CHAPTER–(2)

LITERATURE SURVEY

CHAPTER–2

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2.0.0 ABSTRACT OF LITERATURE ON "LIQUID-LIQUID EXTRACTION OF AROMATICS"

In this Chapter on "literature survey ", information available in the literature with respect to the following aspects have been reviewed critically.

(i) Aromatics feed stocks,(ii) Aromatics recovery processes,

(iii) Solvents for liquid-liquid extraction,

(iv)Mixed solvents and relevant phase equilibria status for ternary and quaternary phase equilibrium data,

(v) Mathematical modeling of phase equilibrium data,

(vi)Liquid-Liquid extraction equipments,

(vii) Application of packed bed extractors,

(viii) Mass Transfer aspects in packed column,

(ix) Generalised correlations for mass transfer coefficients.

2.1.0 Aromatic Feed Stocks:

Instead of coal, the petroleum oil [4] has emerged as the dominant source for aromatic chemicals. It has now exceeded all other raw – materials as a source for benzene and it have been ahead of other sources for toluene and xylenes since 1950 and continues as on today. The requirements of aromatic hydrocarbons in the chemical industry are continually growing. The benzene-toluene-c8 aromatics fraction is presently the principal raw material used to manufacture many petrochemicals. Benzene is a major chemical feedstock used for a wide variety of applications.

The amounts of aromatic hydrocarbons in petroleum vary greatly with the source. A petroleum fraction boiling between 40°C and 180 °C may contain from 2 or 3 percent aromatics to possibly 10 percent. Most of the crude may contain only small amounts of aromatic hydrocarbons. A gasoline fraction from cracking operations may contain 15-20% aromatics but because of the high olefin content, the separation problems become quite complex.

The principal petroleum sources of BTX aromatics[5] continues to be from hydrocarbon reforming or from the dealkylation of toluene or other aromatics which are obtained during the reforming operation. Reformed gasolines contain these aromatics in concentrations ranging from about 30 to 60%. BTX also available from hydrogenated coke oven light oils, cracked gasoline, or hydrogenated dripolenes in which the concentrations can vary from about 70 to 97%.

2.2.0 Aromatics Recovery Processes:

The aromatics present in the reformate must be separated from the paraffin and the residual naphthenes. The earliest large-scale process used to separate BTX from aliphatic was straight distillation..

What happens if benzene is recovered by batch fractional distillation in the presence of aliphatic? First, pure light aliphatic – branched hexanes and all the C_5's- would be removed overhead since they do not form azeotropes with benzene. Then, aliphatic in the 70^0- 80^0 C boiling range would come off and would contain roughly 25% benzene. Thus, it is immediately apparent that one disadvantage of this process is that a good deal of benzene is lost in the light ends. The benzene that is distilled next is only fairly pure and comes off with the aliphatic that boil in the 80^0 – 95 °Crange. With luck, the gasoline fraction might not have too many of these components. However, a substantial amount of high quality benzene cannot be obtained by this process[5] because aliphatic that have boiling points even as high as 100 °C are very difficult (if not impossible) to separate from benzene by fractional distillation. As such, the whole benzene fraction (aliphatic as well as benzene) had to be distilled to get part of the benzene at only a good purity.

Attempts to improve benzene purity by changing the pressure in hopes of altering the relative volatilities has not been very successful. The slope of the vapor pressure curves of benzene and that of aliphatic are essentially parallel. Thus, the relative volatilities are almost unaffected and the compositions of the binary azeotropes will not change much with change in pressure.

Out of various known recovery processes like liquid – liquid extraction, selective absorption, extractive distillation and azeotropic distillation, liquid-liquid extraction has proven to be the most versatile method,[6] capable of operating effectively with a wide range of feedstock and very high product purity can be achieved by this route..

Using a solvent which selectively dissolves the aromatic hydrocarbons while rejecting the paraffin and naphthens, one obtains an extract phase. The extract phase (a solution of almost pure aromatic hydrocarbons in the solvent) is then purified by extractive distillation or back – washing with a non – aromatic of different boiling point to displace the impurities, followed by distillation. The aromatics are then separated from the solvent by distillation[7]. The economics of such a process depend upon the solvent chosen, which will fix the flow rates to be used (power and equipment size) and the reflux ratios during distillation (heat energy).

In the petroleum industry, Liquid-liquid extraction process continues to meet the increased demand, not only for lubricants and for fuels but also for pure aromatics hydrocarbons needed as petrochemicals feed stocks. Pure aromatics are obtained by catalytic reforming of naphtha to increase its aromatic content to 70-80% [8] .After the formation of aromatics by reforming process,as has been already pointed out it is necessary to adopt an efficient method for separation of aromatics from other products of reforming like paraffin. Distillation is ruled out because of closeness of boiling point of aromatics and paraffin required large number of trays in a distillation column. Solvent extraction then becomes the next choice, which at present is the most widely used physical separation technique with variety of solvents.

The most commonly used industrial solvents are glycols [9-11] like diethylene glycol and tri ethylene glycol which have ruled out the use of old solvents like acetonitrile, furfural and di ethanol amine. Somekh[9] has reported that higher molecular weight glycols along with DEG/TEG are being used to increase the capacity for aromatics and at the same time to recover more of the higher molecular weight aromatics. And they have presented equilibrium data and the selectivity data at various temperatures from 25 to 175 °Cand the effects of anti solvent water on the system. They came to the conclusion that higher temp. is essential when using glycol as solvents for aromatic extraction

For the systems using glycols as solvents by decreasing temp, the selectivity of solvent could be increased. An addition of small quantity of water as anti-solvent also increases the selectivity of these solvents. With an increase in the molecular weight of aromatics and paraffin, selectivity of these solvents could also be increased. However, with an increase in molecular weight of glycols (For example di ethylene glycol to tri ethylene glycol) selectivity of these solvents decreases (i.e. less in the case of TEG than DEG). Further an increase in the solubility of aromatics is observed with an increase in the molecular weight of glycols. Hence the value of percentage aromatics extracted increases with an increase in the molecular weight of glycols.

As could be seen from the above discussion, conventional solvents like TEG/ DEG have neither high capacity nor high selectivity under otherwise similar conditions. That is why “newer solvents” are now replacing these conventional solvents[12].

