -W at 20°Cfor all the three anti solvent concentrations namely 0%W, 10%W and 20%W under otherwise identical conditions, , the values of constants A(2,1), A(2,3) and A(2,4)are 465.8, -80.08 and 602.01 respectively.

Thus middle constants A(2,3) is having lowest value i.e. -80.08 which is lower than the remaining two constants- A(2,1) and A(2,4). Further for example for system T-H-Dmf-W at 40°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4) are 271.4, 53.36 and 161.3 respectively.

Thus middle constant A(2,3) is having lowest value i.e. 53.36 which is lower than the remaining two constants- A(2,1) and A(2,4).

(III) For Component Water(3), the three values of NRTL constants namely A(3,1), A(3,2) and A(3,4) follow a similar trend like that is followed for Component

Dmf (2). The value of middle constant-A (3, 2) is always having a lower value in comparison to constants-A(3,1) and A(3,4).

The above statement is true for all the valued of NRTL Constants i.e. A (3, 1), A(3,2) and A(3,4) without any exception.

Thus for example, for system X-H- Dmf -W at 20°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 661.2, 180.6 and 657.0 respectively.

Thus middle value A(3,2) is having lowest value i.e. 180.6 which is lower than the remaining two constants- A(3,1) and A(3,4).

Further for example, for system T-H- Dmf -W at 40°C for all the three anti solvent concentration values 0%W, 10%W and 20%W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 615.6, 250.3 and 616.0 respectively.

Thus middle value A(3,2) is having lowest value i.e. 250.3 which is lower than remaining two constants- A(3,1) and A(3,4).

(IV) For Component Benzene(4), the values of NRTL constants namely A(4,1), A(4,2) and A(4,3) follow exactly an opposite trend than that which is observed for component Hexane (1)

The three values of constants namely A(4,1), A(4,2) and A(4,3) follow an increasing order trend for all the systems consisting of Benzene, Toluene and Xylene and also three temperatures 20°C ,30°Cand 40°C.The main exceptions to this generalized observation are systems consisting of Toluene at 30°Cand Xylene at 40°C

Thus for example, for system B-H- Dmf -W at 30°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical

conditions, the values of constants A(4,1), A(4,2) and A(4,3) are -267.0, 196.7 and 527.0 respectively. Thus NRTL constants follow an increasing trend.

Further for example for system T-H- Dmf -W at 40°Cfor all the three anti solvent namely 0%W, 10%W and 20%W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are -257.9,392.7 and 464.8 respectively. Thus NRTL constants follow an increasing trend.

(V)Thus with respect to NRTL constants for systems consisting of B/T/X-H-Dmf-W under different sets of conditions, the following four generalized conclusions can be drawn:

(i) The various values of NRTL constants involving component- Hexane (1) follow a decreasing trend as component- Dmf (2) gets modified to component water(3) and further gets modified to Component-Benzene (4).

(ii) The values of NRTL constants involving component Dmf (2) follow a trend wherein middle constant value-A(2,3) is lower than remaining two constants namely-A(2,1) and A(2,4).

(iii)) The values of NRTL constants involving component Water (3) also follow a trend like component – Dmf(2). The middle constant value-A(3,2) is lower than remaining two constants namely-A(3,1) and A(3,4).

(iv) The values of NRTL constants involving component Benzene (4) follow an increasing trend as component Hexane (1) gets modified to component Dmf (2) and further gets modified to component-Water (3).

5.8.4 Critical analysis of NRTL constants for different systems-B-H/Hep/Oct-Dmf-W:-

The various values of NRTL constants under different sets of conditions for solvent Dmf and solute Benzene for different systems wherein Hexane has been replaced by Heptane and later on Heptane has been replaced be Octane have been tabulated in Table-72 Component Hexane/Heptane/Octane has been labeled as-1, Component Dmf has been labeled as-2, Component Water has been labeled as-3, and Component Benzene has been labeled as-4

Accordingly, twelve values of NRTL constants have been compared in these tables.

Based on critical analysis of NRTL constants following are the important observations/conclusions:-

(I) For Component H/Hep/Oct (1) the three values of NRTL constants A(1,2), A(1,3) and A(1,4) follows a decreasing order for all systems consisting of Benzene as solute and Hexane/Heptane/Octane as non solute and also at all three temperatures 20° C, 30° C and 40° C.

