CHAPTER -8

SUMMARY & CONCLUSIONS

8.0.0 OUT LINES OF "RESEARCH WORK" CARRIED OUT:-

The newer solvents like dimethyl formamide (Dmf) and dimethyl sulfoxide (Dmso) appear to be very attractive than the conventional solvents like diethylene glycol (DEG) and triethylene glycol (TEG) for liquid - liquid extraction of aromatics as these newer solvents are likely to result in high selectivity and high percentage recovery of aromatics in comparison to solvents like diethylene and triethylene glycol. Further, it appears that the selectivity of these solvents can be increased substantially by the addition of small quantity of water which acts as an antisolvent. These newer solvents containing anti solvent-Water have been labeled as mixed solvent.

However, very limited information was available in the literature regarding quaternary liquid-liquid phase equilibrium data for the systems involving aromatics like Benzene, Toluene and Xylene + aliphatics like Hexane,Heptane and Octane + mixed solvents like (Dmf+W) and (Dmso+W) at different temperatures and the effect of parameters like molecular weight of aromatics & paraffins and the addition of anti solvent water on the values of selectivity and distribution capacity of these newer solvents. Further, if these equilibrium properties of a four component system consisting of aromatics + aliphatics + solvent + water could be derived from those of component ternaries, much of the experimental work could be avoided. Thus there was substantial scope to perform mathematical modeling of quaternary liquid-liquid phase equilibrium data.

Further, practically no information was available in the literature regarding the hold up of the dispersed phase, % recovery of aromatics, % purity of extract, number of transfer units, overall and individual mass transfer coefficients (dispersed side and continuous side) and the effect of variables like continuous and dispersed phase flow rates and solvent to feed ratio etc. on these parameters using Dmf or Dmso as a solvent for the separation of aromatics from aliphatics.

The above mentioned aspects could be studied conveniently in a packed column due to its simplicity.

However, very little information was available in the literature about the suitability of a packed column for liquid - liquid extraction of aromatics using newer solvents like Dmf and Dmso.

Hence, this work was under taken:

(1) To obtain quaternary liquid - liquid phase equilibrium data for liquid - liquid extraction of aromatics using solvent - dimethyl formamide (Dmf) under different sets of conditions

(2) To obtain quaternary liquid - liquid phase equilibrium data for liquid - liquid extraction of aromatics using solvent - dimethyl sulphoxide (Dmso) under different sets of conditions

(3) To compare the performance of these newer solvents (Dmf and Dmso) with the conventional solvents (DEG and TEG) in terms of selectivity and distribution capacity.

(4) To formulate a mathematical model for predicting the quaternary liquid - liquid phase equilibrium data for these two solvents under consideration which has been labelled as"Oza-Puranik" -(O-P) Generalized correlation.

(5) To perform liquid - liquid extraction of aromatics in a packed column under different sets of conditions and to obtain the data on % hold up,% recovery aromatics, number of transfer units, overall mass transfer coefficients -(Kod.a) and (Koc.a) and individual mass transfer coefficients -(Kod and Koc) etc. using these mixed solvents – (Dmf+W) and (Dmso+W).

(6) To perform liquid-liquid extraction of aromatics in a packed column in a stage wise manner in order to increase the values of % aromatics extracted (%A_E) using these mixed solvents.

(7) To compare performance/suitability of these newer solvents with conventional solvents for liquid - liquid extraction of aromatics in a packed column.

8.1.0 Quaternary Liquid-Liquid Phase Equilibrium Data-Experimental Part-I

Quaternary liquid-liquid phase equilibrium data obtained for systems involving two solvents-Dimethyl formamide (Dmf) and Dimethyl sulfoxide (Dmso) included the following.:-

(i) Different systems consisting of B/T/X-H/H'/O-Dmf-W under different sets of conditions.

(ii) Different systems consisting of B/T/X-H/H'/O-Dmso-W under different sets of conditions.

Inclusive of different variations totally 45 systems were investigated using mixed solvent- Dmf+W.

Inclusive of different variations totally 45 systems were also investigated using mixed solvent- Dmso+W.

The quaternary liquid - liquid phase equilibrium data was obtained by determining the points of mutual solubility data by titration method and the tie line data was determined by analyzing extract and raffinate phases by refractive index method. However for a few typical cases, the analysis of the extract and raffinate phases was done by washing method also.

The parameters which were varied and investigated while obtaining quaternary liquid-liquid phase equilibrium data were as under:-

(i) Temperature was varied from 20 °C, 30 °C, to 40 °C.

(ii) Anti solvent concentration was varied from 0%W, 10%W to 20%W

(iii) Effect of molecular weight of aromatics: Benzene -→ Toluene→ Xylene.

(iv) Effect of molecular weight of aliphatics: Hexane -→ Heptane→ Octane.

8.2.0 Liquid-Liquid Extraction of Aromatics in a Packed Column-Experimental Part-II

:Liquid-liquid extraction of aromatics was investigated in a packed column using mixed solvent Dmf+W as well as mixed solvent Dmso+W.

Prime parameters varied included – Solvent to feed ratio (S/F), Dispersed phase flow rate (Vd) and Continuous phase flow rate (Vc) . Column diameter was also varied and multi stage operation was also investigated.

For mixed solvent – Dmf+W , all packed column experimental runs were taken in winter season at 30 °C.

For mixed solvent – Dmso+W , all packed column experimental runs were taken in winter season at 40 °C .

Liquid - liquid extraction of aromatics was performed in a packed column of 5 cms dia, packed with 0.63 cm. glass Raschig rings. The feed consisting of 50 % aromatics and 50% aliphatics by weight was used as a dispersed phase. The solvent (Dmf or Dmso) containing 20% water by weight as an antisolvent was used as a continuous phase. The column was operated in the temp. range of 30°C -40 °C and the values of S/F ratio were varied in particular along with the other variables.

For some selected column experiments, liquid - liquid extraction was also performed in a stage wise manner. Due care was taken to see that results obtained were independent of column diameter, packing size and the height of packed bed. This was confirmed by performing however , a few typical very limited column experiments in a packed column of 15 cm dia. already available which was utilized by Sadhana Shukla . Newer solvents being costly, quantity available for these solvents was very limited for performing column experiments in a bigger column. Hence for selected values of S/F ratios, only four typical column experiments per solvent were performed.

The following is the summary of ranges of different parameters which were varied while obtaining experimental data on "Mass transfer rates and relevant aspects"-

Ranges of Variables:-

(i) Vc range:0.20cm/min to 2.0 cm/min,V_d range:0.10 cm/min to 0.70 cm/min for Dmf.

Vc range:0.25 cm/min to 1.0 cm/min ,V_d range: 0.20 cm/min to 2.0cm/ min.for Dmso

(ii) Concentration of antisolvent-water: 20% by wt.

(iii) Temperature :Column operated for Dmf at 30^{0} C (In Winter) .

Column operated for Dmso at 40^{0} C(In Summer)

8.3.0 Conclusions for Part-I:

Quaternary Liquid-Liquid Phase Equilibrium Data-

8.3.1 Mutual Solubility Data i.e. Binodal Curves.

Based on mutual solubility data curves –(Binodal curves for different systems consisting of B/T/X-H/H'/O- (Dmf/Dmso)+W at three different Temperatures 20 ^{0} C ,30 ^{0} C and 40 ^{0} C the following conclusions can be drawn :-

(i) Mutual solubility data depicted in different figures at three different temperatures 20 ^{0} C ,30 ^{0} C and 40 ^{0} C indicated that for concentration of anti solvent being 0%W, all Binodal curves were of closed type. However when antisolvent concentration increases from 0%W to 10%W and subsequently to 20%W,all the Binodal curves became 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)/ (Dmso+W).