2.3.0 SOLVENTS FOR LIQUID- LIQUID EXTRACTION

2.3.1 Conventional Solvents:

Many solvents have been proposed or used for this purpose. Typical conventional solvents used in liquid-liquid extraction of aromatics are following[13,14]:-

Sulphur Dioxide for Edeleanu process, Diethylene glycol for Udex process, Tetramethylene sulphone for Sulfolane processes, n-methyl pyrrolidone (NMP) for Arosolvan process, NMP and ethylene glycol for Distapex process, Monoethyl Methyl Formamide for Mofex process, Methyl carbonate for Carmex process and Morpholine for SNAM process.

Out of these various processes listed above, sulfolane process is most widely used at present.

Other solvents, which have been found to be useful, include nitrobenzene, phenol, furfural, dicholo diethyl ether, methyl ethyl ketone etc. Among new solvents suggested for separating aromatics from non aromatics is etheylene carbonate or its homologues with addition of glycerol or glycol to improve selectivity.

2.3.2 Newer Solvents:

Newer solvents[15] like sulfolane, methyl carbamate, n-methyl-pyrolidone, n-formyl morpholine, nitro methane propionitrile, nitro alcohol acetate, nitro alcohols, dimethyl formamide and dimethyl sulfoxide appear to be very attractive for Lquid-Liquid extraction of aromatics.

Information available in the literature with respect to Distribution Capacity and Selectivity of these newer solvents for different systems under different sets of conditions have been critically evaluated and pesentedas under:-

1. **System:** Benzene – n-heptane – n-formyl morpholine, Toluene- n- heptane - n -formyl formoline, Xylene – n heptane – n formyl morpholine.

Scope of the data available: phase equilibrium data at 25 °C.

Remarks: [15]Solvent could be utilized for the extraction of aromatics from B-T-X feed stocks 10 Possibility of recovery of C_9 and C_{10} aromatics is also sighted.

2. **System:** Benzene – n hexane – methyl carbamate containing 10% water by weight.

Scope of the data available: Phase equilibrium data at 65 °Cand 95 °C.

Remarks: appears to behighly selective at 95 °Cif 10% water by weight is used as anti solvent [17-19]

.3. **System:** Benzene – n heptane – nitro alcohols - Nitro alcohols considered being following three nitro-alcohols:-

(1) 1-nitro propanol-2, (2) 2-nitro propanol, (3) 1-nitro-2 methyl – 2 propanol.

Scope of the data available: Phase equilibrium data at 30 °Cto 95°C, water content varying from 0 to 20% by weight.

Remarks: Nitro alcohols exhibit high selectivity [20] for aromatics due to nitro and hydroxyl groups; selectivity increases as the length of chain increases.

4. **System:** Benzene – n heptane – initro propane – 2 ol acetel and Toluene – iso octane – 1 nitro propane – 2 ol acetal.

Scope of the data available: Phase equilibrium data at 30°C.

Remarks: Nitro alcohol acetate [21] has high dissolving capacities and marked selectivity. Cannot be recommended because these solvents have extensively high dissolving capacities at the temperature 100 °Cto 170 °Cof commercial plant. They may be used as components for other selectivity solvents for increasing their dissolving capacity.

5. **System:** C6 to C8 aromatics – n heptane – oxy and thio – dipropionitrile.

Scope of the data available: Phase equilibrium data at 20°C

Remarks: It appears that propionitrilles [23] are more selective than diethylene glycol. However, these solvents are not tried on industrial scale.

6 Systems: n methyl pyrolidone – aromatic hydrocarbons.

Scope of the data available: Selectivity data at 25°C.

Remarks: Comparison[24] of methyl pyrolidone with diethylene glycol indicates that n methyl pyrolidone is more selective.

7 System: Benzene-n hexane – sulfolane.

Scope of the data available: Phase equilibrium data, at different temperatures

Remarks: Sulfolane appears to be more selective than DEG[4].

8 System: Benzene – n hexane – Dmso.

Scope of the data available: Mutual solubility data at 20 °Cand 40 °Cwith water content varying from 0 to 10% by weight.

Remarks: Appears to be very attractive for the extraction of aromatics[25–28] selectivity increases markedly with addition of anti solvent water. Tie line data is reported only for one feed composition. From the data, Dmso is outstanding for the extraction of benzene from n hexane. High purity of extract could be achieved.

9 System: Benzene – n hexane – Dmf.

Scope of the data available: Mutual solubility data at 20 °Cwith water content varying from 0% to 10% by weight. Comparison of percentage aromatics extracted V.s S/F ratio with triethylene glycol is presented.

Remarks: The data available suggests that Dmf[29, 30] is more effective than triethylene glycol. High purity of extract using Dmf is expected in comparison to triethylene glycol with proper addition of anti solvent water and temperature.

10 System:- Toluene-Heptane-ionic liquids likeBF4,CH3SO4

Scope of the data available:- Phase equilibrium data at 40 ^{0}C ,75 ^{0}C

Remarks:-Selectivity of ionic liquids as a solvent is substantially higher [31] by a factor of 1.5 to 2.5 compared sulpholane temperature being in the range of 40 ^{0}C to 75 ^{0}C

For sulfolane - D_{Tol}=0.31 and $S_{Tol/Hep}$=30.9 at 40 ^{0}C

For ionic liquids D_{Tol}=0.44 and $S_{Tol/Hep}$=53.6 at 40 ^{0}C

.2.3.3 Ideal Solvents:

The ideal solvent for the separation of aromatics by liquid liquid extraction should have the following properties[31].

High distribution coefficient i.e. it gives higher quantity of the desired product in an extract phase. It should also have high selectivity. The higher the distribution coefficient, the greater is the quantity of the desired component in the extract phase.

The difference in critical solution temperature (C.S.T) [30] of aromatics and non-aromatics in the solvent should be high approximately 220 °Ci.e. high solubility for aromatics and low solubility for non-aromatics. Schiebel[34] has provided a chart to select a suitable conventional solvent.