The only single exception being system consisting of non solute Hexane at 30°C wherein this order is not followed.

Thus for example for system B-Oct- Dmf -W at 30° C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(1,2), A(1,3) and A(1,4) are 1069.4,637.5 and -396.0 respectively. Thus NRTL constants follows a decreasing trend.

Further, for example for system, B-Oct- Dmf -W at 40°C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(1,2), A(1,3) and A(1,4) are 715.9,502.3 and -24.2 respectively.

Thus, it is confirmed that NRTL constants for component Hexane (1) follows a decreasing trend .

(II) For Component Dmf (2), the values of NRTL constants namely A(2,1), A(2,3) and A(2,4) follow an interesting trend for all systems consisting of solute Benzene and non solute-Hexane/Heptahe/Octane and also at all three temperatures i.e. middle constants A(2,3) is always having a lower value in comparison to constants A(2,1) and A(2,4). There is only single exception being constant A(2,4) at 30 °C for system consisting of Octane.

Thus for example, for system B-Oct- Dmf -W at 20°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4) are 160.4,-1246.2 and -436.9 respectively.

Thus middle constants A(2,3) is having lowest value i.e. -1246.2 which is lower than the remaining two constants- A(2,1) and A(2,4). Further for example for system B-Oct-Dmf-W at 40°Cfor all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4) are 487.6,-182.7 and 126.6 respectively.

Thus middle constants A(2,3) is having lowest value i.e. -182.7 which is lower than the remaining two constants- A(2,1) and A(2,4).

(III) For Component Water(3), the three values of NRTL constants namely A(3,1), A(3,2) and A(3,4) follow a similar trend like that followed for Component Dmf(2). The values of middle constant-A(3,1) and A(3,4).

The above statement is true for all the valued of NRTL Constants i.e. A(3,1), A(3,2) and A(3,4) without any exception.

Thus for example, for system B-Hept-Dmf-W at 20°C for all the three anti solvent concentrations namely 0%W, 10%W and 20%W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 485.9, -125.7 and 349.8 respectively.

Thus middle value A(3,2) is having lowest value i.e. -125.7 which is lower than the remaining two constants- A(3,1) and A(3,4).

Further for example, for system B-Oct-Dmf-W at 40°C for all the three anti solvent concentration values 0%W, 10%W and 20%W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 458.6,-21.7 and 317.1 respectively.

Thus middle value A(3,2) is having lowest value i.e. -21.7 which is lower than remaining two constants- A(3,1) and A(3,4).

(IV) For Component Benzene(4), the values of NRTL constants namely A(4,1), A(4,2) and A(4,3) follow exactly an opposite trend than that which is observed for component Hexane (1).

The three values of constants namely A(4,1), A(4,2) and A(4,3) follow an increasing order trend for all the systems consisting of Benzene, Toluene and Xylene and also three temperatures - 20° C, 30° Cand 40° C. The main exceptions to this generalized observation being values of constants A(4,2) for systems consisting of Heptane and Octane at 20° C, also systems consisting of Heptahe at 30° C.

Thus for example, for system B-H- Dmf -W at 30° C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are -267.0, 196.7 and 527.0 respectively. Thus NRTL constants follow an increasing trend.

Further for example for system B-Oct- Dmf -W at 40°C for all the three anti solvent namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are -59.9, 187.5 and 384.5 respectively. Thus NRTL constants follow an increasing trend.

(V)Thus with respect to NRTL constants for systems consisting of B-H/Hep/Oct-Dmf-W under different sets of conditions, the following four generalized conclusions can be drawn:

(i) The various values of NRTL constants involving component- H/Hep/Oct (1) follow a decreasing trend as component- Dmf (2) gets modified to component water(3) and further gets modified to Component-Benzene (4).

(ii) The values of NRTL constants involving component Dmf (2) follow a trend wherein middle constant value-A(2,3) is lower than remaining two constants namely-A(2,1) and A(2,4).

(iii)) The values of NRTL constants involving component Water (3) also follow a trend like component – Dmf(2). The middle constant value-A(3,2) is lower than remaining two constants namely-A(3,1) and A(3,4).

(iv) The values of NRTL constants involving component Benzene (4) follow an increasing trend as component Hexane (1) gets modified to component Dmf (2) and further gets modified to component-Water (3).

