Al-Khwarizmi
Engineering
Journal

Al-Khwarizmi Engineering Journal, Vol. 4, No. 4, PP 9-25 (2008)

Extraction of Phenol From Industrial Water Using Different Solvents

Mahmoud Omar Abdullah*, Khalid Farhod Al-Jiboury**
and Bushra Yaseen***
**Chemical Engineering Department/ Al-Nahrain University*
***Chemical Engineering Department/ University of Technology*
****Chemical Engineering Department/ Al-Mustanserya University*

(Received 7 October 2007; Accepted 11 Septerber 2008)

Abstract

The analysis and efficiency of phenol extraction from the industrial water using different solvents, were investigated. To our knowledge, the experimental information available in the literature for liquid-liquid equilibria of ternary mixtures containing the pair phenol-water is limited. Therefore the purpose of the present investigation is to generate the data for the water-phenol with different solvents to aid the correlation of liquid-liquid equilibria, including phase diagrams, distribution coefficients of phenol, tie-lines data and selectivity of the solvents for the aqueous phenol system.

The ternary equilibrium diagrams and tie-lines data for systems containing Water-Phenol-Benzene, Water-Phenol-Chloroform, Water-Phenol-iso-Butyl Acetate, Water-Phenol-Butanol, Water-Phenol-Ethyl Methyl Keton and Water-Phenol-Toluene, were determined at 303 K and atmospheric pressure.

The capacity and selectivity of these organic solvents in each of these systems were determined from the tie-lines data. The capacity of the isobutyle acetate was found to be the highest among the other solvents, and its selectivity was also the highest. Similar results also were obtained for the ethyl methyl keton but gave less capacity and selectivity as compared to the isobutyle acetate. It can be concluded that both isobutyle acetate and ethyl methyl keton are good solvents for extraction of phenol from industrial water.

The liquid-liquid equilibrium data of ternary systems were correlated to the NRTL, UNIQUAC and UNIFAC models of activity coefficient to determine their adjustable parameters. The standard deviations from experimental compositions were calculated. Results show that the correlation may be greatly improved by applying the NRTL model with the regression criteria based on minimizing the experimental and calculating distribution coefficients S_K to give an average value of the root mean square deviation about 1.436 % and in terms of the average errors in the distribution ratio for all tie-lines about 10.776 %.

Keywords: Liquid -Liquid Equilibria, Extraction of Phenol, Activity Coefficient.

1. Introduction:

Phenol is an example of a highly toxic chemical substance. The maximum amount sanctioned by the World Health Organization in drinking water is 0.001 mg/L., Macedo and Soares (1996). This component is found in large quantities in the effluents of different petrochemical factories and is regularly released into the rivers. Therefore there is great need for elimination phenol from the water, on the other hand, phenol constitutes a valuable component in the production of various chemicals and could be reclaimed from the water to great advantage.

The separation process most widely used in the industry is the extraction with solvents. To design new equipment or to simulate the performance of existing units, it is important to have access to liquid-liquid equilibrium data.

Solvent extraction is a major unit operation based entirely on limited liquid miscibility and the distribution of solute between two liquid phases. In the design of a separation process and indeed whenever solvents are used in chemical technology it is unconditionally necessary to know from data or from calculation, the composition of the two phases in equilibrium.

For many types of mixture containing for example strongly polar molecules, it is necessary to use activity coefficient and hence expression for the excess Gibbs function G^E for the calculation of liquid phase fugasities, Hull and Kronberg (2006).

The aim of this research is to obtain the necessary liquid-liquid equilibrium data for the extraction of phenol from water. Phase equilibrium data of the ternary systems water-phenol-organic compounds were generated including phase equilibrium diagrams, distribution coefficients of phenol, tie-lines data and selectivity of the solvent. Tie-lines of two phase conjugate layers were determined by use of cross-section method and the accuracy of experimental tie-line data for the ternary was checked for six different solvents.

The NRTL, UNIQUAC and UNIFAC models were used to correlate the experimental data obtained for the ternary systems under study. The results showed whether the above model is fitted or not to the systems under consideration. A computerized procedure for predicting or representing multicomponent liquid-liquid phase equilibrium was developed by using the combination of optimization theory and thermodynamic.

The systems studied in this investigation were Water-Phenol-Benzene, Water-Phenol-Chloroform, Water-Phenol-Isobutyle Acetate, Water-Phenol-Butanol, Water-Phenol-Butanone and Water-Phenol-Toluene.

2. Experimental Work Chemicals:

The chemicals used was supplied from local markets. The selection of the six solvents is based on the available solvents in the local market which is considered to be controlling factor in this study. In spite of that the solubility parameters of the six selected solvents is within the range of 10.4 – 8.9. These chemicals were presented in Table 1 with their purities. Physical properties such as density of these materials used in this study were measured experimentally by measure the refractive index and compared with values in the literature (Frances, 1963; Fredenslund and Rasmussen, 1985; Jone and Theodore, 1986).

3. Refractive Index Measurement:

The refractive index was determined by a refractometer of the specification ABBE, the precision of the refractive indices was 0.0002 units. Refractive indices for the samples of liquid were measured and the values presented were the average values of at least three independent readings for each sample. The samples were thermostated by circulating water from a constant temperature bath through the refractometer. The constant temperature at which the measurements were taken was 30 °C and atmospheric pressure.

4. Experimental Apparatus:

The experimental work was carried out using Erlenmeyer flask with a stopper to prevent evaporation with a capillary inserted into the stopper, whilst maintaining a constant agitation by means of a magnetic stirrer. The flask has jacket through which water from a Haake thermostat bath was circulated. Temperature was measured by means of a precision thermometer, with an accuracy of ± 0.1 °C. The apparatus shown diagrammatically in figure 1.