High value of di electric constants of a solvent gives greater solvent power and the other desirable properties are the following[31]:

(1) High boiling point (2) Density between 1 to 1.3 (3) Low surface tension (4) Low viscosity. (5) Low toxicity (6) Low cost (7) Easy availability (8) Non corrosive (9) High thermal stability and (10) Chemical stability.

Neither the conventional nor the newer solvents possess all the above-mentioned properties. However by addition of either anti solvent, co solvent or additive to the solvent better results with respect to liquid – liquid extraction of aromatics could be achieved. Such solvents are popularly known as the mixed solvents.

2.4.0 Mixed Solvents and relevant Phase Equilibrium Studies.

With the growing demand for petrochemicals and high-octane gasoline, more and more extraction capacity will be needed for mixed solvents in coming years. It has been the trend in the industry to employ solvents of increasing solvency to achieve this capacity increase. Mixed solvents[35] increase the Aromatics capacity. For illustration purpose Diethyl glycol, Tri ethyl glycol and Tetra ethyl glycol have been considered[36].

Diethylene glycol solvent is very selective as it does not dissolve much aliphatic in it. However, it does not dissolve much benzene either. The limited solubility with benzene reduces extraction capacity, so that benzene distributes in only about 1 to 4 ratio between extract and raffinate. The distribution coefficients with toluene and C* aromatics (which determine the effective capacity of the solvent) are also substantially lower.

With Trietylene glycol at 121.5 °Cthe results are better. In this case the solvent contains 5% water as anti solvent and its boiling point is about 130°C. This solvent is also very selective and the extracts have low heptane solubility. Benzene distributes in a ratio just under 1 to 2 between extract and raffinate. Triethylene glycol has nearly twice, the extraction capacity of diethylene glycol. It is also important to realize that even highly aromatic feeds can be treated.

However, tetraethylene glycol is the best of the various glycols studied. The solvent contains 39% water so that it also has a boiling point of about 140 °C. Benzene distributes quite favorably in tetra ethylene glycol. The tie lines are rather flat. at 100 °C temperature. Highly aromatic feeds can also be treated.

The average distribution coefficient with diethylene glycol is about 0.25 and that with triethylene glycol is about 0.4 and higher. However, toluene and C_8 aromatics are so much more easily extracted with triethylene glycol that about half as much solvent is needed compared with DEG. Some refiners have increased capacity by adding dipropylene glycol to their diethylene glycol solvent. At about 25% DPG, the solvent is similar to trietylene glycol. However, individual solvents are preferred over mixtures to avoid having to control solvents are preferred over mixtures to avoid having to control solvent composition. The distribution coefficient with TETRA is about 0.6 compared with 0.4 with triethylene glycol. Here again the comparison is that the solvent / feed ratio with TETRA would be nearly half of that with triethylene glycol.

Somekh[9-10] studied addition of di propylene glycol to E.G. (as mixed solvent) and concluded that it improves the selectivity as well as capacity. Johnson and Francis[11] have studied effect of addition of water to E.G. and concluded that the addition of water decreases the capacity. They have also studied the system Benzene – n heptane – DEG – water at various temperatures ranging from 25⁰ C to 175⁰ C. They conclude that higher temperature is favorable. Decrease in temperature increases the selectivity. Small amount of anti solvent water increases the selectivity. Replacing DEG to TEG decreases the selectivity.

Baites and Coworkers[16] studied effect of 0-20% water for Benzene – n hexane – Dmf system and concluded that Dmf is more useful than TEG and DEG.

The process also has been developed[33] and is licensed by the Institute Francais du petrole (IFP). using solvent dimethylsulfoxide (DMSO), CH_3-SO-CH_3 containing a small amount of water as antisolvent.

Cousserans[20] studied the effect of water on the selectivity of solvent and reported that methyl carbamate is more selective at 95⁰ C, if 10% water is added.

Diyarov and Coworkers[22] studied the effect of water-nitro-alcohols at different temperature for aromatics extraction. Nitro alcohol acetate is a favourable co solvent for aromatic extraction.

Meeler and Hochfield[24] studied various combinations of mixed solvents of DMSO, NMP, DMF, furfural, aniline and Phenols also of phenols with E.G., DEG, MEA, DEA and water and concluded that in case of mixed solvents selectivity gets improved substantially.

Choffle and Coworkers[25] used Benzene – n heptane – Dmso – Water mixed solvent in concentration 3% to 15% and concluded that it is an excellent solvent at ambient temperature due to low viscosity and high thermal stability. They have recommended water washing for the separation of Benzene from Dmso.

Ripe and Coworkers[37] have reported that the distribution coefficient of Dmf is so favorable that only small quantity of water is needed for Dmf.

Tare and Puranik have also utilized mixed solvent for the extraction of furfural from its aqueous solution.

Vesilev and Coworkers[39] used caprolactum with DEG and concluded that it increases the capacity.

Deshpande[40] studied a mixed solvent-Dmso+water at various compositions and various temperatures and concluded that these newer solvents are more attractive than DEG and TEG. The systems which have been studied are as under:

Benzene – n Hexane – Dmso and Benzene – n Hexane – Dmf under various operating conditions. The following important conclusions could be drawn:

1. The selectivity of both the solvents Dmso and Dmf increases with a decrease in temperature or with an increase in the molecular weight of aromatics or paraffins and with an increase in concentration of anti solvent-water.

2. With an increase of the molecular weight of aromatics and aliphatics, the value of distribution coefficient increases. However with an increase in the concentration of anti solvent, the values of distribution coefficient decrease. Values of distribution coefficients obtained for mixed solvents-Dmso and Dmf containing mixed solvent-water are substantially higher than the values of distribution coefficient obtained for triethylene and diethylene glycol under other wise comparable conditions. Hence the values of percent aromatics extracted are expected to be very high in the case of Dmf and Dmso as solvent in comparison to TEG or DEG, as a solvent.

Surana[41] has also studied the phase equilibrium data for systems consisting of Benzene-n-Heptane/cyclohexane-using mixed solvents-Dmf+water, E.G.+water, and Dmf+E.G.

The effect of addition of solid caprolactum as additive in E.G. was also investigated by the author.