5.8.5 Critical analysis of NRTL constants for different systems-B/T/X-H-Dmso-W:-

The various values of NRTL constants under different sets of conditions for solvent Dmso for different systems wherein Benzene has been replaced by Toluene and later on Toluene has been replaced by Xylene have been tabulated in Table-73

Component Hexane has been labeled as-1,Component Dmso has been labeled as-2, Component Water has been labeledas-3,and Component Benzene/Toluene/Xylene has been labeled as-4

Accordingly, twelve values of NRTL constants have been compared inTable-73.

Based on critical analysis of NRTL constants following are the important observations/conclusions:-

(I) For Component Hexane (1) the three values of NRTL constants A(1,2), A(1,3) and A(1,4) follow a decreasing order for all systems consisting of Benzene, Toluene and Xylene as solute and also at all three temperatures 20° C, 30° C and 40° C.

The exceptions for the above observation being systems consisting of Xylene at 40°C wherein this order is not followed.

Thus for example for system B-H-Dmso-W at 20°C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(1,2), A(1,3) and A(1,4) are 1123.6, 680.5 and 319.7 respectively. Thus NRTL constants follow a decreasing trend.

Further, for example for system, X-H- Dmso -W at 20° C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(1,2), A(1,3) and A(1,4) are 879.1, 521.1 and 189.9 respectively.

Thus, it is confirmed that NRTL constants for Hexane (1) follow a decreasing trend.

(II) For Component Dmso(2), three values of NRTL constants A(2,1), A(2,3) and A(2,4) follow an interesting trend for all systems consisting of Benzene, Toluene and Xylene and also at all three temperatures i.e. middle constants A(2,3) is always having a lower value in comparison to constants A(2,1) and A(2,4). There is not a single exception to this trend for component Dmso.(2).

Thus for example, for system T-H- Dmso -W at 20°C for all the three anti solvent namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4) are 681.99, -3240.4 and 102.2 respectively.

Thus middle constants A(2,3) is having lowest value i.e. -3240.4 which is lower than the remaining two constants- A(2,1) and A(2,4). Further for example for system T-H-Dmso-W at 40°Cfor all the three anti solvent namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3)and A(2,4) are 704.2, -189.4 and 64.5 respectively.

Thus middle constants A(2,3) is having lowest value i.e. -189.4 which is lower than the remaining two constants- A(2,1) and A(2,4).

(III) For Component Water(3), the three values of NRTL constants namely A(3,1), A(3,2) and A(3,4) follow a similar trend like that is followed for Component Dmf(2). The value of middle constant-A(3,2) is always having a lower value in comparison to constants-A(3,1) and A(3,4).

The above statement is true for all the valued of NRTL Constants i.e. A(3,1), A(3,2) and A(3,4) without any exception.

Thus for example, for system X-H- Dmso -W at 20°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 845.4, 140.2 and 906.8 respectively.

Thus middle value A(3,2) is having lowest value i.e. 140.2 which is lower than the remaining two constants- A(3,1) and A(3,4).

Further for example, for system T-H- Dmso -W at 40°Cfor all the three anti solvent concentration values 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 953.3, 280.2 and 1304.9 respectively.

Thus middle value A(3,2) is having lowest value i.e. 280.2 which is lower than remaining two constants- A(3,1) and A(3,4).

(IV) For Component Benzene/Toluene/Xylene(4), the values of NRTL constants namely A(4,1), A(4,2) and A(4,3) follow exactly an opposite trend than that which is observed for component Hexane (1)

The three values of constants namely A(4,1), A(4,2) and A(4,3) follow an increasing order trend for all the systems consisting of Benzene, Toluene and Xylene and also three temperatures- 20°C ,30°C and 40°C. The main exceptions to the generalized observation are systems consisting of Xylene at 30°C and 40°C.

Thus for example, for system B-H- Dmso -W at 30°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are 237.0, 814.5 and 1206.0 respectively. Thus NRTL constants follow an increasing trend.

Further for example, , for system T-H- Dmso -W at 40°C for all the three anti solvent namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are 553.2, 741.4 and 1158.1 respectively. Thus NRTL constants follow an increasing trend.

(V)Thus with respect to NRTL constants for systems consisting of B/T/X-H-Dmso-W under different sets of conditions, the following four generalized conclusions can be drawn: (i) The various values of NRTL constants involving component- Hexane (1) follow a decreasing trend as component- Dmso (2) gets modified to component water(3) and further gets modified to Component-Benzene (4).