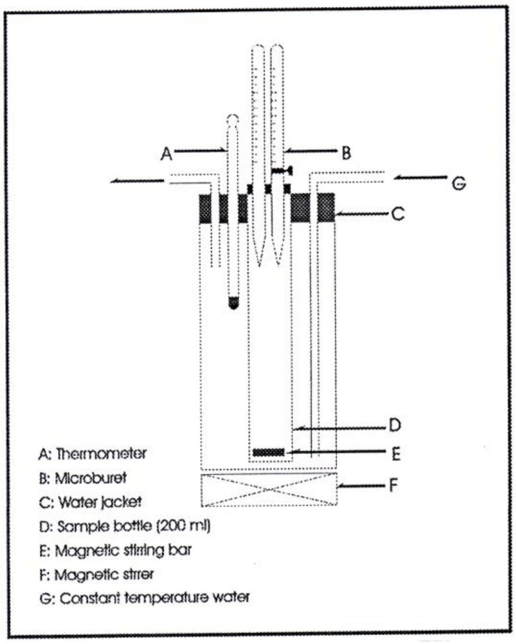

Fig.1. Cloud Point Titrator for Liquid-Liquid Equilibria.

5. Experimental Procedure:

The procedure involves operating the apparatus at steady state in order to predict the properties of liquid-liquid equilibria for ternary systems.

6. Determination of The Binodal Curves;

The binodal curves of the ternary systems were determined by the method of titration as described by (Alders, 1959). The solvent 3 was added to the mixture of water 1 and phenol 2 in the sample bottle inside the constant temperature water-jacket. As soon as the cloud point was reached, phenol 2 was then added to make the liquid homogenous again. The procedure was repeated a number of times, and the successive cloud points were connected up to produce the binodal curve. The maximum error of binodal points determination was ± 0.2 %.

Table 1
Physical Properties of Chemicals Used at 303 K.

Component	M. wt.	Density		Refractive index		Boiling point ^oC	Purity %	Supplier
		Exp.	Lit.	Exp.	Lit.			
Benzene	78.114	0.8683	0.8685	1.496	1.4962	80.1	99 %	BDH
Butanol	74.12	0.8053	0.8057	1.3970	1.3971	117.7	99.5 %	BDH
Butanone	72.11	0.7941	0.7941	1.3770	1.3773	79.6	99.5 %	BDH
Chloroform	119.38	1.4693	1.4706	1.4400	1.4401	61.2	99 %	BDH
Iso-butyl acetate	116.16	0.8621	0.8599	1.3880	1.3880	117.5	99 %	BDH
Toluene	92.14	0.8575	0.8577	1.4930	1.4935	110.6	99 %	BDH
Water	18.015	0.9951	0.9956	1.3340	1.3342	100.0	99.5 %	BDH
Phenol	94.113	1.588	1.587	1.5423	1.5395	181.8	99.5 %	Merck

7. Determination of the Tie Lines:

The determination was carried out using a double-walled similar to that described by (Novak, 1987). The separating funnels containing heterogeneous mixture of three components were placed in a thermostat bath. Temperature was controlled within an accuracy of ± 0.01 ^oC by using a temperature regulator as shown in fig.2. The prepared heterogeneous mixtures were shaken for at least 20 min., equilibration of the two phases took place in a thermostatted double-walled separating funnels (250 ml) over a period of 20 hr. After equilibrium had been reached, the refractive index of one of the separated phases was measured. The composition of the tie-lines was calculated numerically from the calibration data by polynomial regression analysis. The third order polynomial was the best approximation (stand. dev. = 1.5*10-4) of the relation between refractive index and composition.

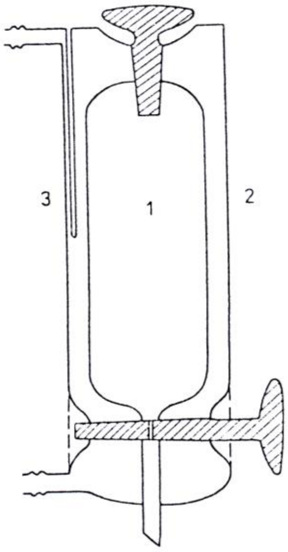

Fig.2. Thermostatted Separating Funnel for Determining Tie-Lines 1-Separating Funnel, 2-Thermostatting Mantle, 3-Thermometer Holder, 4-Stop Cock.

To determine the tie-lines of the two conjugate layers, ternary two phase systems were analyzed by the so-called cross-section method reported by (Radecki and Grzyboski, 1975). This method consists of plotting the refractive index of a mixture against concentration of one of the components at a constant ratio of the remaining two components.

8. Results and Discussion Tie-Line Data:

The tie-line data between the two conjugate phases were obtained from the cross-section method. The liquid-liquid equilibrium data (tie-line data) obtained experimentally for the series of the ternary systems water-phenol-benzene, water-phenol-chloroform, water-phenol-isobutyl acetate, water-phenol-butanol, water-phenol-butanone and water-phenol-toluene at 30°C were plotted in figures 3 to 8, the data of (Macedo and Soreas, 1996) for the system water-phenol-benzene was plotted in figure 3 for comparison only.

The tie-lines data were used to determine the selectivity (K_i) and distribution coefficients (S_{ij}) for the systems under investigation according to the following relationships:

$$K_i = \frac{Concentration\ of\ i\ in\ extract\ phase}{Concentration\ of\ i\ in\ raffinate\ phase} \qquad ...(1)$$

$$S_{ij} = \frac{K_i}{K_j} \qquad ...(2)$$

The subscript (i) is referred to phenol component and (j) is referred to water component one.