(iii) As solute component Benzene/Toluene gets replaced by component – Xylene under otherwise identical conditions, the ratio of non-solute/solute decreases.

Thus selectivity of mixed solvent is expeted to increase with an increase in molecular weight of aromatics.

(iv)It is interesting to observe that under otherwise identical conditions 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 selectivity values are expected to be highest for system consisting of non solute Octane and lowest for non solute consisting of Heptane. However, the reason for such abnormal behavior is not clear.

8.3.2 Tie Line Data and Plait Points:-

Tie line data diagrams were constructed for following two categories.:-

Category-I: For Systems consisting of B/T/X-H/H'/O-Dmf+W

Category-II: For Systems consisting of B/T/X-H/H'/O-Dmso+W

Totally 45 diagrams for mixed solvent –Dmf+W and additional 45 diagrams for mixed solvent –Dmso+W presented in this thesis were divided in five groups as under:-

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

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

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

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

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

Tie line Data Diagrams:-

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 were of closed type for both mixed solvents-(Dmf+W) & (Dmso+W).

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 as well as 45 systems for mixed solvent- Dmso+Water.

(3)When systems under consideration were of closed type, the value of plait point composition were 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 was discussed in details and interesting conclusions have been obtained.

(4)Tie line data obtained in this investigation was correlated by different Tie line correlations available in the literature out of which Hand's correlation was more appropriate and sound for correlating the data.

(5)Nature of slopes of different tie line data straight lines were analyzed which offered explanation for effect of different parameters on plait points.

(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.

Plait Point Data:-

The following are the important conclusions w. r. t. "Plait Point Data" presented in this investigation for different systems consisting of mixed solvents – (Dmf+W) & (Dmso+W).

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

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

(2)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→T→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 ($\%X_{B/T/X}$) in plait point increases.

(3)Effect of temperature and effect of molecular weight of aromatics on plait point follows a peculiar trend i.e. with an increase in temperature the value of $\% X_B$ in plait point decreases and with an increase in molecular weight of aromatics, the value of $\%X_B$ in plait point increases.

(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/Dmso) with systems consisting of B-Hept- (Dmf/Dmso) under different sets of conditions of temperatures, the composition of Benzene ($\%X_B$) in plait point value decreases.

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

8.3.3 Extraction Capacity and Selectivity of Solvents- 'Dmf'& 'Dmso':-

Quaternary liquid - liquid phase equilibrium data were obtained in the case of liquid - liquid extraction of aromatics at 20^0 30^0 and 40^0 C and antisolvent concentration was varied from 0%, 10% and 20% for the following systems:

(1) Benzene + Hexane + Dmf + Water.
(2) Toluene + Hexane + Dmf + Water.
(3) Xylene + Hexane + Dmf + Water.
(4) Benzene + Heptane + Dmf + Water.
(5) Benzene + Octane + Dmf + Water.
(6) Benzene + Hexane + Dmso + Water.
(7) Toluene + Hexane + Dmso + Water.
(8) Xylene + Hexane + Dmso + Water.
(9) Benzene + Heptane + Dmso + Water.
(10) Benzene + Octane + Dmso + Water.

Using the above exhaustive data, the values of extraction capacity and selectivity were calculated for these two solvents under different sets of conditions.Further distribution and selectivity diagrams were also constructed.

The following are the important conclusions based on sets of distribution and selectivity diagrams presented in this investigation.

(i)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 it's composition in a solvent from 0 % to 20% by wt.

(ii)It is observed that under otherwise identical conditions, as the extraction capacity of a given solvent increases, its selectivity decreases.

(iii)By increasing the quantity of antisolvent and by decreasing temperature, the selectivity of a mixed solvent increases; however its distribution capacity decreases under otherwise identical conditions.

(iv)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.

(v) Further with an increase in molecular weight of aromatics/aliphatics extraction capacity decreases and under otherwise identical conditions, selectivity of mixed solvent increases.

(vi)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.

8.3.4 Distribution Coefficient (m) Values for Solvents Dmf and Dmso:

The effect of different parameters on the values of distribution coefficients for mixed solvents – (Dmf+W) & (Dmso+W) is as under:-

(1)The values of distribution coefficient decreases with an increase in concentration of anti solvent water. Further, addition of water appears to have substantial effect on the values of (m) with an increase in anti solvent concentration of water, the solubility of Benzene in solvent –(Dmf+W)/(Dmso+W) decreases and hence the value of distribution coefficient (m), consequently decreases under otherwise identical conditions.

(2)When temperature is increased from 20 °C to 30 °C, effect of temperature on values of 'm' 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.

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'.

(3) 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. However There are some exceptions to this normal trend which have been listed in the thesis.

(4) When in a particular system Hexane is replaced by Heptane and Heptane is further replaced by Octane under otherwise identical conditions, the values of distribution coefficient (m) also decrease with an increase in molecular weight of aliphatics. However There are some exceptions to this normal trend which have been listed in the thesis.

8.3.5 Tie Line Data and Modified Hand's Plots:-

Quaternary liquid-liquid phase equilibrium data for the following five groups for different systems involving solvent Dmf and additional five groups for different systems involving solvent- Dmso at three temperature 20^0, 30^0 and 40^0 C along with variation in water concentration 0%, 10% and 20% as a parameter for both solvents were correlated satisfactorily by modified Hand's plots..

Group Number	For solvent Dmf	Group Number	For solvent Dmso
(i)	B-H-Dmf-W	(vi)	B-H-Dmso-W
(ii)	T- H-Dmf-W	(vii)	T-H-Dmso-W
(iii)	X-H-Dmf-W	(viii)	X-H-Dmso-W
(iv)	B-Hep-Dmf-W	(ix)	B-Hep-Dmso-W
(v)	B-Oct-Dmf-W	(x)	B-Oct-Dmso-W

From these totally ninenty straight line plots, it was observed that under different sets of operating conditions for different systems- consisting of B-H-Dmf-W and B-H-Dmso-W, sets of different parallel lines were obtained with distinct intercept and single value of slope at a fixed temperature . Hence, for obtaining Generalized correlation to correlate quaternary 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 which were obtained for other correlations.

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. Thus, the values of 'n' from slope of straight line and the values of 'k' from the corresponding intercept were obtained for all the lines under different sets of conditions.

8.3.6 Hand's constants -'k' and 'n'

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, Hand's equation is thus applicable and can be written as under:

$$\left[\frac{X_{BR}}{X_{HR}}\right] = k\left[\frac{X_{BE}}{X^*_{SE}}\right]^n$$

Wherein $X^*_{SE} = (X_{DE} + X_{WE})$ 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'.

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.

Based on critical analysis of values of "k" & "n" the following are the important conclusions-

(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 systems 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/aliphatics under otherwise identical conditions the value of "k" decreases.

(v) There are some exceptions to this normal trend. All such exceptions are listed.

Thus, 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 were 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.)

$$\text{'k'} = f\left(\left[\frac{T_1}{T_0}\right]^{o}, \left[\frac{S+W}{S}\right]^{p}, \left[\frac{M_1}{C_1}\right]^{q}, \left[\frac{M_2}{C_2}\right]^{r} \right)$$

By using principles of "Dimensional analysis", the optimum values of index- [o,p,q & r] have been obtained . The correlation developed was labelled as Oza-Puranik (O-P) Generalized Correlation.