(ii) The values of NRTL constants involving component Dmso (2) follow a trend wherein middle constant value-A(2,3) is lower than remaining two constants namely-A(2,1) and A(2,4).

(iii)) The values of NRTL constants involving component Water (3) also follow a trend like component - Dmso (2). The middle constant value-A(3,2) is lower than remaining two constants namely-A(3,1) and A(3,4).

(iv) The values of NRTL constants involving component Benzene (4) follow an increasing trend as component Hexane (1) gets modified to component Dmf (2) and further gets modified to component-Water (3).

5.8.6 Critical analysis of NRTL constants for different systems-B-H/Hep/Oct-Dmso-W:-

The various values of NRTL constants under different sets of conditions for solvent Dmso and solute Benzene for different systems wherein Hexane has been replaced by Heptane and later on Heptane has been replaced be Octane have been tabulated in Table-74

Component Hexane/Heptane/Octane has been labeled as-1, Component Dmso has been labeled as-2, Component Water has been labeled as-3 and Component Benzene has been labeled as-4

Accordingly, twelve values of NRTL constants have been compared in Table-74.

Based on critical analysis of NRTL constants following are the important observations/conclusion:-

(I) For Component H/Hep/Oct (1) the three values of NRTL constants A(1,2), A(1,3) and A(1,4) follow a decreasing order for all systems consisting of Benzene as solute and Hexane/Heptane/Octane as non solute and also at all three temperatures 20° C, 30° C and 40° C.

The exceptions for the above Observation being values of constants A(1,2) at 20 °C , 30 °C and 40 °C for systems consisting of Heptane wherein this order is not followed.

Thus for example for system B-H-Dmso-W at 20°C, for all the three anti solvent concentration namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(1,2), A(1,3) and A(1,4) are 1123.62, 680.57 and 319.72 respectively. Thus NRTL constants follow a decreasing trend.

Further, for example for system, B-H- Dmso -W at 30° C, for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants, A(1,2), A(1,3) and A(1,4) are 748.0,452.0 and 400.3 respectively.

Thus, it is confirmed that NRTL constants for Hexane (1) follow a decreasing trend for all the three temperatures.

(II) For Component Dmso (2), three values of NRTL constants A(2,1), A(2,3) and A(2,4) follow an interesting trend for all systems consisting of solute Benzene, and non solute H/Hep/Oct and also at all three temperatures i.e. middle constants A(2,3) is always having a lower value in comparison to constants A(2,1) and A(2,4).

There are three exceptions being values of constants A(2,4) at temperatures 20 °C , 30 °C and 40 °C for system consisting of Heptane

Thus for example, for system B-H- Dmso -W at 20°Cfor all the three values of anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4)are 714.5 -214.42 and -67.4 respectively. Thus middle constants A(2,3) is having lowest value i.e. -214.4 which is lower than the remaining two constants -A(2,1) and A(2,4).

Further for example for system B-H-Dmso-W at 40°Cfor all the three values of anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(2,1), A(2,3) and A(2,4) are 597.3,-316 and -205 respectively. Thus middle constants A(2,3) is having lowest value i.e. -316 which is lower than the remaining two constants- A(2,1) and A(2,4).

(III) For Component Water(3), the three values of NRTL constants namely A(3,1), A(3,2) and A(3,4) follow a similar trend like that followed for Component Dmso (2). The values of middle constant-A(3,2) is having lowest value which is lower than the remaining two constants- A(3,1) and A(3,4).

The above statement is true for all the values of NRTL Constants i.e. A(3,1), A(3,2) and A(3,4) without any exception.

Thus for example, for System B-Oct- Dmso -W at 20°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are -93.0,-634.9 and 1244.6 respectively.

Thus middle value A(3,2) is having lowest value i.e. -634.9 which is lower than the remaining two constants- A(3,1) and A(3,4).

Further for example, for system B-Hep- Dmso -W at 40°C for all the three anti solvent concentration values 0%W, 10%W and 20%W under otherwise identical conditions, the values of constants A(3,1), A(3,2) and A(3,4) are 1111.9,-361.0 and 1190.9 respectively.

Thus middle value A(3,2) is having lowest value i.e. -361.0 which is lower than remaining two constants- A(3,1) and A(3,4).

