SYNOPSIS

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. Further, due to their important advantages like very low viscosity, non-toxicity, low interfacial tension and high solubility of aromatics, these 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.

However, very limited information is 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 is substantial scope to perform mathematical modeling of quaternary liquid-liquid phase equilibrium data.

Further, practically no information is 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. Since the interfacial tension for these systems consisting of aromatics + aliphatics + solvent-Dmf/Dmso is very low in comparison to DEG/TEG, it is expected that the values of effective interfacial area and the rates of extraction are likely to be very high even in packed column. Hence a packed column could be utilized conveniently as a suitable contacting device for liquid-liquid extraction of aromatics

However, very little information is 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 from the respective component ternaries of these solvents where in anti solvent component water is absent.

(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.

Chapter (1) of the thesis is devoted to the introduction just described above.

Chapter (2) presents literature survey with respect to the following important aspects:

(I) Solvents for the liquid - liquid extraction of aromatics: conventional and newer solvents, also mixed solvents.

(II) Ternary and quaternary Liquid - liquid phase equilibrium data available in the literature with respect to different solvents.

(III) Critical over view of Mathematical Modeling of phase equilibrium data.

(IV) Equipments for liquid - liquid extraction of aromatics.

(V) The relevant information available about rates of mass transfer using different solvents pertaining to these equipments.

It has been concluded that very little information is available pertaining to quaternary liquid-liquid phase equilibrium data and liquid-liquid extraction of aromatics in a packed column using mixed solvents – (Dmf+W) and (Dmso+W).

Chapter (3): Theoretical considerations include liquid – liquid phase equilibrium data correlations and the relevant thermodynamic aspects in detail. The relevant details with respect to selectivity, distribution capacity and limiting values of extraction of solute from non solute etc. have also been dealt in. This chapter also includes the generalized correlations available in the literature for correlating the hold up data and the mass transfer coefficients data - dispersed side and continuous side.

Chapter (4): Experimental has been divided in two parts:-

Part (I): Quaternary liquid-liquid phase equilibrium data under different sets of conditions.

Part (II): Liquid-liquid extraction of aromatics in packed column under different sets of conditions. In this Chapter – (4) under part-I, the following aspects have been out lined:-

The quaternary liquid - liquid phase equilibrium data has been obtained by determining the points of mutual solubility data by titration method and the tie line data has been 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 has been done by washing method also.

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

(i) Temperature has been varied from 20 ^{0}C, 30 ^{0}C, to 40 ^{0}C.
(ii) Anti solvent concentration has been 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.

Also in this Chapter – (4) under part-II, the following aspects have been out lined:-

Liquid - liquid extraction of aromatics has been 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 has been used as a dispersed phase. The solvent (Dmf or Dmso) containing 20% water by weight as an antisolvent has been used as a continuous phase. The column has been operated in the temp. range of 30^{0}C - 40 ^{0}C and the values of S/F ratio have been varied in particular along with the other variables.

For some selected column experiments, liquid - liquid extraction has also been performed in a stage wise manner. Due care has been taken to see that results obtained are independent of column diameter, packing size and the height of packed bed. This has been 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 have been 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).

Chapter (5) deals with results and discussion for quaternary liquid - liquid phase equilibrium data for solvents – Dmf as well as Dmso. The following is the summary of some important aspects which have been dealt in this chapter:

Liquid - liquid phase equilibrium data has been obtained in the case of liquid - liquid extraction of aromatics at 20^0 30^0 and 40^0 C with antisolvent concentration being 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.

The values of extraction capacity and selectivity have been calculated for these two solvents under different sets of conditions.

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. 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 data on quaternary liquid-liquid phase equilibrium data has been also analyzed by evaluating the values of distribution coefficient (m). Effect of temperature, antisolvent concentration, molecular weight of aromatics and molecular weight of aliphatics on the values of "m" have also been analyzed critically for mixed solvents – (Dmf+W) and (Dmso+W).

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. Also 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.

Log - Log plots for parameters - log $[X_{BR}/X_{HR}]$ Vs. log $[X_{BE}/(X_{SE}+X_{WE})]$ appear to be straight-line plot 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 straight lines which vary according to a fixed trend, many interesting conclusions have been obtained. Interestingly, a set of many parallel straight lines with different values of antisolvent concentration as a parameter are obtained for both the mixed solvents under consideration.

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 0.5 to 0.6. Based on these values of slopes (k) and intercepts (n), a mathematical modeling has also been attempted in order to correlate quaternary liquid - liquid phase equilibrium data in terms of a generalized correlation consisting of" Dimensionless Groups."

The effect of altering temperature , anti solvent concentration, molecular wt. of aromatics and molecular wt. of aliphatics on the values of 'k' has been analyzed by performing appropriate mathematical modeling and a generalized correlation has been developed for both the mixed solvents. This can be considered as one of the most important contribution of this research work.

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

$$\text{Log } k = \log (T/T')^{o} + \log[(S+W)/S]^{p} + \log(M_1/C_1)^{q} + \log(M_2/C_2)^{r}$$

The values of index- 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 listed below:-

Quaternary Systems	o	p	q	r
B/T/X-H/H'/O-Dmf+W	+1	-3	-0.5	-2*
		*However,'r'for Oct being (-0.5)		
B/T/X-H/H'/O-Dmso+W	+1	-3 *	-0.5*	-0.75^{X}
		*However,'p'and'q'for Xylene being (-0.333) and (-1) respectively.		
		^{X} However,'r'for Octane being (-1).		