8.3.7 Oza - Puranik (O-P) Correlation for Quaternary Liquid - Liquid Phase Equilibrium Data:

The following generalized Oza-Puranik (O-P) correlation proposed in this investigation can be considered as one of the most important and unique contribution of the present work.

$$\log k = \log \left[\frac{T}{T_0}\right]^{o} + \log\left[\frac{S+W}{S}\right]^{p} + \log\left[\frac{M_1}{C_1}\right]^{q} + \log\left[\frac{M_2}{C_2}\right]^{r}$$

The above correlation constitutes four dimensionless groups as

$$\left[\frac{T}{T_0}\right], \left[\frac{S+W}{S}\right], \left[\frac{M_1}{C_1}\right], \left[\frac{M_2}{C_2}\right]$$

with index values o, p, q & r.

The terms in the denominator namely T_0, C_1 and C_2 are having values 273 ^{0}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:

$p_{B,T,X} = -3$, $p_{H',O} = -0.75$, $q_{B,T,X} = -0.5$, $r_{H'} = -2$ & $r_o = -0.5$

For quaternary systems : B / T / X - H / H' / O - Dmso + W :

Index values are as under :

$p_{B,T,X} = -3$, $p_X = -0.333$ & $p_{H',O} = -0.75$

$q_{B,T} = -5$, $q_x = -1$ & $r_{H',O} = -1$

8.3.8 Predicting Values of X_{BE}, X_{SE} & X_{BR}, X_{HR} :

Stepwise procedure mentioned by Dhabe and Puranik,(43) Bansod 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 fee composition, the ratio of E / R can be assumed.

(iv) Stepwise procedure mentioned by Dhabe and Puranik [43]has 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 equation 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.

(vi) Thus extract phase composition of solute and solventi.e.(X_{BE} & X_{DE}), raffinate phase composition of solute and non-solute (X_{BR} & X_{DR}) can be predicted.

8.3.9 Computer programming & NRTL Equation:-

(I) Computer programmes:-

Exhaustive work has been done by Kolah and Puranik[77] 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.

.In particular using NRTL, UNIVAC and UNIFAC models available in literature, various computer programmes have been prepared by these investigators:

It was 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 model.

(II) NRTL Constant values:-

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 180 values of constants minimum.

(III)Critical Analysis of 180 values of Constants:-

Based on critical analysis of NRTL constants obtained for different systems involving B/T/X-H/H'/O-(Dmf+W)/(Dmso+W), the following are the important conclusions.:-

(A)With respect to NRTL constants for systems consisting of B/T/X-H--(Dmf+W)/(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- -(Dmf)/(Dmso) (2) gets modified to component water(3) and further gets modified to Component- Benzene /Toluene/Xylene(4).

(ii)The values of NRTL constants involving component -(Dmf)/(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 – -(Dmf)/(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 /Toluene/Xylene(4).follow an increasing trend as component- Hexane (1) gets modified to component Dmf (2) and further gets modified to component-Water (3).

(B)With respect to NRTL constants for systems consisting of B-H/Hep/Oct-(Dmso-W) /(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- (Dmf/Dmso) (2) gets modified to component water(3) and further gets modified to Component- Benzene (4).

(ii) The values of NRTL constants involving component (Dmf/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 – (Dmf/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/Dmso) (2) and further gets modified to component-Water (3).

(IV) Error analysis for different systems for both solvents:-

Based on 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, following important 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%.

(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 40^0 C and for system- B-Hept- Dmf-W also at 40^0 C, the values of absolute mean deviations are of the order of 4% which is also relatively 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 one single system i.e. system- X-H- Dmso-W at 40^0 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.

(vi)Hence computer programming based on methodology adopted by Kolah and Puranik[77] could be extended and 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 (X_{BE}, X_{HE}, X_{DE} & X_{WE}) and reffinate phase compositions (X_{BR}, X_{HR} X_{DR} & X_{WR}) satisfactorily.

8.4.0 Conclusions for Part-II Liquid-Liquid Extraction of Aromatics in Packed Column:-

8.4.1 Preliminary considerations:-

Liquid- Liquid extrication of aromatics was carried out using two mixed solvents- (Dmf + W and Dmso + W). Preliminary consideration included fixing the ranges of dispersed phase flow rate (Vd) and continuous phase flow rate (Vc) for operation of a packed column, range of S/F ratio, feed composition, composition of mixed solvent and column characteristics like packed column height, size of packing etc. to be used.

Various mass transfer aspects like hold up of the dispersed phase, %aromatics extracted were considered. The values of NTU, HTU K_{oc}.a and K_{od}.a etc. were determined.

Multistage operation was also carried out. It was observed that values of percentage aromatic extracted can be increased considerably by carrying out multistage operation.

Exhaustive experimental data were obtained in a packed column of 5 cms. in diameter. In order to confirm that experimental data obtained is free from End effects and Wall effects, some limited experimental observations were taken in a packed column of 15 cms. in diameter. However only very limited data and experimental runs were taken in column of 15 cms. diameter due to financial constraints.

8.4.2 Hold Up of Dispersed Phase:-

In case of a packed column, rate of mass transfer is always governed by effective interfacial area available for mass transfer. Rate of mass transfer is directly proportional to effective interfacial area and effective interfacial area is directly proportional to hold up of the dispersed phase. Hence data on values of dispersed phase hold up (% X) appears to be of prime importance.

Hence, values of dispersed phase hold up were measured by displacement technique during Liquid-Liquid extraction of aromatics under different sets of conditions of dispersed phase flow rate (Vd) and continuous phase flow rate (Vc) for the system:- B-H-80%Dmf+20%Water and also for the system:- B-H-80%Dmso+20%Water.

The following are the important conclusions:-

(i)With an increase in Vd, the value of dispersed Phase hold up increases substantially.Under otherwise constant value of Vd with an increase in continuous phase f rate (Vc) appears to have very marginal effect on the values of dispersed phase hold up (X).

Hence, it can be concluded that dispersed phase hold up appears to be a strong function of Vd and at the same time a very weak function of Vc.

(ii)The well-known Pratt and coworker's hold-up data correlation can be utilized to correlate hold up data terms of Vd and Vc wherein a plot of Vd + (X/1-X) Vc Vs X(1-X) resulted in a straight line and the slope of straight line was utilized to obtain the value of characteristic droplet velocity (Vo).

The straight-line nature obtained for all hold up plots indicates the plots clearly indicated that the holdup data obtain for the system:B-H-Dmf+W and also for the system:B-H-Dmso+W can be correlated satisfactorily by Pratt's correlation.

(iii)The values of V_o obtained experimentally for the two mixed solvents-(Dmf+W) & (Dmso+W) have been compared with the values of Vo obtained by Ladha's correlation. The said correlation is as under:-

$\in V_o = C/(a_p \rho_c/\in^3 g\Delta\rho)^{1/2}$

From physico chemical properties of the system, fractional voidage of packing and surface were a of packing, one can thus estimate the value of Vo. The agreement between these two values of V_0 experimental and V_0 predicated is reasonably good for both the mixed solvents.

(iv) The comparison of Hold up of dispersed phase under otherwise comparable conditions of Vc and Vd for mixed solvents- Dmf and Dmso indicates that the values of Hold up for solvent Dmso were higher than for solvent Dmf.

Hence it is expected that values of effective interfacial area available for mass transfer for solvent Dmso were expected to be higher than the value of effective interfacial area available for mass transfer for solvent Dmf.