A simple graph of distribution curve for phenol compound between the two immiscible phases were obtained by plotting the concentration of phenol compound in organic phase against its concentration in the aqueous phase, and presented in figure 9. This type of diagram could be compared to a Y-X plot for the presentation of vapor-liquid equilibrium data, and the deviation of each curve from the Y-X line is a measure of the selectivity of solvent. As the deviation increases the selectivity of the solvent increases.

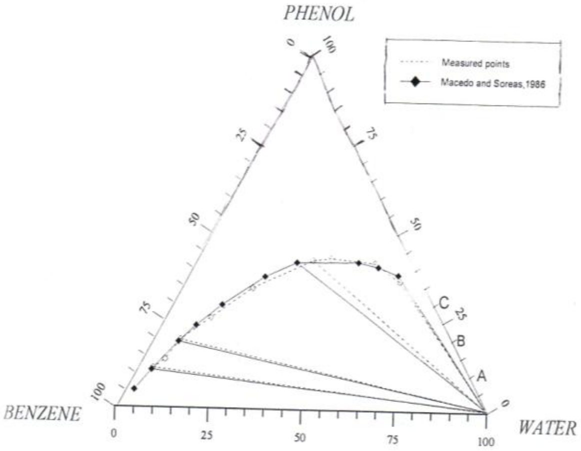

Fig. 3. **Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol-Benzene.**

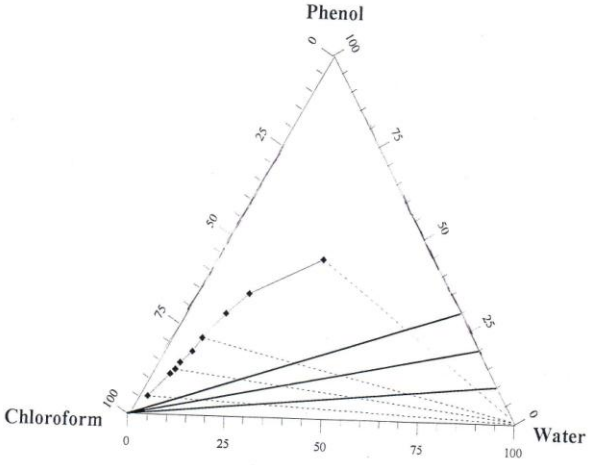

Fig. 4. **Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol- Chloroform.**

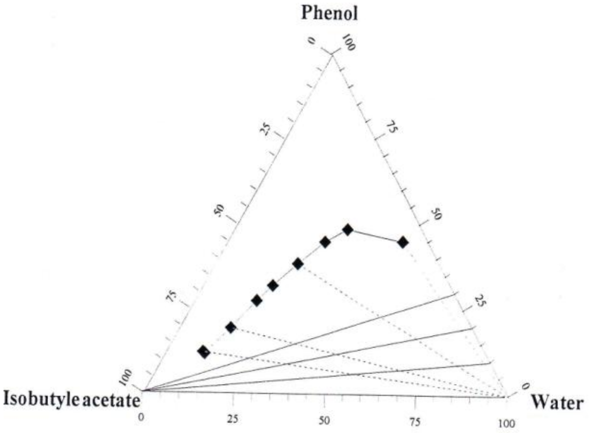

Fig. 5. **Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol-Isobutyl Acetate.**

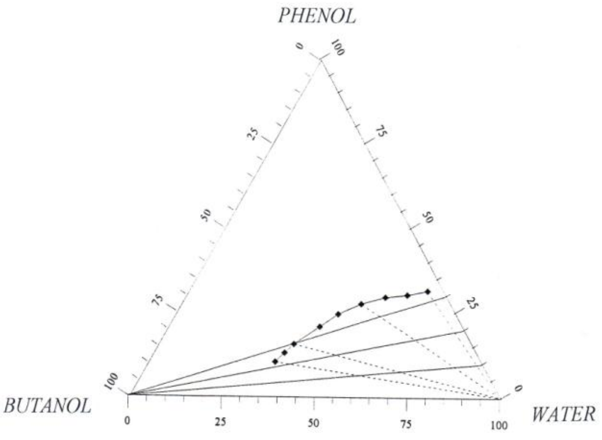

Fig.6. Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol-Butanol.

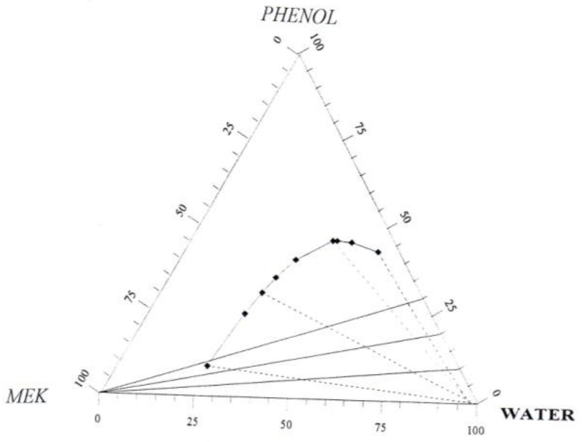

Fig.7. Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol-Butanone.

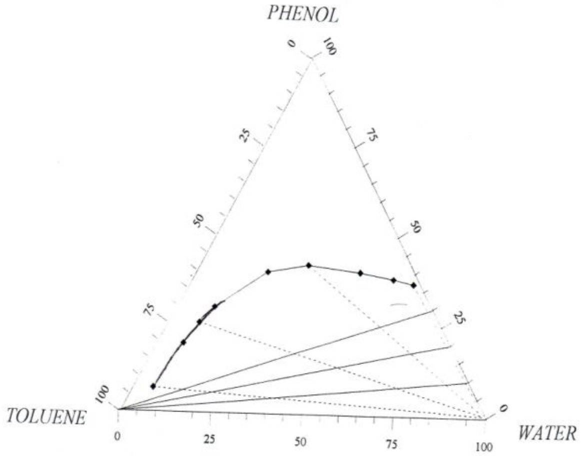

Fig.8. Experimental Liquid-Liquid Equilibrium of Ternary System Water-Phenol-TOLUENE.