From the results obtained for mixed solvent , the following are the summarized conclusions:-

1. Both water and ethylene glycol improves the selectivity of DMF. However the increase in the selectivity of Dmf is higher with water than with E.G. when same concentration is used.

2. Almost pure benzene is obtained as the extract phase when 50% E.G. is mixed with 50% Dmf.

3. In the region of higher values of solvent capacity, E.G. + Dmf combination has higher selectivity than that of Dmf + water combination. However in the region of lower values of solvent capacity, the selectivity of Dmf + water has higher values than that of Dmf + E.G. combination.

4. The addition of caprolactum considerably improves the solvent capacity of E.G. at higher solute concentrations.

Characterization [42] of the extracts and residues obtained during extraction using mixed solvent CS_2-N-methyl-2-pyrrolidinone[45] appear to be informative. Behavior of a mixed solvent-triethylene glycol (TEG) – N. methyl pyrrolidone (NMP) solvent for aromatics [46]extraction. may be mentioned as under:-

Solvent selectivity behavior of a mixed solvent of TEG and NMP may be adapted appropriately to the required solvent characteristics for aromatics extraction. Mutual solubility of pure C_7 - C_{10} hydrocarbons in the pure and mixed solvents does not increase appreciably with change in volume percentage of NMP or also with temperature variation for non aromatics. The relative increase in mutual solubility data of aromatics is more for aromatics than for non aromatics with variation in temperature or % of NMP in mixed solvent.

The extraction of aromatics[47] from naphtha and kerosene with sulfolane T.E.G, furfuryl amine, tetra hydrofurfuryl ale morpholine, 2-nethoxyethanl and nitro methane at

30-120 °Cwas studied. The equilibrium data generated in single stage batch runs under varying conditions of aromatic content in the fixed temperature, solvent – fixed ratio and water content in the solvent were correlated with the operating variables by a multiple regression model.

The stabilization also accelerates phase [48] separation during extraction. The stabilized extraction mixture is especially suitable for recovery of benzene and toluene from reformatees and pyrolysed gasoline.

Liquid-liquid equilibrium studies have been made for the extraction of aromatics from naphtha reformate by dimethylformamide/ethyleneglycol mixedsolvent. [49-50] The phase equilibrium for the extraction of aromatics from naphtha reformate (b.p.60–135 °C) in a mixed solvent of dimethylformamide (DMF) and ethylene glycol (EG) have been correlated using the UNIFAC group contribution model. The interaction parameters of DMF and EG with different hydrocarbon groups present in the reformate, such as CH_2 (paraffin CH_2), ACH (aromatic CH) and $ACCH_2$ (aromatic CCH_2), and each of the two solvents were fitted to experimental concentrations of ternary systems containing these groups. The extraction runs were carried out at different temperatures, solvent compositions and solvent-to-feed ratios. The experimental results compared favorably with those predicted from the UNIFAC method. The minimum required energy for separation was achieved at 57 °Cusing a 44% EG solvent with a solvent-to-feed ratio of 2.2 on a volume basis.

Liquid-liquid equilibrium; and Activity coefficients for Aromatics;from Naphtha reformate; solvents Dimethyl formamide (DMF); Ethylene glycol (EG); & UNIFAC approach forselection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures has been dealt in by authors.[51-52]

Measurements and Mathamatical modeling of quaternary liquid-liquid equilibrium data for mixtures of methanol+water / ethanol + water - toluene - n-dodecane) has been discussed in details for the above systems. [53]

Liquid-liquid equilibrium for the extraction of aromatics from naphtha reformate by dimethylformamide/ethylene glycol mixed solvent has been investigated and interesting conclusions have been drawn with respect to mixed solvents.[56]

Extraction of toluene/o-xylene from heptane and benzyl alcohol from toluene has also been investigated[56]. From the results obtained for mixed solvents-EG+Dmf, Dmf+water and EG+caprolactum following critical remarks could be made:

1. Both water and ethylene glycol improves the selectivity of DMF. However the increase in the selectivity of Dmf is higher with water than with E.G. when same concentration is used.

2. Almost pure benzene is obtained in the extract when 50% E.G. is mixed with Dmf

3. In the region of higher values of solvent capacity, E.G. + Dmf combination has higher selectivity than that of Dmf + water combination. However in the lower solvent capacity region the selectivity of Dmf + water has higher values than that of Dmf + E.G. combination.

4. The addition of caprolactum considerably improves the solvent capacity of E.G. at higher solute concentrations.

Skinner and Coworkers have reported[57] the phase equilibrium data of C_6 to C_{10} aromatics – n heptane – BB' thio di-propionitrile and B,B – oxydipropionitride at 25 °C. Their study indicated that nitrile is more selective solvent than DEG and TEG.

Phase equilibrium data for Benzene – methanol – n-heptane/ n -hexane systems at 20 °C, 40 °Cand 60 °Chave been reported by Labinits[58]. He showed that for all solute concentrations of benzene, the solvent selectivity decreases as temperature increases.

Procedure in detailed has been out lined[59] by Fuchs for prevention or decrease of residue formation in (N-methyl pyrrolidone-E.G.) containing extension agent mixture for aromatic recovery . T.E.G. – N.M.P, mixture [60] . for "Solvent and its Selectivity behaviour of (TEG-NMP) mixed Solvent for aromatics extraction" has been critically evaluated.

2.5.0 Mathematical Modeling of Phase Equilibrium Data:

Design of an aromatic extractor requires the knowledge of multi-component liquid–liquid equilibrium (LLE) data. Such experimental LLE data are usually not available and therefore can be predicted using various activity coefficient models. These models require proper binary interaction parameters, which are not yet available for all aromatic extraction systems. Furthermore, the parameters available for most of the ternary systems are specific to that system only and cannot be used for other ternary or multi-component systems. An attempt has been made to obtain these parameters that are globally applicable. For this purpose, the parameter estimation procedure has been modified to estimate the parameters simultaneously for different systems involving common pairs. UINQUAC and UNIFAC models have been used for parameter estimation. The regressed parameters are shown to be applicable for the ternary as well as for the multi-component systems. It is observed that UNIQUAC parameters provide a better fit for ternary LLE data, whereas, as one moves towards the higher component systems (quaternary and quinary) the UNIFAC parameters, which are a measure of the group contributions, predict the LLE better. Effect of temperature on UNIQUAC binary interaction parameters has been studied and a linear dependence has been observed.