(IV) For Component Benzene (4), the values of NRTL constants namely A(4,1), A(4,2) and A(4,3) follow exactly an opposite trend than that which is observed for component Hexane (1)

The three values of constants namely A(4,1), A(4,2) and A(4,3) follow an increasing order trend for all the systems consisting of Hexane, Heptane and Octane and also three temperatures 20°C, 30°C and 40°C. However single exception to above trend is a system consisting of aliphatic- Octane at teure of 30°C.

Thus for example, for system B-H- Dmso -W at 30° C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are 237.0, 814.5 and 1206.0 respectively. Thus NRTL constants follow an increasing trend.

Further for example, , for system B-Hep- Dmso -W at 40°C for all the three anti solvent concentrations namely 0%W, 10%W and 20% W under otherwise identical conditions, the values of constants A(4,1), A(4,2) and A(4,3) are -184.0,1056.5 and 1276.9 respectively. Thus NRTL constants follow an increasing trend.

(V)Thus with respect to NRTL constants for systems consisting of B-H/Hep/Oct-Dmso-W under different sets of conditions, the following four generalized conclusions can be drawn:

(i) The various values of NRTL constants involving component- Hexane (1) follow a decreasing trend as component- Dmso (2) gets modified to component water(3) and further gets modified to Component- Benzene (4).

(ii) The values of NRTL constants involving component Dmso (2) follow a trend wherein middle constant value-A(2,3) is lower than remaining two constants namely-A(2,1) and A(2,4).

(iii)) The values of NRTL constants involving component Water (3) also follow a trend like component - Dmso (2). The middle constant value-A (3,2) is lower than remaining two constants namely-A(3,1) and A(3,4).

(iv) The values of NRTL constants involving component Benzene (4) follow an increasing trend as component Hexane (1) gets modified to component Dmf (2) and further gets modified to component-Water (3).

5.8.7 Error analysis for different systems for both solvents:-

The values of absolute mean deviations in mole percent for different systems consisting of B/T/X - H/Hep/Oct - Dmf + W and B/T/X - H/Hep/OCT - Dmso + W are reported in Table- 75. Based on the values of absolute mean deviations in mole percent reported in Table- 75, following conclusions can be drawn.

(i) All the quaternary liquid-liquid phase equilibrium data obtained for different systems B/T/X- H/H'/Oct- Dmf + W can be correlated satisfactorily within average absolute mean deviations in mole percent of the order of 2.5%.

(ii) All quaternary liquid-liquid phase equilibrium data obtain for different systems B/T/X- H/H'/Oct- Dmso + W can be correlated satisfactorily within average absolute mean deviations in mole percent of the order of 1.5%.

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Error Analysis: Absolute mean deviations for Tie line data-Experimental and Predicted by NRTL model.

Table No.	System	*ABSOLUTE MEAN
		DEVIATION (MOLE %)/Error
-i		
1.1	B - H - Dmf - W at 20 ° C	1.54815*
1.2	B - H - Dmf - W at 30 ° C	2.89683*
1.3	T - H - Dmf - W at 20 ° C	5.10046*
1.4	T - H - Dmf - W at 30 $^{\circ}$ C	1.87058*
1.5	T - H - Dmf - W at 40 ° C	3.09568*
1.6	X - H - Dmf - W at 20 ° C	2.98251*
1.7	X - H - Dmf - W at 40 ° C	1.32106*
1.8	B - Hep - Dmf - W at 20 ° C	2.94784*
1.9	B - Hep - Dmf - W at 40 ° C	3.92413*
1.10.	B - Hep - Dmf - W at 30 °C	1.669075*
1.11	B - Oct - Dmf - W at 20 ° C	1.66133*
1.12	B - Oct - Dmf - W at 30 ° C	2.44740*
-1.13	B - Oct - Dmf - W at 40 0 C	3.89405*
	• •	
2.1	B - H - Dmso - W at 20 °C	1.68877*
2.2	B - H - Dmso - W at 30 °C	1.54738*
2.3	B - H - Dmso - W at 40 °C	0.83040*
2.4	T - H - Dmso - W at 20 °C	1.54738*
2.5	T - H - Dmso - W at 30 °C	0.99164*
2.6	T - H - Dmso - W at 40 °C	1.69440*
2.7	X - H - Dmso - W at 20 °C	0.83067*
2.8	X - H - Dmso - W at 30 °C	1.65215*
2.9	X - H - Dmso - W at 40 ° C	2.23821*
2.10.	B - Hep - Dmso - W at 20 ° C	1.08454*
2.11	B - Hep - Dmso - W at 30 ° C	1.09647*
2.12	B - Hep - Dmso - W at 40 ° C	1.70940*
2.13	B - Oct - Dmso - W at 20 ° C	1.12518*
2.14	B - Oct - Dmso - W at 30 °C	1.24104*
2.15	B - Oct - Dmso - W at 40 °C	1.02741*