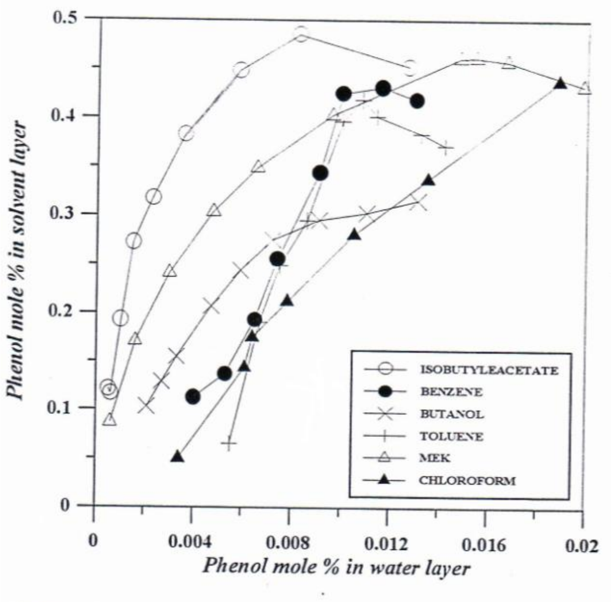

Fig.9. Distribution Coefficient of Phenol Between Water Layer and Solvent Layer at 303 K.

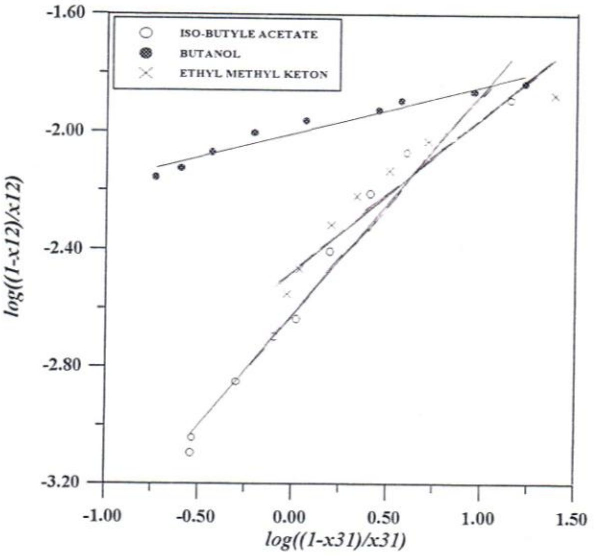

Fig.10. Othmer-Tobias Correlation for Water-Phenol-Solvent at 303 K.

9. Evaluation of the Consistency of the Experimental Tie-Lines:

The accuracy of the experimental data for the six ternary systems at 30 ^{o}C was checked by plotting in figures 10 and 11, the Othmer-Tobias correlation (Othmer and Tobias, 1942):

$$\log\frac{1\text{-}X_{ww}}{X_{ww}} = m\log\frac{1\text{-}X_{ss}}{X_{ss}} + n \qquad ...(3)$$

Figures 10 and 11 can be useful to check whether experimental data have a regular or not. This can help to identify some tie-lines with high random errors.

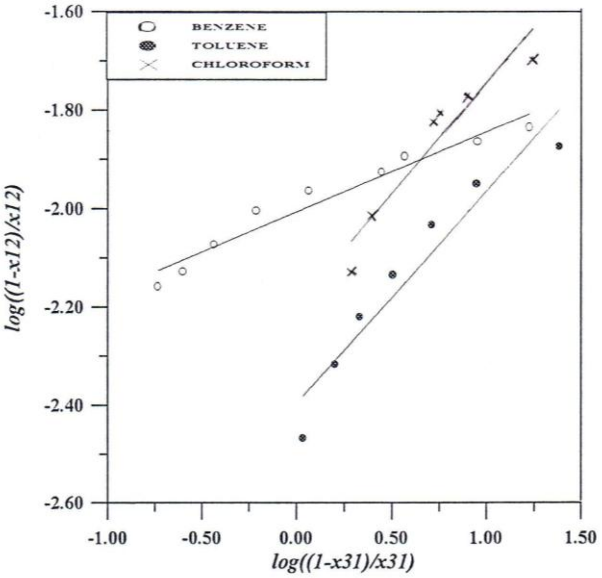

Fig. 11. Othmer-Tobias Correlation for Water-Phenol-Solvent at 303 K.

Figures 3 to 8 show the equilibrium diagrams of the systems water-phenol-organic solvent (benzene, chloroform, isobutyle acetate, butanol, butanone (MEK) and toluene). The six solvents are totally miscible with phenol. For butanol system the two phase area is small. A small area has the disadvantage that the purity of the extract is low and that, more over, only mixtures of limited concentrations can be extracted (Alders, 1959). Thus it follows for figure 6 that with butanol as extractive solvent at 303 K, no mixtures can be separated that contain more than 40 % of phenol. For benzene the area under the binodal curve is large and for figure 3 it can be seen that mixtures of 70 % phenol can be extracted with benzene. In figures 4, 5, 7 and 8 the same conclusions can be reached for the other solvents. Figure 9 verifies this result. It shows the distribution curves of benzene, chloroform, isobutyle acetate, butanol, butanone and toluene. The distribution coefficient of phenol was higher towards isobutyle acetate and butanone than for the other solvents.