Hence, a detailed study has been reported in the literature with respect to liquid-liquid extraction of aromatics using sulfolane as solvent.[61] Interaction parameters for multi component liquid- liquid extraction of aromatics using solvent sulfolane have been reported.

Predicting Liquid-Liquid phase equilibria by group contribution method for system involving hydrocarbons involving carbon number – 10 to 20 and solvent Dmf has been also reported.[62]

This work describes a method of calculating liquid-liquid aromatics extraction of a middle distillate. The group contribution models of the ASOG and UNIFAC type are investigated. Four vapour liquid equilibrium (VLE), two solid-liquid equilibrium (SLE), three binary and six ternary liquid-liquid equilibrium (LLE) have been measured. The parameters of the models are based mainly on the data of the systems having 10–20 carbon number. VLE, SLE, and infinite dilution activity coefficient data (17–245 °C) have been used for calculating interaction parameters between hydrocarbon groups and LLE data (20–80 °C) for interaction parameters of dimethylformamide-hydrocarbon groups. Middle distillate representation is based on mass spectrometric and gas chromatographic analysis and on limited data of middle distillate-DMF liquid-liquid equilibrium. It is shown that the performance of ASOG and UNIFAC models are sufficiently valid in representation of database and in extraction calculations. Considering the predictive character and the rapidity of its application this method can be useful in the preliminary study of extraction processes.

Liquid-Liquid extraction of aromatics from middle distillates and equilibrium data prediction by group contribution method [63] [64] is available in the literature as a critical review. Liquid—liquid phase equilibrium for dearomatisation of ATF fraction and Selectivity of Solvents for Liquid-Liquid Extraction of C7-C10 Aromatics is also available in the literature[65-66] as a deailed study.

A detailed study of quaternary system converted in to double binary system: Benzene – Ethyl isovalerate – Ethyl alcohol – Water has been reported by Moulton and change[13]. The quaternary correlation equation may be written as

$$\frac{X_{AR}}{A_{WR}}=\left(\frac{X_{AE}}{k_1 x_{BE}+k_2 X_{CE}}\right)^{n_2-m(n_1-n_2)}$$

where A, B, C, W are components ethyl alcohol (A), benzene(B), ethyl isovalerate(C), water(W) respectively.

Here, n_1, n_2 n_1, k_1, k_2 are constants for quaternary system which may be derived from ternary phase equilibrium data only i. e. for equivalent ternary phase equilibrium data systems.

n_1, n_2 are slopes and k_1, k_2 are intercepts in the Hand's plot of the corresponding Benzenes/Ester– ternary systems.

Bansod and Puranik[44] have studied quaternary system Benzene – hexane –Dmf–water and basic ternaries Benzene – Dmf–water and Hexane–Dmf–water systems at 30°C. The tie line data obtained by these investigators have also been correlated by the equations proposed by Moulten and Chang.[13]

The comparison between the experimental and predicated tie line data with the help of correlations proposed is quite satisfactory within + 15%.

Dhabe and Puranik [67] have studied quaternary systems consisting of components-

Benzene – Hexane – Dmso – water at 30 ^{0}C. They have also investigated basic ternarie systems:

Benzene – hexane – water and Hexane – Dmso – water at 30^0 C. Tie line data obtained have been correlated satisfactorily by the following equation:-

$$\log\frac{X_{DR}}{X_{WR}} = \log\left(\frac{X_{DE}}{k_1\, x_{BE} + k_2\, X_{HE}}\right)^{n_2 - m(n_1 - n_2)}$$

This equation is very similar to the equation proposed by Bansod and Puranik[44] except that the power of m_R required is 0.75 instead of 0.5.

The generalized correlations developed by mathematical modeling thus could be utilized conveniently for predicting the equilibrium composition of extract and raffinate phase for the case of liquid-liquid extraction of aromatics.[67]

The extraction of aromatics from naphtha and kerosene with sulfolane T.E.G, furfuryl amine, tetra hydrofurfuryl ale morpholine, 2-nethoxyethanl, nitromethane and furfuryl are at 30-120 °Cwas studied. The equilibrium data generated in single stage batch runs under different sets of operating conditions were correlated with the operating variables by a multiple regression model. [68]

Prediction of phase equilibrium data for the extraction of aromatics from naphtha reformate byusing solvent tetra ethylene glycol [69]was done by UNIFAC method.

The extraction of aromatics from naphtha reformate was carried out by the use of solvent tetra ethylene glycol at six temperatures and three solvent to feed ratios. The concentrations of paraffin, naphthenes and aromatics in the extract and raffinate phase were measured and compared to values predicted by the UNIFAC group contribution model. It was shown that the UNIFAC model is capable of predicting the concentrations in this multicomponent system with an overall RMSD of 1.27 mol. %.

A simulation model[71] for dearomatictisation of the straight-run fraction that boils in the range 140–240 °C(also called Aviation Turbine Fuel fraction) of Bombay high crude (India—offshore) was developed by using solvent- Sulpholane The group contribution model, UNIFAC, has been investigated for the prediction of the multicomponent liquid—liquid equilibrium data. The compositions of the extract and raffinate phases, thus predicted[71], compare closely with single stage experimental data.

Bansod and Puranik[72] have studied quaternary systems consisting of components – Benzene _ Hexane –Dmf-water at 30 0C and developed a generalized correlation for predicting quaternary liquid-liquid phase equilibrium data , However their work is limited to single temperature only.