8.4.3 Values of % AE and % PE:-

The values of percentage aromatic extracted (%AE) and percentage purity of extract for systems:- B-H-Dmf-W and B-H-Dmso-W were obtained under different sets of conditions . Continuous phase flow rate (Vcavg) was varied from 0.3 cm/min to 1.8 cm/min and dispersed phase flow rate (Vdavg) was varied from 0.1 cm/min to 0.6 cm/min for system B-H-Dmf-W. Further, continuous phase flow rate (Vcavg) was varied from 0.1 cm/min to-0.9-cm/min and dispersed phase flow rate (Vdavg) was varied from 0.13 to 1.8 cm/min for system B-H-Dmso-W.

The following are the important conclusions:-

(i)As could be seen from different graphs with an increase in Vdavg at constant value of Vcavg, the value of percentage aromatic extracted increases.However, with an increases in Vdavg value of percentage aromatic extracted increases marginally .As such with an increase in Vdavg under otherwise identical conditions for a constant value of Vcavg, S/F ratio decreases. Hence value of percentage aromatic extracted is expected to decrease .However with an increase in Vdavg, the value of dispersed phase hold up increases. Hence effective interfacial area available mass transfer increases, consequently rate of extraction also increases. Hence value of percentage aromatic extracted increases, however very marginally.

(ii)As could be seen from graph with an increase in Vcavg, under other wise constant value of Vdavg, the value of percentage aromatic extracted increases substantially.

For a fixed value of Vdavg when Vcavg increases, the value of S/F ratio also increases. It is known that as S/F ratio increases value of percentage aromatic extracted also increases. Similar conclusions can be drawn from phase equilibrium data obtained for two quaternary systems under consideration wherein with an increase in [S/F] ratio, the limiting values of %AE also increase under other wise identical conditions. Hence with an increase in Vc, the values of $\%A_E$ increase substantially.

(iii)Favorable operating condition for liquid-liquid extraction of Aromatics using solvent either Dmf or Dmso are expected to be the following for **single stage extraction:-**

Contact Time Ø = 50 to 60 min, S/F by wt. = 3.5

Feed composition = 50% Benzene + 50% Hexane

Under these conditions the values of Aromatic extracted for solvents Dmf and Dmso are expected to be 58% and 48% respectively.

It is known from quaternary liquid-liquid phase equilibrium data that by adding anti solvent water to solvent (Dmf/Dmso),% purity of extract $\%P_E$ can be increased considerably

Both solvents-(Dmf/Dmso) contain anti solvent water and its composition in solvent either Dmf or Dmso was of the order of 20% by wt. The values of % purity of extract ($\%P_E$) obtained in liquid-liquid extraction in packed column under these conditions were of the order of 97-98% which agrees fairly well with the values obtained from quaternary liquid-liquid phase equilibrium data.

8. 4.4 Mass Transfer aspects for Mixed Solvent-(Dmf+W):-

Liquid- liquid extraction of aromatics was carried out in a paked column under different sets of conditions of flow rates(Vc, Vd) and S/F ratios to study various mass transfer parameters like the following.:

(i) Number of transfer units on dispersed side as well as continuous side.(NTUod, NTUoc)

(ii) Over all Height of transfer unit on dispersed side as well as continuous side.(HTUod, HTUoc).

(iii) Height of transfer unit on dispersed sideas well as on continuos side (HTUd,HTUc).

(iv) Overall volumetric mass transfer coefficient based on dispersed side as well as continuous side (Kod.a, Koc.a).

Based on critical analysis of these results the following are the important conclusions:-

(i)Based on the values of HTUod and HTUoc obtained for the system-B-H-80%Dmf+20%W at 30 ^{0}C, the range of values of HTUod is slightly higher than the range of HTUoc. Thus for the present system under consideration, resistance to mass transfer for transfer of aromatics from dispersed phase to continuous phase is in film of both the phases.

(ii)From a plot of (HTU)oc Vs. Gc/Gd, the slope of the straight line happens to be 5 and the slope of equilibrium diagram under consideration is 0.1. Thus, the value of HTUd from the slope of plot is expected to be 50 cm which compares very well with the intercept value obtained from a plot of HTUod Vs. Gd/Gc which is being 40 cm.

(iii)From a plot of (HTU)od Vs. Gd/Gc the slope of the straight line happens to be 330 . The inverse of slope of equilibrium diagram under consideration is 10. Thus, the value of HTUc from the slope of plot is expected to be 33 cm which compares reasonably well with the intercept value obtained from a plot of HTUoc Vs. Gc/Gd which was 50 cm.

(iv)Thus the average value of HTUc avg and HTUd avg. were expected to be 41.5 cm and 45 cm respectively.Thus the values of HTUc were expected to be slightly lower than the HTUd values.

(v)The above data clearly indicates that for the system B-H-80%Dmf-20%W when Benzene gets transferred from dispersed phase to continuous phase, the following is the interesting observation. :-

Major resistance to mass transfer lies in dispersed phase film as well as continuous phase film because of the fact that the value of HTUd is little higher than HTUc.

Hence , mass transfer aspect in a packed column for transfer of benzene from dispersed phase to continuous phase using solvent dimethyl formamid (Dmf) were expected to be totally different than from the mass transfer aspect in a packed column for transfer of benzene from dispersed phase to continuous phase wherein solvent used is dimethyl sulfoxide (Dmso)

(vi) It is observed from different graphs that the values of over all (volumetric) mass transfer coefficient (dispersed side) Kod. a appears to have very little effect of continuous phase flow rate (Vc).Thus, Kod. a is a strong function of Vd and weak function of Vc.

In general it is observed that when Vd increases by a factor of 1.5, increase in Kod.a is of the order of 1.8. Thus Kod.a appears to be a strong function of Vd.

As could be seen from different graphs the values of over all volumetric mass transfer coefficient continuous side ,appear to have little effect of dispersed phase flow rate (V_d). Thus $K_{oc..}$a is a strong function of Vc and a weak function of V_d.

(vii)The value of Kod. a appears in the range of $1x10^{-3}$ min^{-1} to $4x10^{-3}$ min^{-1} Further,the range of Koc.a value appears to be from $4x10^{-3}$ min^{-1} to $12x10^{-3}$ min^{-1}.Thus, the range of Koc. a value appears to be higher than the value of Kod.a

It has been already concluded that the values of HTUc were expected to be slightly lower than the values of HTUd. Hence resistance to mass transfer is expected to be little higher in dispersed phase film than that in continuous phase film. Hence while calculating rates of mass transfer during liquid-liquid extraction of aromatics in packed column using mixed solvent-(Dmf+W), Koc.a as well as Kod.a values were going to play a major role.

8.4.5 Mass Transfer Aspects for Mixed Solvent-(Dmso+W) :-

Liquid- liquid extraction of aromatics was carried out in a packed column under different sets of conditions of flow rates(Vc, Vd) and S/F ratios to study various mass transfer parameters like the following.:

(i)Number of transfer units on dispersed side as well as continuous side (NTUod, NTUoc)

(ii) Over all Height of transfer unit on dispersed side as well as continuous side (HTUod, HTUoc).

(iii)Height of transfer unit on dispersed sideas well as on continuous side (HTUd,HTUc).

(iv)Overall volumetric mass transfer coefficient based on dispersed side as well as continuous side (Kod.a, Koc.a).

Based on critical analysis of these results , the following are the important conclusions:-

(i)Based on the values of HTUod and HTUoc obtained for the system-B-H-80%Dmso+20%W at 40 ^{0}C, the range of values of HTUod is substantially higher than the rang of HTUoc. Thus for the present system under consideration , major resistance to mass transfer for transfer of aromatics from dispersed phase to continuous phase is expected to lie in dispersed phase film only. Further, resistance to mass transfer in continuous phase film is expected to be low.