Also, the liquid-liquid equilibrium data presented were plotted in figure 10 in the form of separation factor (S) versus the equilibrium distribution ratio of phenol (K), in the range of concentration under observation. This study showed that, for all the solvents considered, the organic ester and keton emerge as the most indicated for the separation of phenol from water. Although isobutyle acetate and MEK have similar distribution curve. The boiling point and specific gravity of MEK differ greatly from those of phenol, and so MEK is a more suitable solvent for phenol.

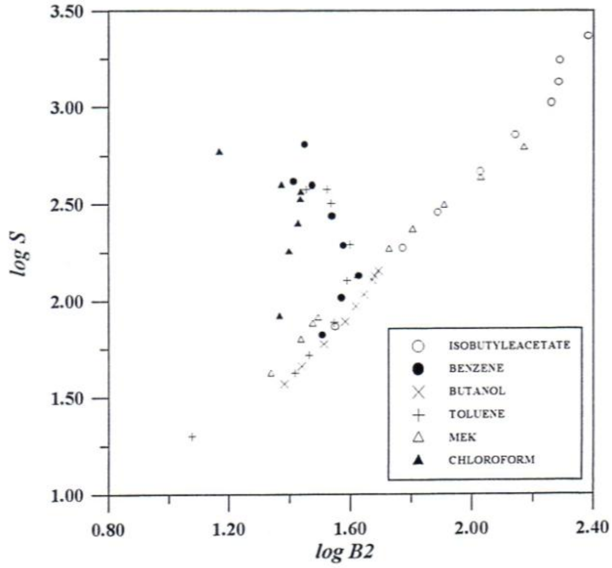

Fig.12. Separation Factor Versus Equilibrium distribution Ratio for Extraction of Phenol From Water With Solvents at 303 K.

10. Correlation Methods Estimation of Parameters:

The NRTL equation (Renon and Prausnitz, 1968), the UNIQUAC equation (Anderson and Prausnitz, 1978) and the UNIFAC equation (Fredenslund and Prausnitz, 1982) were used to correlate the experimental phase equilibrium data. Binary parameters were calculated using the maximum likelihood procedure for the minimization of the following objective functions

$$F1 = \sum_{K=1}^{M}\sum_{i=1}^{N}\left[\ln\left(x_i^{II}\big/x_i^{I}\right) - \ln\left(\gamma_i^{I}\big/\gamma_i^{II}\right)\right]_k^2 \quad \dots(4)$$

$$F2 = \sum_{k=1}^{M}\sum_{i=1}^{N}\sum_{j=1}^{2}\left(\hat{x}_{ijk} - x_{ijk}\right)^2 \quad \dots(5)$$

The calculation begins using the objective function F1 and when the parameters are near optimum value the calculation continues with the objective function F2. For ternary mixtures nine parameters for the NRTL equation must be fitted, six parameters for the UNIQUAC equation and the predictive method for UNIFAC equation for describing a ternary data set.

This procedure gives a set of parameters shown in tables 2 and 3

11. Calculation of Tie-Lines:

The above mentioned procedure for estimated – parameters were employed to calculate the tie-lines. Computation started from the heterogeneous mixture:

$$Z_i = \frac{x_i^{I} + x_i^{II}}{2} \qquad ...(6)$$

The computation of tie-lines was based on the algorithm published by (Null, 1970)

Figures 13, 14, 15, 16, 17 and 18 represent NRTL models correlation with two regression criteria for the systems under study.

A good representation was obtained in figures 13, 15, 16, 17 and 18 for the two regression criteria Sa, Sk and the residuals to the experimental data were low but residuals to the distribution coefficients was better for the regression criteria Sk than the regression criteria Sa for all the systems.

For chloroform system, the NRTL model represents the correlation with the regression criteria Sk only and give a good residuals for both the experimental data and the distribution coefficients.

Figures 19, 20, 21, 22, 23 and 24 represent the UNIQUAQ modeling to the ternary system under study. For all the systems the residuals were higher for the experimental data and the distribution coefficient, and representation was better for the NRTL model than the UNIQUAC model.

For all the systems above it can be seen that, at low concentration of the solute both the NRTL model and UNIQUAC model fit the experimental data. But at high concentrations the deviation from experimental are obvious.

Figures 25, 26, 27, 28, 29 and 30 represent UNIFAC models correlation for the systems under study. In figures 25, 26, 27, 28, 29 and 30 the residuals were higher for the experimental data, and representation was better for both the NRTL model and UNIQUAC model than the UNIFAC model.

For Butanol system, the UNIFAC model gives good residuals for both the experimental data and the distribution coefficients than the UNIQUAC model.

Table 2
NRTL Correlation Parameters for Ternary System in kJ/mol at 303 K.

Solvent	i-j	A_{ij}	A_{ji}	$\square_{ij}$
Benzene	1-2 1-3 2-3	1267.83346 1595.76351 -265.14854	-125.07542 1108.3348 858.27337	0.21906 0.31233 0.42423
Chloroform	1-2 1-3 2-3	1084.83814 2024.50135 116.82185	154.68756 473.8733 263.54813	0.5169 0.19131 0.60211
iso butyl acetate	1-2 1-3 2-3	1552.05204 1973.83952 2190.65119	136.07517 651.2274 20.7399	0.5743 0.28968 0.67227
Butanol	1-2 1-3 2-3	1244.98256 2193.96024 782.10278	119.92193 501.96555 379.55085	0.53109 0.34753 0.69905
MEK	1-2 1-3 2-3	1527.03582 3037.4255 2299.1531	-448.7063 148.9289 -2185.0569	0.16978 0.21666 0.06204
Toluene	1-2 1-3 2-3	1370.2677 1376.6916 -476.4699	-208.4991 822.2341 1533.0258	0.2116 0.2566 0.2385

Table 3
Uniquac Correlation Parameters for Ternary System in kJ/mol at 303 K.