An attempt has also been made to correlate Quaternary liquid-liquid phase equilibrium data obtained in this investigation by NRTL equation. The sets of NRTL Constants obtained for different systems using mixed solvents-(Dmf+W) and (Dmso+W) have also been analyzed critically.

This critical analysis is likely to be very helpful to obtain the values of interaction parameters namely – Dmf-CH, Dmf-ACH and Dmf-W for solvent Dmf and Dmso-CH, Dmso-ACH and Dmso-W for solvent- Dmso.These interaction parameters then can be utilized conveniently while predicting liquid-liquid phase equilibrium data by "Group contribution method".

In summary, it can be concluded that the generalized correlations developed in this investigation by mathematical modeling using different approaches can be utilized conveniently for predicting the equilibrium compositions of extract and raffinate phases for the case liquid – liquid extraction of aromatics.

Chapter (6) deals with results and discussion for liquid – liquid extraction of aromatics in a packed column. The following is the summary of some important aspects which have been dealt in this chapter:

For liquid – liquid extraction of aromatics, the solvent consisting of 80% Dmf and 20% water was used as a continuous phase and feed consisting of 50% aromatics + 50% aliphatics was used as a dispersed phase. All the experiments were performed at temperature 30 ^{0}C in a 5.0 cms. diameter column packed with glass Raschig rings/ceramic Raschig rings under different sets of conditions. However, some selected experiments were also performed in a 15 cm diameter packed column in order to confirm that the results obtained in 5 cm diameter column are free of end effects and wall effects.

The operating variables studied were the following :

(i) Continuous phase flow rate (Vc) varied from 0.1 cm/min to 0.7 cm/min

(ii) Dispersed phase flow rate (V_d) varied from 0.2 cm/min to 2.0 cm/min

(iii) Solvent to feed ratio (S/F) by wt. varied from 1.0 to 10

The values of % hold up of dispersed phase, % aromatic extracted and % purity of extract were determined under different sets of conditions. The values of mass transfer rates, Number of transfer units (NTU), Height of transfer unit (HTU) and mass transfer coefficients (dispersed phase side as well as continous phase side) were also estimated.

Experiments were also performed at 40 ^{0}C using the second solvent consisting of 80% Dmso and 20% water as a continuous phase under otherwise similar conditions mentioned above for solvent – 80% Dmf and 20% water where in range of operating variables were as under:-

- (i) Continuous phase flow rate (Vc) varied from 0.25 cm/min to 1.0 cm/min
- (ii) Dispersed phase flow rate (V_d) varied from 0.2 cm/min to 2.0 cm/min
- (iii) Solvent to feed ratio (S/F) by wt. varied from 0.5 to 5.0

The following are some of the important conclusions: -

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

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

(ii) The values of dispersed phase hold up can be satisfactorily correlated by the correlation proposed by Pratt and co–workers. The agreement between the values of characteristic droplet velocity (Vo) obtained experimentally and predicted by Laddha's correlation 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) The values of %A_E and %P_E:-

(i) With an increase in the dispersed phase flow rate, for a fixed value of continuous phase flow rate, 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 increases considerably. The values of % P_E remain practically the same i.e. of the order of 95-98%.

(iii) Some selected experimental observations were also taken by carrying out liquid- liquid extraction of aromatics in a packed column of 15 cm dia. The values of %AE and %PE obtained for the two cases under consideration are 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 could be utilized conveniently for the scale up purpose.

(iv) Favorable 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 have been 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 to continuous phase (80%Dmf+20%W), the resistance to mass transfer lies in both the phases.

(ii) The values of NTUod , NTUoc, HTUod and HTUoc have been 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 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:-

(i) The values of Kod.a and Koc.a have been obtained under different sets of operating conditions for liquid-liquid extraction of aromatics using solvents- (Dmf +W) and (Dmso+W). 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 value 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.

(iv) Mass transfer data on Kod..a and Koc..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) Multi stage operation in a packed column:-

(i) Since the range of values of %AE obtained during single stage extraction are relatively on lower side for both the mixed solvents under consideration , it is preferable to carry out liquid-liquid extraction of aromatics 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.

(ii) Favorable 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 up to three stages , the value of % aromatics extracted (%AE) appear to be of the order of 95% and %PE is expected to be of the order of 96%.

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

Obtaining "Limiting values of %AE and%PE" for multi component liquid-liquid extraction of aromatics performed in a multistage manner involves exhaustive "Thermodynamic Calculations" .That is why practically no information is available in the literature about these aspects. Hence, Chapter-(7) appears to be an "Unique Feature" of this investigation wherein Multicomponent Liquid-Liquid Extraction of

Aromatics-"Thermodynamics Aspects" have been presented. It also incorporates suggestions for further work with special reference to "Multicomponent Liquid-Liquid Extraction of Aromatics" in a packed column.

The last Chapter presents summary and conclusions of the present work. At the end , a list of 172 references referred in this investigation has been incorporated under the heading of "References."

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