(ii)From a plot of (HTU)oc Vs. Gc/Gd, the slope of the straight line happens to be 11.35 and the slope of equilibrium diagram under consideration is 0.08. Thus, the value of HTUd from the slope of plot is expected to be 140 cm which compares very well with the intercept value obtained from a plot of HTUod Vs. Gd/Gc which was 125 cm.

(iii)From a plot of (HTU)od Vs. Gd/Gc the slope of the straight line happens to be 75 . The inverse of slope of equilibrium diagram under consideration is 12.3. Thus, the value of HTUc from the slope of plot is expected to be 6.5 cm which compares reasonably well with the intercept value obtained from a plot of HTUoc Vs. Gc/Gd which was 10 cm.

(iv)Thus the average value of HTUc avg and HTUd avg. are expected to be 8.25 cm and 82.5 cm respectively.Thus the values of HTUc are expected to be 10 times lower than the HTUd values.

(v)The above data clearly indicates that for the system B-H-80%Dmso-20%W when Benzene gets transferred from dispersed phase to continuous phase the following are the interesting observations. :-

Major resistance to mass transfer lies in dispersed phase film and not in continuous phase film because of the fact that the value of HTUd is substantially higher than HTUc. Tare and coworkers[38] have studied extraction of furfural from its aqueous solution in a packed column wherein they have used two solvents benzene and ethyl acetate respectively. It is interesting to observe that resistance to mass transfer of furfural from aqueous phase to solvent phase appears to be negligible because value of HTUc is substantially smaller than the value of HTUd. Hence, resistance to mass transfer lies in dispersed phase film only and not in continuous phase film.

Hence , mass transfer aspect in a packed column for transfer of benzene from dispersed phase to continuous phase using solvent dimethyl sulfoxide (Dmso) are expected to be totally different than from the mass transfer aspect in a packed column for transfer of benzene from dispersed phase to continuous phase wherein solvent used is dimethyl formamid (Dmf).

(vi) It is observed from different graphs that the values of overall (volumetric) mass transfer coefficient (dispersed side) Kod.a appear to have very little effect of continuous phase flow rate (Vc).Thus, Kod. a appears to be a strong function of Vd and a very weak function of Vc.

In general it is observed that when Vd is increased by a factor of 5.5, the value of Kod.a also increases by a factor of 4.4. Thus, Kod. a appears to be a strong function of Vd.

As could be seen from different graphs, continuous phase flow rate exercises very little effect on the value of K_{oc}a The parameter Vd is having distinct effect i.e. with an increase in Vd, the value of Koc.a increases.

(vii)The value of Kod. a appears in the range of $1x10^{-3}$ min^{-1} to $10x10^{-3}$ min^{-1} Further, the range of Koc.a value appears to be from $4x10^{-3}$ min^{-1} to $25x10^{-3}$ min^{-1}.Thus, the range of Koc.a value appears to be substantially higher than the value of Kod.a

It has been already concluded that the values of HTUc were expected to be 10 times lower than the values of HTUd. Hence resistance to mass transfer is expected to be substantially higher in dispersed phase film and not in continuous phase film. Hence while calculating rates of mass transfer during liquid-liquid extraction of aromatics in packed column using mixed solvent-(Dmso+W), Koc.a values were going to play a major role.

8.4.6 Comparison of Performance of Mixed Solvents:-

The values of aromatic extracted (% AE) and purity of extract(%PE) for liquid-liquid extraction of aromatic using mixed solvents namely (Dmf+W) and (Dmso+W), have been compared under otherwise identical conditions in order to evaluate the performance of these mixed solvents.

Based on this critical comparison, the following is the important conclusion:-

In general it is observed that the values of % aromatic extracted (% AE) are higher for solvent-Dmf+W than that for solvent-Dmso+W under otherwise identical conditions of Vc,Vd and S/F. However, for higher values of S/F ratio of the order of 3.5 and above, the values of % AE for both the solvents appear to be comparable.

Under otherwise comparable conditions, the values of distribution coefficient (m) for mixed solvent (Dmf+W) are generally higher than that for mixed solvent (Dmso+W). Hence , the values of %AE are also higher for mixed solvent- (Dmf+W) than that for mixed solvent- (Dmso+W).

However as the value of S/F ratio increases, resistance to mass transfer for mixed solvent- (Dmf+W) is relatively higher than that for mixed solvent-(Dmso+W).As a result for higherv S/F ratios, the rate of mass transfer for mixed solvent(Dmf+W) decreases than that for mixed solvent-(Dmso+W). As a result, the values of %AE which werec inititially on higher side for solvent – (Dmf+W) start decreasing. Hence as a over all cosequence, the values of %AE for both the mixed solvents became comparable under otherwise identical conditions.

8.4.7 Multi Stage Operation for Liquid-Liquid Extraction of Aromatics:-

(i)Three stage operation for Solvents- (Dmf+W) & (Dmso+W):

During liquid liquid extraction of aromatics if the value of solute extracted were on lower side, then by carrying out liquid liquid extraction in a stage wise manner happens to be the appropriate method for liquid liquid extraction of aromatics

Since the information available in the literature was scanty, liquid liquid extraction of aromatics using solvents- Dimethyl formamide (Dmf) and Dimethyl sulfoxide (Dmso) was carried out in a packed column in multi stage manner.

Instead of using three packed columns in series for multistage extraction, only single column was used but thrice. Thus, raffinate phase coming out of column no.I became feed for column no.II. Likewise raffinate phase coming out of column no.II became feed for column no. III. Thus stage wise operation was performed in a single column in this manner as if it was multi stage extraction consisting of three stages.

Case-I Multi stage operation for mixed solvent 80%Dmf+20%W at 30 ^{0}C:-

By performing a stage wise operation in a packed column,the value of % aromatic extracted of the order of 95% was obtained with purity of extract being of the order of 93 % for system B-H-80%Dmf-20%W under following set of operating conditions :-

(i)Temperature of column for all three columns=30 ^{0}C
(ii)Vcavg =0.591 cm/min
(iii)Vdavg =0.131 cm/min
(iv) S/F=5.41 by wt.

Case-II Multi stage operation for mixed solvent 80%Dmso+20%W at 40 ^{0}C

By performing a stage wise operation in a packed column, the value of % aromatic extracted of the order of 86% was obtained in a packed column with purity of extract of the order of 93.5 % for system B-H-80%Dmso-20%W under following set of operating conditions:-

(i)Temperature of column for all three columns=40 ^{0}C
(ii)Vcavg =0.62 cm/min
(iii)Vdavg =0.207 cm/min
(iv) S/F=4.187 by wt.

(ii)Mass transfer aspects during Multi stage operation:-

During single stage operation , mass transfer of solute (Benzene) in feed to continuous phase (solvent) occurs as under:-

Solute from bulk phase i.e. dispersed phase gets transferred to dispersed phase film. From dispersed phase film solute gets transferred to the interphase of dispersed phase film and continuous phase film. From continuous phase film, solute gets transferred to bulk phase- solvent phase. Thus, solute (Benzene) gets transferred from bulk phase – feed- to bulk continuous phase- solvent during liquid - liquid extraction in packed column. This mechanism of mass transfer is based on two film theory.