Solvent	i-j	B_{ij}	B_{ji}
Benzene	1-2 1-3 2-3	-7.1734 220.908 -53.1383	164.64 514.0597 91.1305
Chloroform	1-2 1-3 2-3	52.6238 643.2392 81.6293	345.7274 425.8234 78.7847
iso butyl acetate	1-2 1-3 2-3	267.108 158.795 2141.241	322.71 1106.435 -282.265
Butanol	1-2 1-3 2-3	90.3247 2514.7869 827.905	80.0523 473.0648 -270.6094
MEK	1-2 1-3 2-3	93.4385 949.4014 1543.2946	396.148 546.9067 423.9119
Toluene	1-2 1-3 2-3	-103.013 47.108 -246.023	375.872 1139.4387 904.198

Table 4
Classical and Statistical Regression Criteria.

$$S_a = \sum_{k=1}^{M}\sum_{i=1}^{N}\left(x_{ik}^{I}\gamma_{ik}^{I} - x_{ik}^{II}\gamma_{ik}^{II}\right)^2 \qquad \ldots(7)$$

$$S_{a'} = \sum_{k=1}^{M}\sum_{i=1}^{N}\left[\frac{a_{ik}^{I} - a_{ik}^{II}}{a_{ik}^{I} + a_{ik}^{II}}\right]^2 \qquad \ldots(8)$$

$$S_k = \sum_{k=1}^{M}\sum_{i=1}^{N}\left[\ln\left(\frac{x_i^{II}}{x_i^{I}}\right) - \ln\left(\frac{\gamma_i^{II}}{\gamma_i^{I}}\right)\right]_k^2 \qquad \ldots(9)$$

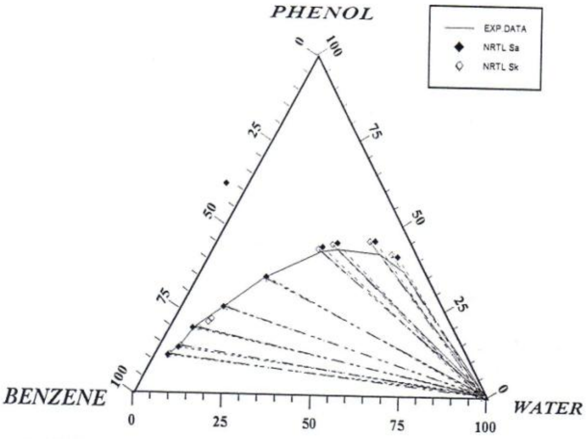

Fig. 13. Representation of the Ternary System Water-Phenol-Benzene by NRTL Model With Parameters Obtained From LLE Data at 303 K.

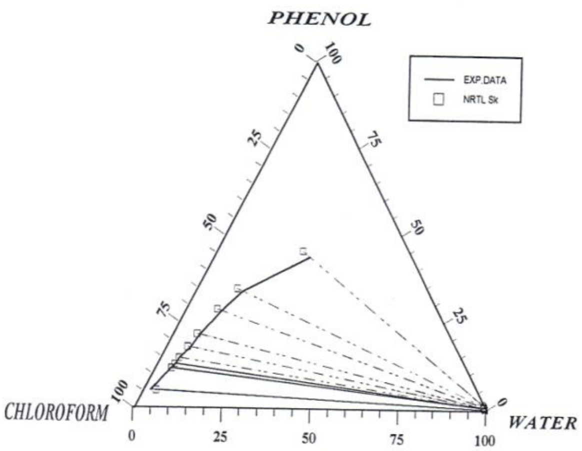

Fig.14. Representation of the Ternary System Water-Phenol-Chloroform by NRTL Model With Parameters Obtained from LLE Data at 303 K.

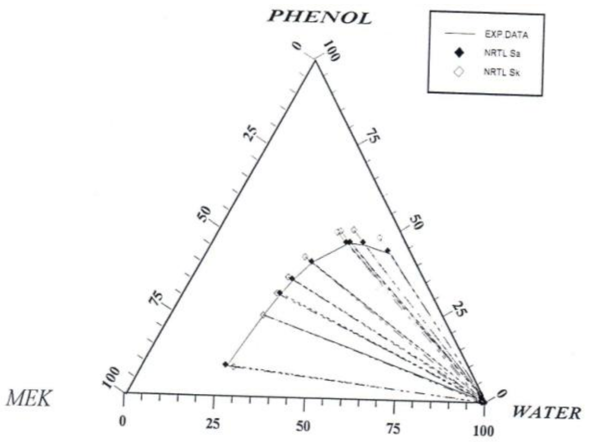

Fig.17. Representation of the Ternary System Water-Phenol-MEK by NRTL Model With Parameters Obtained From LLE Data at 303 K.

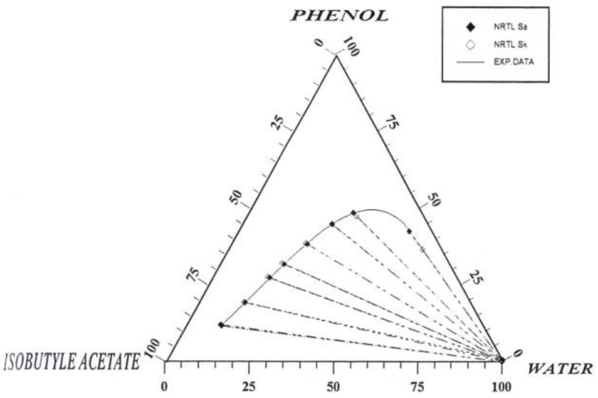

Fig.15. Representation of the Ternary System Water-Phenol-Isobutyle Acetate by NRTL Model With Parameters Obtained from LLE Data at 303 K.