In petroleum processing, the intermediate streams contain compounds of the five homologous series—n-paraffins, iso-paraffins, olefins, naphthenes and aromatics (PIONA). To attain a quantitative description of the phase equilibrium of such mixtures, a novel shortcut method, which is based on only one key component and the ratio of the adjacent distribution coefficients for homologous series has been developed[73,75]. At a particular temperature the recursive ratios of the distribution coefficients in a homologous series indicate a fixed value on the main branch. The dependency of relative distribution coefficients on temperature and solvent to feed ratio has been estimated. For all the PIONA families, exponentially distributed feed has been used in the AspenPlus simulator to calculate the distribution coefficients K. The shortcut PIONA LLE simulation program has been trained using the above distribution coefficients to obtain the relative distribution parameter α. For testing PIONA LLE proposition, single-stage liquid–liquid extraction experiments for gamma (continuous) and random (discrete) distributed feeds were done. n-Paraffin and aromatic families were investigated independently. Using this novel approach, shortcut simulation prediction results match well with the experimental data points.Interaction parameters for multi component liquid-liquid extraction of aromatics using solvent –sulpholane are also available in the literature.[76]

Kolah and Puranik [77] have done exhaustive work and developed various computer programmes for correlating and predicting ternary as well as quaternary liquid-liquid phase equilibrium data inclusive of VLE data.

These authors have used various novel approaches as under:-

(i) Correlaing basic component binary vapour-liquid phase equilibrium data to correlate ternary vapou-liquid equilibrium data.

(ii) Correlaing basic ternary liquid -liquid equilibrium data to correlate quaternary liquid -liquid phase equilibrium data.

(iii) Using vapour-liquid phase equilibrium data to predict liquid -liquid phase equilibrium data

(iv) Using liquid -liquid phase equilibrium data to predict vapour -liquid phase equilibrium data

(v) Also using LEMF, NRTL, UNIVAC and UNIFAC models available in the literature, various computer programmes have been prepared by these investigators.

Liquid + liquid equilibrium (LLE) results for the ternary mixtures of (solvent + aromatic hydrocarbon + alkane) at different temperatures from (298.15 to 313.15) K are reported[78] where the aromatic hydrocarbon is toluene or m-xylene and the alkane is n-heptane or n-octane or cyclohexane and the solvent is tetramethylene sulfone (i.e., sulfolane) or dimethyl sulfoxide (DMSO) or ethylene carbonate. The exhaustive data were correlated with the UNIQUAC and NRTL equations. The partition coefficients and the selectivity factor of the solvents are also calculated. Then, the selectivity of solvents for the extraction of aromatic hydrocarbons from alkanes has been compared. The phase diagrams for the ternary mixtures are presented and the correlated. Tie line results have been compared with the experimental data. The comparisons indicate the applicability of the UNIQUAC and NRTL activity coefficients model for prediction of multi component Liquid-Liquid phase equilibrium data.

Ternary liquid - liquid equilibrium data has been reported [79,80] for mixtures of mixed solvent-tetrafluoroborate or hexafluorophosphate- benzene- an alkane at T=298.2 K and p=0.1MPa. Also extraction of aromatic compound-toluene from higher alkane-dodecane by mixed solvents (water + methanol), (water + ethanol) and (methanol + ethanol) have been studied [81]by (liquid + liquid) equilibrium (LLE) measurements at three temperatures (298.15, 303.15, and 313.15)^0 K and ambient pressure. NRTL equations can be utilized to correlate all the above data.

The comparisons indicate that the selectivity factor for mixed solvent (methanol + ethanol) is higher than the other two mixed solvents at the three studied temperatures.

NRTL equations could be utilised conveniently to correlate obtained experimental data for the different systems and mixed solvent under consideration.

2.6.0 Liquid-Liquid Extraction Equipments and Applications of Packed Bed Extractors:

(i) Liquid-Liquid Extraction Equipments

Various equipments used for liquid-liquid extraction are as follows:

(I) Vertical Column type Extractor:

(A) Unaggitated:

1 Spray column, 2 Packed column,3 Plate column.

(B) Rotor agitated Contactor.

1 Rotary Disc contactor (RDC) Asymmetric, 2 Mixo contactor,

3 Rotary annular column.

(C) Pulse agitated column:

1 Pulsed Spray column, 2 Pulsed Packed column,3 Pulsed Plate column

(II) Horizontal Extractor:

1 Mixer settlers, 2 Centrifugal extractors, 3 Horizontal Rotating Disc contactor,

4 Raining bucket extractor.

Out of these Packed column[82] is well known for its simpilcity, ease of operation, efficiency and economy.

(ii) Important Applications of packed bed extractors:

Packed bed extractors [82] due to their simple and economical construction, less corrosion problems and lesser pressure drops are widely used in the chemical industries. New packing which offer more efficiency and high intimacy of the phase in contact are also being investigated continuously.

Some of the chemical processes wherein packed bed extractors are utilisede have been listed below.

Edeleanu process[83] use liquid-sulphur dioxide as a solvent. Light distillates like heavy naphtha are usedas feed stock to recover aromatics. Lubricating oils can also be treated however with mixed solvent like benzene and sulphur dioxide.

Udex process[84] is mainly used for recovery of aromatics with high degree of purity. Extractive distillation process, widely used nowadays, employs phenol as solvent. Addition of 8% to 12% water to diethylene glycol in the Udex process increases the selectivity of mixed solvent. Recovery of aromatics from coke oven oils using Ethyl acetate as a solvent is also an important application.[85]

Furfural extraction process[86] is used in the manufacture of lubricating oils. Tower packed with wood slots and maintained at a temperature of 95 °C was used previously. Use of rotating disc contactors in the commercial operations is now gaining importance, due to high flexibility of the equipment to handle various feedstocks.

Dimethyl sulphoxide[87] is widely used solvent in the recovery of aromatics from catalytic reformate and kerosene feed stocks as solvent shows high selectivity.

Using light oil as a solvent, acetic acid can be recovered [88] from very dilute solution of acetic acid.

Phenex process[89]also uses unit operation –liquid-liquid extraction to obtain phenol.

Acetic acid can also be recovered[90] from its aqueous solution with ethyl acetate as solvent. Due to high latent heat of vaporization of water, distillation cannot be employed and hence lquid-liquid extraction is recommended. However, high efficiency packing is necessary for such operations.

2.7.0 Mass Transfer Aspects in Packed Columns:

(i) Hydrodynamics and Mass transfer in packed column with Ceramic Rings, [90] were studied for systems consisting of toluene – acetone – water and n-BuOH – succinic acid – water.

A film flow was observed when the packing was wetted by the dispersed phase rather than by the continuous phase. The constants in the flow equation for Hi-flow ceramic rings were calculated for film flow as well as drop flow.