During stage wise operation i.e. during stage-II in a packed column operation of liquid- liquid extraction , raffinate phase from column-1 in stage –I becomes feed for column -2 –stage-II where in composition of benzene in the feed decreases and that of hexane in the feed increases. During further stage wise operation i.e. during stage –III operation of liquid –liquid extraction of aromatics, raffinate phase coming out of stage-II becomes feed for column- 3- stage-III where in composition of benzene in the feed for stage-III further decreases in comparison to stage-II and that of hexane in the feed for stage-III further increases in comparison to stage II. It is observed that amount of benzene transferred during stage-II gets decreased than that transferred during stage –I. Mass transfer mechanism either during stage-I or stage-II being the same, one has to perform critical analysis as to why benzene amount in stage –II was decreased . Further, rate of mass transfer of benzene from dispersed phase to continuous phase for stage –I is higher than that for stage –II.

Thus , resistance to mass transfer in dispersed phase film in stage-II is more than that in stage-I .Continuous phase film in stage-I of column -1 or stage-II of column -2 or stage-III of column -3 is expected to remain same as fresh solvent along with water was used in all the three stages.

Hence, the value of overall dispersed phase side mass transfer coefficient (Kod.a) is expected to decrease in stage –II in comparison to stage-I. It will get decrease further in stage-III in comparison to stage –I and stage-II. However , the value of over all continuous phase side mass transfer coefficient (Koc.a) is expected to be the same as continuous phase is 80% solvent +20% water in all the three stages. However, composition of benzene in dispersed phase (feed) in stage-I ,II and III gets decreased continuously and composition of hexane in feed in stage-I ,II and III gets increased continuously. It appears that when composition of component- Hexane in feed increases and that of component- Benzene in the feed decreases, resistance to mass transfer progressively gets increased from stage-I to stage-III .As a result rate of mass transfer of benzene decreases progressively under other wise identical condition from stage-I to stage-III when one operates a set of three columns in stage wise manner.

Thus for any observation for system B-H-80%Dmf-20%W or B-H-80%Dmso-20%W, the value of Kod .a for stage –I is expected to be highest and that for stage-III ,it is expected to be lowest. The corresponding value of Koc.a for all three stages is expected to remain same.

Thus in summary it can be stated as under:-

Since for stage –I or stage-II or stage-III solvent phase (Vci) happens to be (80% Dmf +20% W) /(80% Dmso +20% W) for all the three stages , resistance to mass transfer in continuous phase film is expected to remain same for all the three stages .However resistance to mass transfer in the dispersed phase film increases continuously from stage-I to stage- III. Thus when liquid- liquid extraction of aromatics in a packed column is performed in multistage manner using three stages , mass transfer of solute from dispersed phase to continuous phase occurs in same manner as in single stage operation; however as number of stages are increased , resistance to the rate of mass transfer increases progressively.

8.4.8 Overview of Performance of Mixed Solvents:-

Single stage Operation Comparison:-

Since mass transfer data on %AE values obtained in 5 cm. dia column compares very well with mass transfer data obtained in 15 cm. dia column it can be concluded that all the Mass transfer data obtained in this investigation for both the mixed solvents--(Dmso + W) &(Dmso + W) in a 5 cm. dia column is free from "End effects" and "Wall effects".

Hence exhaustive "Experimental Data"obtained in a 5 cm. dia column for both the mixed solvents--(Dmf + W) &(Dmso + W) can be utilized conveniently in Industrial Practice.

Multi stage Operation Comparison:-

Results obtained for multi stage liquid-liquid extraction of aromatics with respect to % aromatic extracted (%AE) and purity of extract (%PE) for both the solvents have been compared below under otherwise comparable operating conditions for 5 cm. diameter column Vs. 15 cm. diameter column.

For mixed solvent- (Dmf +W) under conditions of Vc =0.9 cms/ min, Vd=0.315 cms/ min, and S/F ratio of 3.42 by weight, when liquid liquid extraction of aromatics was performed in a stage wise manner (multistage operation) ,the values of (%AE) obtained in stage (I) and last stage – stage (IV) in a 5 cm diameter column were 39% and 77.64% respectively

Further for the same mixed solvent- (Dmf +W) under otherwise comparable conditions of Vc=0.819 cm/ min, Vd=0.279 cm/ min and S/F ratio of 3.48 by weight, when liquid liquid extraction of aromatics was performed in a stage wise manner (multistage operation), the values of %AE obtained in stage-(I) and the last stage i.e. stage-(IV) in a 15 cm diameter column were 41.12% and 79.76% respectively.

Further for second mixed solvent- (Dmso +W) under conditions of Vc =0.62 cms/ min, Vd=0.207 cms/ min, and S/F ratio of 4.18 by weight, when liquid liquid extraction of aromatics was performed in a stage wise manner (multistage operation), the values of (%AE) obtained in stage (I) and last stage – stage (IV) in a 5 cm diameter column were 46.52% and 86.09% respectively.

Further for the same second mixed solvent- (Dmso +W) under otherwise comparable conditions of Vc=0.558 cm/ min, Vd=0.186 cm/ min and S/F ratio of 3.88 by weight, when liquid liquid extraction of aromatics was performed in a stage wise manner (multistage operation), the values of %AE obtained in stage-(I) and the last stage i.e. stage-(IV) in a 15 cm diameter column were 49.28% and 88.82% respectively.

The above comparisons in the case of both mixed solvents-(Dmf+W) & (Dmso+W) indicates that results obtained in a 5 cm diameter column are free from the "End Effects" and "Wall Effects" because of the fact that values of % AE for both the categories are comparable under otherwise comparable operating conditions.

Thus for both the newer solvents – (Dmf+W) & (Dmso+W) when S/F ratio is in the range of 3.5 to 4.0 by weight the values of (%AE) are expected to be in the range of 65% to 75%. By increasing S/F ratio range to 5to6 by wt., the values of % aromatics extracted (%AE) are expected to be in the range of 90%. Thus newer solvents- Dmf and Dmso appear to be attractive for liquid liquid extraction of aromatics in comparison to conventional solvents DEG and TEG wherein for the second case liquid liquid extraction column has to be operated at 120 °C because of very low values of distribution coefficients at 30 °C for solvents-DEG/TEG.

The information available in the literature [2,,6] regarding the values of distribution coefficient (m) for solvents DEG and TEG and the values of distribution coefficient(m) for solvents- Dmf and Dmso obtained in this investigation are listed below:-

Sr.	System	Temperature	"m" Value
(i)	B+Hept+92.29%+DEG+7.71%W	120 °C	0.125
(ii)	B+Hept+92.79%+TEG+7.21%W	120 °C	0.175
(iii)	B+Hex+80%+Dmf+20%W	30 °C	0.25
(iv)	B+Hex+90%+Dmso+10%W	30 °C	0.35

The corresponding values of selectivity and relevant details for the above mentioned four systems are critically analyzed as under:-

For a fixed temperature of 120 °C and for a fixed value of benzene in raffinate phase of the order of 25% by weight, the corresponding value of Benzene in extract phase for mixed solvent- (92.29% DEG+7.77%W) is **78%** and under otherwise identical conditions , the corresponding value of Benzene in extract phase for mixed solovent –(92.79%TEG +7.21%W) is **70%. For a fixed temperature of only 30 °C** and for a fixed value of benzene in raffinate phase of the order of 25% by weight, the corresponding values of benzene in extract phase for solvent-(80% Dmf.+20%W) and (90%Dmso + 10% W) are **95%** and **92%** respectively. From the above data it is crystal clear that the value of benzene in extract phase for newer solvent is of the order of 95% and the corresponding values of benzene in extract phase for conventional solvents- DEG and TEG is of the order of 70%-75% only. Thus separation load for conventional solvents is expected to be higher than that for newer solvents. Further, the values of distributions coefficients (m) for newer solvents are approximately double than the values of distribution coefficients (m) for conventional solvents. Thus rates of liquid-liquid extraction of aromatics are expected to be substantially higher for newer solvents. Further to have reasonable values of distribution coefficient (m), the temperature of extraction for conventional solvents is of the order of 120 °C. By chance this temperature of extraction is reduced to 30 °C, the value of distribution coefficient (m) is expected to be very low for conventional solvents- DEG and TEG wherein to carry out liquid liquid extraction is probably not feasible. However for solvents-(Dmf/Dmso) liquid liquid extraction column could be operated conveniently at temperature of the order of 30 °C to 40 °C.