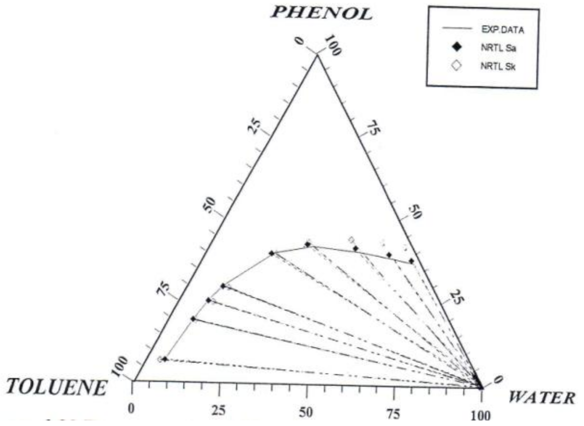

Fig.18. Representation of the Ternary System Water-Phenol-Toluene by NRTL Model With Parameters Obtained From LLE Data at 303 K.

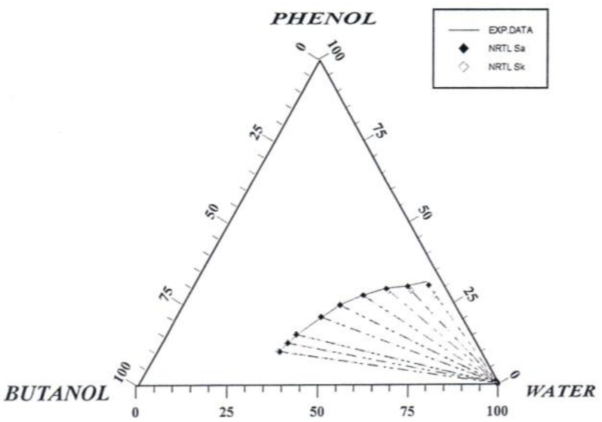

Fig.16. Representation of the Ternary System Water-Phenol-Butanol by NRTL Model with Parameters Obtained From LLE Data at 303 K.

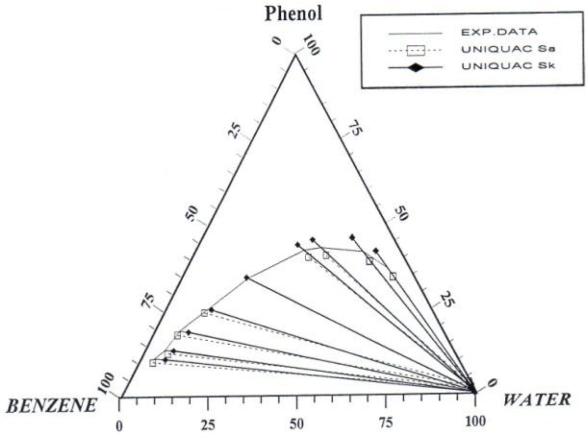

Fig.19. Representation of the Ternary System Water-Phenol-Benzene by UNIQUAC Model with Parameters Obtained From LLE Data at 303 K.

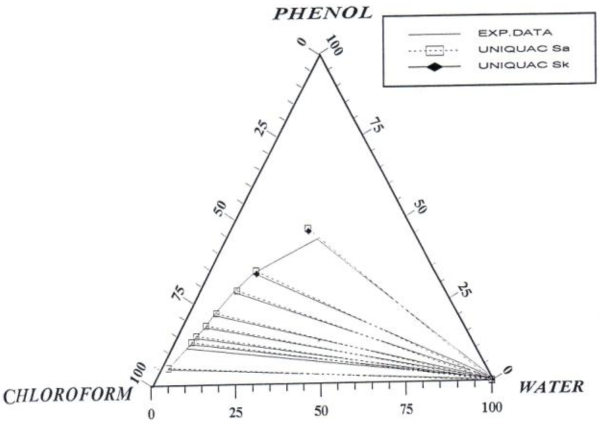

Fig.20. Representation of the Ternary System Water–Phenol-Chloroform by UNIQUAC Model with Parameters Obtained From LLE Data at 303K.

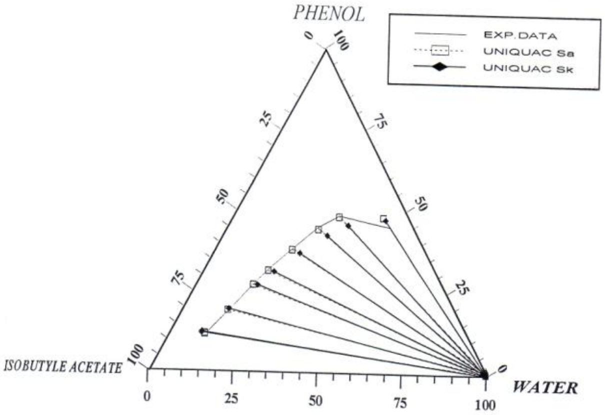

Fig.21. Representation of the Ternary System Water-Phenol-Isobutyle Acetate by UNIQUAC Model with Parameters Obtained From LLE Data at 303 K.