(iii)Error analysis based on absolute mean deviation values for mixed solvent Dmf+W indicates that for systems T-H- Dmf-W at 20 ⁰ C, the value of absolute mean deviation is highest of the order of 5.1%. When one compares this value with remaining values of absolute mean deviation for other remaining different systems, this value appears to be highest.

Even for system- B-Oct- Dmf-W at 40° C and for system- B-Hept- Dmf-W also at 40° C, the values of absolute mean deviations are of the order of 4% which is also on higher side. The reason for such a high error value is not clear.

(iv) Based on Error analysis of absolute mean deviation values for mixed solvent Dmso+W indicates that the maximum value of deviation appears to be only for single system i.e. system- X-H- Dmso-W at 40° C having absolute mean deviation value of 2.2%. For all the others systems, values of absolute mean deviation lie below 1.7%. Thus for mixed solvent Dmso+W data can be correlated by NRTL method satisfactorily and predicting the values of extract phase and raffinate phase compositions can be done with least error of the order of 1.5%.

(v) Comparison of absolute mean deviation values for both the solvents under consideration indicates that absolute mean deviation values for mixed solvent Dmf+W are on higher side in comparison to absolute mean deviation values for mixed solvent Dmso+W. Hence, it can be concluded that the fitting of data for mixed solvent-Dmso+W by NRTL method is more sound and appropriate than fitting of data for mixed solvent Dmf+W.

Hence computer programming based on methodology adopted by Kollah and Puranik⁷⁷ could be extended utilized conveniently to correlate all the experimental data obtained in this investigation for mixed solvents Dmf+W and Dmso+W satisfactorily.

The values of constants (A1,2), (A1,3), (A1,4), (A2,1), (A2,3), (A2,4), (A3,1), (A3,2), (A3,4), and (A4,1), (A4,2), and (A4,3); obtained in this investigation for different systems could be utilized conveniently to predict the values of extracts phase compositions (XBE, XHE, XDE & XWE) and reffinate phase compositions (XBR, XHR XDR & XWR) satisfactorily.

5.9.0 SUMMARY OF QUATERNARY LIQUID - LIQUID PHASE EQUILIBRIUM DATA:

(i) Quaternary liquid - liquid phase equilibrium data have been obtained in this investigations using mixed solvents-(Dmf + W) and (Dmso + W) under different sets of condition by varying temperature, anti solvent concentration, molecular weight of aromatics and molecular weight of aliphatics.

Thus for mixed solvent-(Dmf + W) it constitutes mutual solubility data and tie line data for 45 systems. Also for mixed solvent-(Dmso + W) it constitutes mutual solubility data and tie line data for additional 45 systems.

(ii)When anti solvent concentration is of the order of 0%W or a value near to 0%W Binodal curves is of closed type. However, when anti solvent concentration is in the range of 10%W and 20%W, all Binodal curves are of open type for all temperatures.

Values of plait points have been obtained for different systems where in Binodal curves are of closed type. Effects of various parameters like temperature, anti solvent concentration, molecular weight of aromatics and molecular weight of aliphatics have been discussed in detail.

The values of extraction capacity and selectivity have also been calculated for these two mixed solvents under different sets of condition.

(iii)It appears that extraction capacity of a solvent and its selectivity can be altered by changing the temperature of extraction from 20^{0} C to 40^{0} C and by addition of antisolvent - water by changing its composition in a solvent from 0 % W to 20%W by wt. It is observed that under otherwise identical conditions, as the extraction capacity of a given solvent increases, its selectivity decreases. By increasing the quantity of antisolvent, the selectivity of a mixed solvent increases; however its distribution capacity decreases under otherwise identical conditions. In comparison to effect of temperature, the effect of antisolvent concentration appears to have appreciable effect on the values of extraction capacity and selectivity of these mixed solvents. Further with an increase in molecular weight of aromatics/aliphatics extraction capacity decreases and under otherwise identical conditions, selectivity of mixed solvent increases.