(ii) As droplets pass through a contractor such as packed tower, investigators[91] experienced a sequence of hydro dynamic events as listed below:- (a) free movement within the packing voids (b) collision with the packing on subsequent distortion (c) collision followed by breaking into two daughter droplets. (d) passage through narrow voids accompanied by droplet elongation, and (e) coalescence with a stationery drop in the inter sheets of the packing followed by dispersion. Each of these events is characterized by its own rate of mass transfer, which can be expressed in terms of partial mass transfer coefficients.

(iii) Mass Transfer aspects have been investigated [92] in packed bed and pulsed plate columns with respect to important factors like drop diameter, drop velocity; contact time ; or solvent modifiers; agitation of the continuous phase, drop break-up; coalescence and drop distortions. It is necessary to isolate these factors and to determine how to predict coefficients in larger diameter columns. A mass transfer system where in "a stream of single drops traveling widely apart to eliminate drop interactions and to avoid drop break-up or coalescence" is employed in which most of the resistance to solute transport can be assumed to reside in the drops i.e. dispersed phase. It was observed that mass transfer coefficients obtained for pulsed plate columns and packed columns are enhanced due to drop interactions with packing elements.

(iv) Characteristics of extraction in packed columns were compared[93] with those in rotary disk columns. Experiments were done for refining of lubricating oils by extraction with furfural. The packed columns can replace the disk columns, especially in systems with low interfacial tension. Intensification of extraction was also examined by adding on inert gas by following two methodologies:-

(a) Mixing the gas with dispersed phase in a droplet distributor.

(b) Feeding the gas through a separate distributor into the column to form droplets containing two phases.

(v) The drop size distribution and residence time of both phases were photographically studied[94] at four positions of a packed extraction column on industrial scale having packed bed height of five meters. The effects of various pulsation intensities and component exchange directions and rates on the sauter diameter were established and analyzed for system consisting of n-Butyl acetate, water and acetone.

(vi) Empirical correlations for the prediction of droplet size, dispersed phase holdup, slip velocity, and maximum throughputs in packed columns using random and ordered packing are considered[95]. The drop size correlation, which is based on measurements form 376 runs with and without mass transfer from nine different sources for conditions when the continuous phase wets the packing, reproduces the data with an Absolute Value of the relative deviation of 15.7%.

(vii) Based on data from 645 measurements with both continuous phase and dispersed – phase wetting, an equation for maximum throughout is derived[96] which reproduces the data with an average abs. Value of the relative deviation of 19.5%.

(viii) Thornton and Rahman [97] have studied single drop collisions with packing elements and shown temporary enhancement (for fractions of a second) of the mass transfer rate.

2.7.1 Hold-up of dispersed phase under no mass transfer conditions.

The initial investigations for the hold-up in packed columns are that of Appeal and Elgin [98]

The equation has been proposed by Gayler and Pratt [99] which correlates hold-up data below flooding point with dispersed and continuous phase flow rates and a characteristic velocity $\overline{V}_o$ characterizing the packing and liquid-liquid system employed.

Another equation was obtained by the same investigators [100] where $\overline{V}_a$ can be obtained as the slope of the straight line plot of

Vd+[X/(1-X)].Vc Vs. X(1-X)

Gayler and Pratt[100] have proposed the correlation for the estimation of the 'characteristic velocity using Raschig ring and Berl saddles.

Sitaramayya and Laddha [101] equation for correlating hold up data showed 10.97% average deviation. This equation can be considered as a generalized correlation for correlating the hold-up data below flooding velocity. Generalised hold up data correlation was also proposed by Johnson and Laverng [102] with A', B' and n constants.

Burdett, et at[103] devised a new technique for measurement of static and dynamic hold-up. However, the usefulness of the method for general purpose is doubtful.

In a subsequent modification, Chandra Shekharan and Laddha[104] obtained a new equation with modified constants in order to correlate dispersed phase hold up data at flooding.

All these equations listed so far are specifically under the conditions of no mass transfer between the contacted phases.Under solute transfer conditions, relevant equations /expressions/correlations are expected to be different.

2.7.2 Hold-up of Dispersed phase under solute transfer conditions::

Gayler and Pratt [105] correlated their data nd solute transfer conditions. Degaleesan and Laddha[106] obtained the generalized hold up data correlations for transfer from continuous to dispersed phase (c→d) and for solute transfer from dispersed phase to the continuous phase (d→c). These equations give the estimation of hold-up of the dispersed phase under solute transfer conditions.

2.7.3 Correlations for maximum through put:-

In the succeeding paragraphs, the correlations available in the literature for the flooding velocities of dispersed and continuous phases are discussed and analysed critically.

Blanding and Elgin[107] presented their results as the plot of square root of continuous phase flow rates against that of the dispersed phase.

An equation for flooding velocity was also proposed by Breckenfeld and Wilke[108] which predicts flooding velocity within ±20% deviations.

Row, Koffolt and Withrow[109] represented their data graphically in the form of flooding curves.

Bailard and Piret [110] defined the flooding in way that is more precise and presented an entirely different correlation when dispersed phase does not wet the packing.

Extensive variation in column size (up to 150 mm dia) and packing size and type was done by Dell and Pratt[111] who proposed the correlation also taking into account the data of previous investigators. Values of constant are available for different packing types and sizes.

Crawford and Wilke [112] used large size packing 12.5 mm to 37.5 mm carbon Raschig rings and large diameter column of 300 mm diameter under the specified conditions. The proposed correlations are similar to those proposed by Breckenfeld and Wilke[108]. Comparison of the two correlations shows that for geometrically similar systems, similar conditions of hydrodynamics prevail.

Treybal[152] modified the equation of Hoffing and Lockhart[35] and expressed Vc as a function of packing characteristic and physical properties of the systems with deviations within ±10% in flooding velocities.

Sakiadis and Johnson [114] modified the correlation proposed by Dell and Pratt [111,105] by adding a viscosity term to it and modified the constant by accounting for packing characteristic, fractional voids and surface tension effect. It is claimed that the correlation proposed is useful even for gas-liquid systems.