Thus using newer solvents-(Dmf) and (Dmso) however as mixed solvents in combination with antisolvent water to increase their selectivity, appears to be a very attractive proposition for liquid liquid extraction of aromatics.

8.5.0 Multi Component Liquid- Liquid Extraction of Aromatics- “Thermodynamic Approach”:-

Practically no information is available in the literature on "Multicomponent Liquid- Liquid Extraction of Aromatics"-neither “Theoretical” nor “Experimental”. Hence an” Unique Attempt" was made in this investigation to study-“ Thermodynamics Aspects of Multicomponent Liquid- Liquid Extraction of Aromatics, " wherein the values of % Aromatic extracted (% A_E) and %Purity of extract (%P_E) were calculated in this investigation based on "Quaternary Liquid- Liquid Phase Equilibrium Data" obtained for Liquid- Liquid extraction of aromatics.

All "Theoretical Aspects" w. r. t. Multicomponent Liquid- Liquid Extraction of Aomatics were considered and the relevant exhaustive calculations w. r. t. %AE and corresponding %PE values for different categories were performed. Based on these results obtained, further experimental work on Multicomponent Liquid- Liquid Extraction of Aromatics" can be undertaken.

The values presented in this investigation for Multicomponent Liquid- Liquid Extraction of Aromatics" are "Limiting Values". These are the maximum values of % AE and % PE which can be achieved/ obtained in actual practice under appropriate and suitable operating conditions.

Actual experimental values for "Multicomponent Liquid- Liquid Extraction" will be always less than these values. In limiting case actual values can be equal to these "Limiting Values".

8.5.1 Conclusions for Multi Component- Multi Stage Liquid-Liquid Extraction:-

Mixed feed consisting of six components- three solutes- (B+T+X), three non solutes – (H+H'+O) and Mixed Solvents- consisting of (80% Dmso + 20% W) & (80% Dmf + 20% W) was used as feed (F) and solvent (S). The ratio of solvent to feed (S/F) was kept as one only. Temperature of extraction was kept as constant value of 30 ^{0} C.

Under the above set of operating conditions for Multicomponent Liquid- Liquid Extraction Aromatics, the limiting values of % AE and %PE obtained for Mixed solvents (Dmso + W) and (Dmf + W) are (%AE = 6.02%, %PE = 98.66%) and (%AE = 18.17%, %PE = 76.8%) respectively. This has been labeled as stage – I of Multicomponent Liquid- Liquid Extraction of Aromatics.

Raffinate phase (R_I) coming out of Stage- I after liquid-liquid extraction, becomes Multicomponent feed stock for stage- II for performing Multicomponent Liquid- Liquid Extraction of Aromatics. Raffinate phase (R_{II}) coming out of Stage- II after liquid-liquid extraction, becomes Multicomponent feed stock for stage- III for performing Multicomponent Liquid- Liquid Extraction of Aromatics.Raffinate phase (R_{III}) coming out of Stage- III after liquid-liquid extraction, becomes Multicomponent feed stock for stage- IV performing out Multicomponent Liquid- Liquid Extraction of Aromatics.

Thus the limiting values of %AE and %PE obtained in the case of multistage Liquid- Liquid Extraction of Aromatics consisting of four stages are reported as under:-

Stage No.	Solvent 80% Dmso + 20% W		Solvent 80% Dmf + 20% W	
	% AE	% PE	% AE	% PE
I	6.02	98.66	18.17	76.8
II	12.14	89.25	33.53	75.44
III	21.53	82.9	45.41	74.85
IV	30.18	88.9	68.62	70.05

Thus by carrying out Multicomponent Liquid- Liquid Extraction of Aromatics in a multistage manner, the values of %AE can be increased considerably. Thus for example, under otherwise comparable operating conditions, the limiting values of %AE for mixed solvent- 80% Dmso + 20% W can be increased from 6.02% obtained in (Stage- I) to 30.18% obtained in (Stage- IV).

Similarly for second mixed solvent (80% Dmf + 20% W) by carrying out Multicomponent Liquid- Liquid Extraction of Aromatics in a multistage manner consisting of four stages, under otherwise comparable operating condition, the limiting values of %AE can be increased from 18.17% obtained in (Stage- I) to 68.62% obtained in (Stage- IV).

The relevant data presented in this investigation is having the main basis of solvent to feed ratio equal to one (1) by weight. By increasing S/F ratio and by keeping the same of the order of five (5) by wt, it is expected that the "Limiting Values "of %AE of the order of 95% can be achieved by carrying out Multicomponent Liquid- Liquid Extraction of Aromatics using four stages.

8.5.2 Suggestions for Further Work:-

It has been shown in this investigation that limiting values of %AE calculated based on "Thermodynamic Principles" can be obtained in actual practice for binary feed stock involving aromatic- Benzene (B) and aliphatic- Hexane(H) under a particular set of conditions having fixed values of continuous phase flow rate (Vc), dispersed phase flow rate (Vd), solvent to feed ratio (S/F), residence time (∅) and carrying out multistage operation.

Hence "Liquid- Liquid Extraction of Aromatics" using multicomponent mixed feed stocks can also be carried out on "Laboratory Scale" in a similar manner as has been done in this investigation for a feed stock consisting of two components – Aromatics – Benzene (B) and Aliphatics- Hexane(H).

The four variables to be studied can include-Vc, Vd, S/F and (∅) "Single Stage and Multistage Operation" under different sets of operation conditions can be carried out for feed consisting of multicomponent mixture of aromatic components & aliphatic components.

Thus, **favorable operating conditions can be suggested for carrying out "Multicomponent Liquid- Liquid Extraction of Aromatics"** in a multistage manner. Under the favourable operating conditions obtained by experimentation, it is expected that the "Limiting Values" of %A_E and %P_E presented in this investigation can also be achieved in actual practice.

8. 6.0 High Lights of Conclusions for Part-I

Quaternary Liquid-Liquid Phase Equilibrium Data:-

(i) Quaternary liquid - liquid phase equilibrium data was obtained in this investigation 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) constituted mutual solubility data and tie line data for 45 systems.Also for mixed solvent-(Dmso + W) constituted mutual solubility data and tie line data for additional 45 systems.

(ii)When anti solvent concentration was of the order of 0%W or a value near to 0%W,Binodal curves was of closed type. However, when anti solvent concentration is in the range of 10%W and 20%W, all Binodal curves were of open type for all temperatures.

Values of plait points were obtained for different systems where in Binodal curves were of closed type by graphical technique. Effect of various parameters like temperature, anti solvent concentration, molecular weight of aromatics and molecular weight of aliphatics on the values of plait point was attempted in detail wherein interesting trends were observed.

(iii)The values of extraction capacity and selectivity were also calculated for these two mixed solvents under different sets of conditions. The following are the important conclusions:-

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 % 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.

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 Quaternary liquid-liquid phase equilibrium data has been also analyzed 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).