(iv)In comparison to the molecular weight of Benzene/Toluene, the effect of molecular weight of Xylene on distribution capacities appears to be more stringent. Further in comparison to the molecular weight of Hexane/Octane, the effect of molecular weight of Heptane on distribution capacities appears to be more stringent. The entire data on Quaternary liquid-liquid phase equilibrium data has been also analysed by evaluating the values of distribution coefficient(m). Effect of temperature, anti solvent concentration , molecular weight of aromatics and molecular weight of aliphatics on the value of "m" have also been analyzed critically for mixed solvents –(Dmf+W) and (Dmso+W).

(v)The well known Hand's equation popularly utilized in the literature for correlating the ternary liquid-liquid phase equilibrium data , has been extended with modifications to correlate the quaternary liquid-liquid phase equilibrium data. The values of 'k'and 'n' have also been obtained for 45 systems under considerations for mixed solvent- Dmf+W consisting of systems involving components- B/T/X-H/H'/O-Dmf+W. Further the values of 'k' and 'n' have also been obtained for 45 systems under considerations for mixed solvent- Dmf+W. Further the values of 'k' and 'n' have also been obtained for 45 systems under considerations for mixed solvent- Dmso+W consisting of systems involving components- B/T/X-H/H'/O-Dmso+W.

(vi)Log-Log plots for parameters - log $[X_{BR}/X_{HR}]$ Vs. log $[X_{BE}/(X_{SE}+X_{WE})]$ appear to be straight-line plots for all the systems under consideration under different sets of operating conditions. Based on the values of slopes (k) and intercepts (n) of these ninety lines which vary according to a fixed trend, many interesting conclusions have been obtained. Interestingly, a set of many parallel lines for antisolvent concentration as a parameter are obtained for both the solvents under consideration.

(vii)The range of values of (k) varies from 0.03 to 1.8 for Dmf and for Dmso the range of values of (k) varies from 0.02 to 0.6 Further the range of values of (n) for Dmf varies from 0.8 to 0.9 and for Dmso it varies from 0.4 to 0.6. Based on these values of slopes (k) and intercepts (n), a mathematical modeling has also been attempted to correlate Quaternary liquid - liquid phase equilibrium data in terms of a generalized correlation.
(viii)The effect of altering temperature, anti solvent concentrations, molecular wt. of aromatics and molecular wt. of aliphatics on the value of 'k' has been analyzed by performing appropriate mathematical modeling and generalized correlations have been developed for both the mixed solvents. This can be considered as one of the most important contribution of this research work.

(ix)The pertinent generalized correlation Oza-Puranik (O-P) correlation containing four parameters is the following:-

$$\log k = \log \left[\frac{T_1}{T_0}\right]^0 + \log \left[\frac{S+W}{S}\right]^p + \log \left[\frac{M_1}{C_1}\right]^q + \log \left[\frac{M_2}{C_2}\right]^r$$

The values of indices 'o', 'p', 'q' and 'r' for different systems involving two mixed solvents under considerations – i.e. (Dmf+W) and (Dmso+W) obtained by use of optimization technique are the following:-

Systems	0	р	q .	r
B/T/X-H/H'/O-Dmf+W	+1	-3	-0.5	-2
				0.5(for Oct)
B/T/X-H/H'/O-Dmso+W	+1	-3	-0.5	-0.75
		0.333(for X)	-1(for X) -1(for Oct)

(x)An attempt has also been made to correlate Quaternary liquid-liquid phase equilibrium data obtained in this investigation by NRTL equation. The sets of NRTL Constants obtained for different systems using mixed solvents-(Dmf+W) and (Dmso+W) have also been analyzed critically.

This critical analysis is likely to be very helpful to obtain the values of interaction parameters namely – Dmf-CH, Dmf-ACH and Dmf-W for solvent Dmf and Dmso-CH, Dmso-ACH and Dmso-W for solvent Dmso.These interaction parameters then can be utilized conveniently while predicting liquid-liquid phase equilibrium data for Aromatics+ Aliphatics+(Dmf/Dmso)+W by "Group contribution method".

In summary, it can be concluded that the generalized correlations developed in this investigation by mathematical modeling using different approaches can be utilized conveniently for predicting the equilibrium compositions of extract and raffinate phases for the case:- Liquid – Liquid Extraction of Aromatics.