Numunaitis, et al [115] suggested that the group (a_t/e) – called as packing factor with two constants C_1 and C_2 which empirically accounts for the high capacity of the intelox saddles and Pall rings can be introduced in flooding velocities correlations. Thus, C_1 and C_2 are specified for different types of packing. In terms of these packing factors, Numunaitis[115] et al also suggested a graphical correlation.

Watson and McNeese [96] studied the hydrodynamics of counter-current flow of high-density difference fluids such as mercury and water and proposed a correlation based on the assumption of constant superficial slip velocity. But this correlation does not apply over a wide range of fluid properties and thus it's use is very limited. In a later development [116] they covered the wide range of fluid properties but covering only Raschig rings as the packing material.

2.8.0 Generalised correlation for Mass transfer coefficients:

Gayler and Pratt[117] have proposed the equations for dispersed phase and continuous phase mass transfer coefficients which relates the area based dispersed phase/continuous phase mass transfer coefficients in terms of a characteristic Reynolds number Re, phase velocities, fractional voidage and hold up of the dispersed phase.

Laddha and Smith[118]have correlated their results on mass transfer studies in terms of the height of transfer units.

Similar investigations were made by Gayler and Pratt[105] also who presented the graphical correlations showing influence of flow velocities on the mass transfer coefficients.

The equation was developed by Smith and Beckman[119] that correlated height of transfer units of continuous phase (HTUoc) to that of height of transfer units of dispersed phase(HTUod).

Critical theoretical analysis has been done about Kod.a and Koc.a equations by Handlos and Baron[120] also by Kronig and Brink[121]

Krishnan, et al[122] extended the theoretical analysis of Handlos and Baron [120] and also that of Kroning and Brink[121] and proposed Kod.a and Koc.a equations The Kod.a and Koc.a correlations proposed by Krishnan, et al [120] show 15% average deviations from experimental values of Kod.a and Koc.a.

The estimation of overall mass transfer coefficient was done by Gayler and Pratt[105]. Laddha, et al[123] also proposed the equation for the prediction of volumetric overall mass transfer coefficient based on the dispersed phase hold up.

Gopalrao and Ramamurty[124] obtained the area based overall mass transfer coefficients (Koc.a) in terms of dispersed phase flow rate and characteristic droplet diameter d_{sv}. They found that Koc.a was independent of the continuous phase flow rates.

2.8.1 Effective interfacial area in packed columns:

The volumetric overall mass transfer coefficients (Kod .a and Koc. a) could be reduced to true mass transfer coefficient (Kod and Koc) based on knowledge of values of effective interfacial areas under otherwise similar conditions.

Pratt, et al[125] proposed relevant equations for Kod and Koc based on aw wetted surface area assuming that effective interfacial area is equal to wetted surface area .Later on Gayler and Pratt[126] suggested corrections to these equations.

In an entirely novel approach Puranik and Sharma[127] applied the theory of 'extraction with fast-Pseudo-first order reaction' to to find out the values of effective interfacial area in a packed column. These authors [51] have utilised the following equation:-

$$a = \frac{R_a}{[C^*.(D.K_2.B)^{0.5}]}$$

Where Ra=specific rate of extraction

C*=equilibrium solubility of solute in solvent.

K_2=Second order reaction velocity constant.

B=concentration reacting species in solvent.

a=Effective interfacial area available for mass transfer during liquid-liquid extraction.

In a further development[128] it was shown that with the help of kinetics of coalescence and breakage of droplets, it is possible to calculate the interfacial area of contact. Billet and Mackowiak [129] have studied the new types of columns called as "packed tube columns". Here the diameter of packing is slightly less than the diameter of the column itself. Thus, the packings are regularly stacked in the tube column. Main advantage with such type of columns is that systems with extreme differences of physical properties can successfully be separated, again throughput from such columns are high compared to conventional packed columns. Regularly stacked packing reduces axial mixing and thus higher efficiencies could be obtained.

Billet and Mackowiak[129] have proposed correlations for true mass transfer coefficients- Kod and Koc inclusive of correlations for the flooding velocities.

The graphical generalized correlations are also proposed[130] in terms of (HTU) against total column capacity.

These correlations are expected to be very useful while performing scale up of packed columns on commercial scale by utilizing laboratory scale experimental data.

2.9.0 Summary:-

Based on the above review of "Liquid –liquid extraction of aromatics" the important observations/ comments have been summerised in the following paragraphs.

The newer solvents like Dimethyl sulfoxide (Dmso) and Dimethyl formamide (Dmf) appear to be very attractive than the conventional solvents like diethylene glycol (DEG) and triethylene glycol (TEG) for liquid - liquid extraction of aromatics. This is because of the fact that these newer solvents are having 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.

However, as could be seen from critical review of literature survey, very limited information is available in the literature regarding the ternary and quaternary liquid-liqui phase equilibrium data for the systems involving aromatics + aliphatics + newer solvents at different temperatures and the effect of parameters like molecular weight of aromatics and paraffins and the addition of anti solvent – water on the selectivity and distribution capacity of these newer solvents. Further, if these equilibrium properties of a four-component system (aromatics + aliphatics + solvent + water) could be derived from those of component ternaries, much of the experimental work could be avoided. However information available in the literature about these newer solvents –Dmf and Dmso – is very limited.

Further,except the work done by Deshpande and Puranik[2,6,40] practically no information is available in the literature regarding the effect hold up of the dispersed phase, % recovery of aromatics, % purity of extract, number of transfer units, mass transfer coefficients (dispersed side and continuous side.) using Dmf or Dmso as a solvent for the separation of aromatics.

The above-mentioned aspects could be studied conveniently in a packed column due to its simplicity. Since the interfacial tension for these systems (aromatics + aliphatics + solvent-Dmso/Dmf) is very low in comparison to DEG/TEG, it is expected that even in a packed column, the values of effective interfacial area and the rates of extraction are likely to be very high. Hence, a packed column could be utilized conveniently as a suitable contacting device for liquid - liquid extraction of aromatics.

However, practically very less / no information is available in the literature about the suitability of a packed column for liquid extraction of aromatics using these newer solvents like "Dmf" and "Dmso"