(iv)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 different 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- Dmso+W consisting of different systems involving components- B/T/X-H/H'/O-Dmso+W.

(v)Log-Log plots of 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.

(vi)The range of values of (k) varies from 0.03 to1.8 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.

(vii)The effect of altering temperature , anti solvent concentrations, molecular wt. of aromatics and molecular wt. of aliphatics on the value of 'k' was 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.

(viii)The pertinent generalized correlation Oza-Puranik (O-P) correlation containing four parameters is the following:-

$$\log k = \log \left[\frac{T_1}{T_0}\right]^{o} + \log\left[\frac{S+W}{S}\right]^{p} + \log\left[\frac{M_1}{C_1}\right]^{q} + \log\left[\frac{M_2}{C_2}\right]^{r}$$

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	**o**	**p**	**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 0.333(for X)	-0.5 -1(for X)	-0.75 -1(for Oct)

(ix)An attempt was also 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) were analyzed critically.

This critical analysis is likely to be very helpful further 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".

(x)In summary, it can be concluded that Oza-Puranik(O-P) generalized correlation developed in this investigation by mathematical modeling can be utilized conveniently for predicting the equilibrium compositions of extract and raffinate phases for the case:- "Liquid – Liquid Extraction of Aromatics".

8. 7.0 High Lights of Conclusions for Part-II

Liquid-Liquid Extraction of Aromatics in Packed Column:-

(I) Hold-up of the dispersed phase:-

(i)As dispersed phase flow rate (Vd) increases, the value of dispersed phase hold up (%X) increases. The continuous phase flow rate (Vc) exercises little effect on the values of dispersed phase hold up.

(ii) The values of dispersed phase hold up were satisfactorily correlated by the correlation proposed by Pratt and co–workers[100] The agreement between the values of characteristic droplet velocity (Vo) obtained experimentally and predicted by Laddha's correlation[101]appears to be satisfactory. Hence the well known Laddha's correlation can also be used in a petroleum refinery engineering field for liquid – liquid extraction of aromatics.

(II) Values of %AE and %PE:-

(i)With an increase in the dispersed phase flow rate (Vd) for a fixed value of continuous phase flow rate(Vc),the value of % aromatic extracted decreases., however marginally.

(ii)Further with an increase in the ratio of S/F, for a fixed value of dispersed phase flow rate, the values of % aromatic extracted %(A_E) increases considerably. The values of % P_E remain practically the same i.e. of the order of 95-98%.

(iii)The values of %A_E and %P_E obtained in two different packed columns of 5cm.dia. and 15 cm. dia were comparable. Hence, it has been concluded that the exhaustive mass-transfer data obtained in a packed column of 5 cm. diameter is free from "End effects " and "Wall effects". Thus mass transfer data obtained in this investigation in a column of 5 cm diameter, could be utilized conveniently for the scale up purpose.

(iv) Favourable operating conditions for single stage liquid-liquid extraction of aromatics have been mentioned for both the mixed solvents under consideration- i.e.- (Dmf+W) and (Dmso+W).

(III) Mass Transfer data on NTU and HTU :-

(i)The values of NTUod , NTUoc, HTUod and HTUoc were obtained under different sets of operating conditions for liquid –liquid extraction of aromatics using mixed solvent – Dmf+W. Based on the average values of HTU)d and HTU)c obtained in this investigation , it can be concluded that during liquid-liquid extraction of aromatics when benzene gets transferred from dispersed phase consisting of Benzene& Hexane to continuous phase consisting of (80%Dmf+20%W), the resistance to mass transfer lies in both the films.

(ii)The values of NTUod , NTUoc, HTUod and HTUoc were also obtained under different sets of operating conditions for liquid –liquid extraction of aromatics using mixed solvent – Dmso+W. Based on the average values of HTU)d and HTU)c obtained in this investigation , it can be concluded that during liquid-liquid extraction when benzene gets transferred from dispersed phase consisting of Benzene+ Hexane to continuous phase consisting of 80%Dmso+20%W, the major resistance to mass transfer lies in the dispersed phase film and not in the continuous phase film.

(iii) Mass transfer data on NTU and HTU values is expected to be very useful while designing a packed column to be utilized on industrial scale for liquid-liquid extraction of aromatics using newer solvents –Dmf and Dmso.

(IV)Mass transfer coefficients – Kod.a and Koc.a:-

The values of Kod.a and Koc.a were obtained under different sets of operating conditions for liquid-liquid extraction of aromatics using solvents-(Dmf +W) and (Dmso+W). Critical analysis of these values indicates the following:-

(i)The values of Kod.a appear to be a strong function of dispersed phase flow rate (Vd) and continuous phase flow rate(Vc) exercises little effect on the values of Kod.a for both the cases under consideration..

(ii) The range of values of Koc.a appear to be higher than the range of values of Kod.a in the case of liquid-liquid extraction of aromatics using mixed solvent- (Dmf +W). Thus , resistance to mass transfer for transfer of aromatics – benzene from dispersed phase to continuous phase lies in the both phases- i.e. dispersed phase film as well as continuous phase film.

(iii)The range of values of Koc.a appear to be substantially higher than the range of values of Kod.a in the case of liquid-liquid extraction of aromatics using mixed solvent- (Dmso +W). Hence, resistance to mass transfer for transfer of aromatics benzene from dispersed phase to continuous phase basically lies in the dispersed phase film only.

(iv)Mass transfer data on(K_{od}.a) &(K_{oc}.a) values is expected to be very contributory and useful while designing a packed column on industrial scale for liquid-liquid extraction of aromatics.

(V) Multistage operation in a Packed Column:-

Since the range of values of %A_E obtained during single stage extraction were relatively on lower side for both the mixed solvents under consideration , liquid-liquid extraction of aromatics was carried out in a multi stage wise manner . "The mass transfer data obtained" in this regard can also be considered as **one of the most important contribution** of this research work.

Favourable operating conditions for both the mixed solvents under consideration have been mentioned. It has been concluded that by utilizing S/F ratio of the order of 5 to 6 by wt. having (Vc)avg in the range of 0.6 cm/min to 0.8 cm/min and (Vd)avg in the range of 0.15 cm/min to 0.2 cm/min , when one performs liquid-liquid extraction in a stage wise manner consisting of three stages , the value of % aromatics extracted (%A_E) appear to be of the order of 95% and %P_E is expected to be of the order of 96%.

(VI) Comparison of %A_E & %P_E Values with Limiting Values:-

It is interesting to observe that the "Limiting Values of %A_E and %P_E" calculated based on the" Quaternary Liquid-Liquid Phase Equilibrium Data " obtained in this investigation can be achieved in actual practice; however only under a fixed set of operating conditions of (Vc, Vd, S/F & θ)for both the mixed solvents -(80% Dmf+20% W) & (80%Dmso+20%W).

Obtaining "Limiting Values of %A_E and %P_E" for multi component feed mixture is very tedious and time consuming. Still an attempt was made in this investigation to obtain such limiting values for multicomponent feed mixture and extraction being carried out in a multi stage manner.

It is expected that these "Limiting Values of % A_E & %P_E" can also be achieved in actual practice under a fixed set of operating conditions of (Vc, Vd, S/F, & ∅) for both the mixed solvents (Dmf+W) & (Dmso+W).

(VII) Designing of Packed column for Liquid-Liquid Extraction

In summary, it can be concluded that "Mass Transfer Data" for extraction of aromatics obtained in this investigation could be utilized conveniently while designing of extraction column/ columns for liquid – liquid extraction of aromatics.