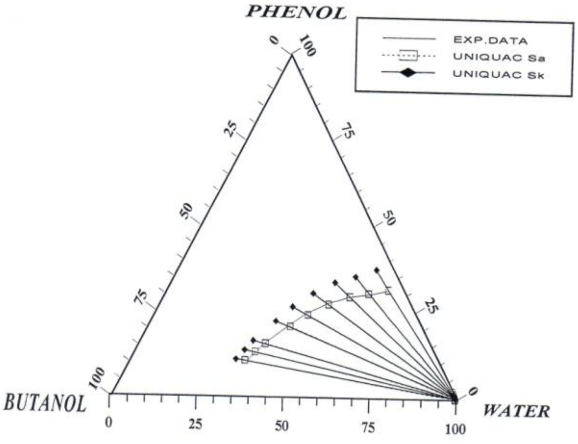

Fig.22. Representation of the Ternary System Water-Phenol-Butanol by UNIQUAC Model with Parameters Obtained From LLE Data at 303 K.

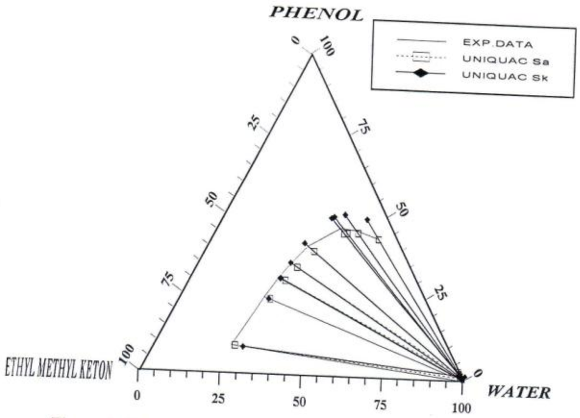

Fig.23. Representation of the Ternary System Water-Phenol-MEK by UNIQUAC Model with Parameters Obtained From LLE Data at 303 K.

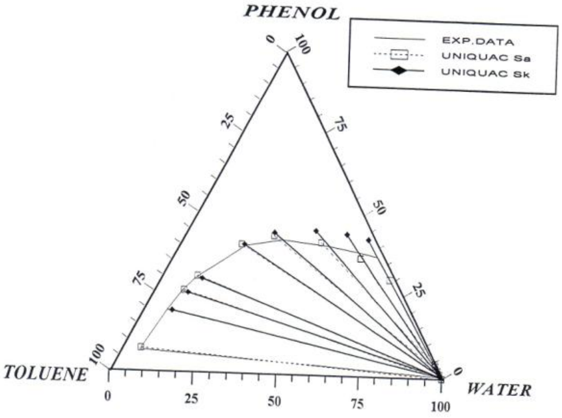

Fig.24. Representation of the Ternary System Water-Phenol-Toluene by UNIQUAC Model with Parameters Obtained From LLE Data at 303 K.

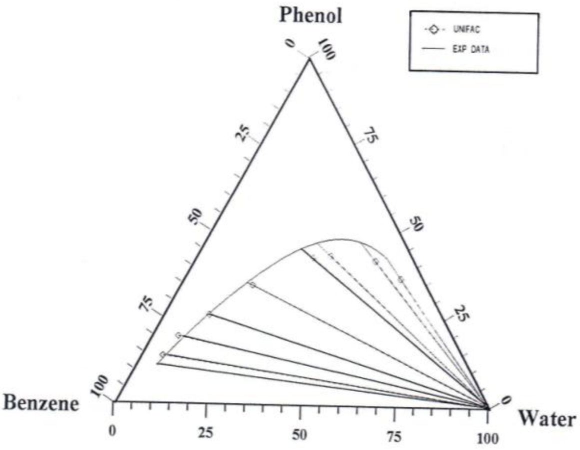

Fig.25. Representation of the Ternary System Water-Phenol-Benzene by UNIFAC Model with Parameters Obtained From LLE Data at 303 K.

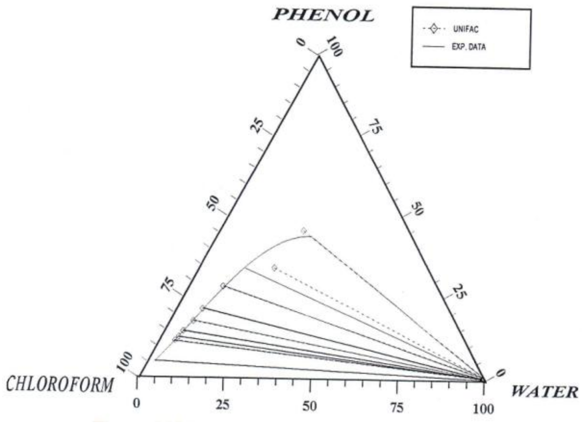

Fig.26. Representation of the Ternary System Water-Phenol-Chloroform by UNIFAC Model with Parameters Obtained from LLE Data at 303 K.

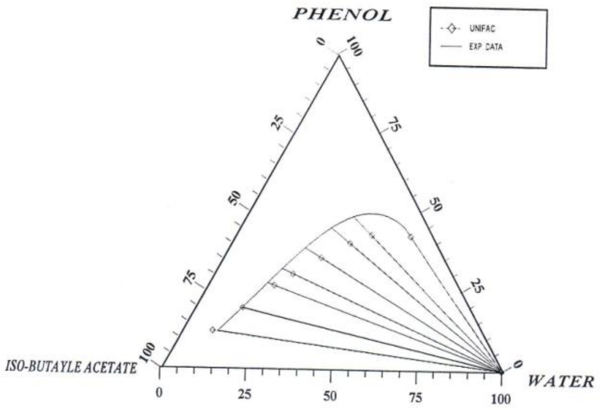

Fig.27. Representation of the Ternary System Water-Phenol-Isobutyle Acetate by UNIFAC Model with Parameters Obtained From LLE Data at 303K.

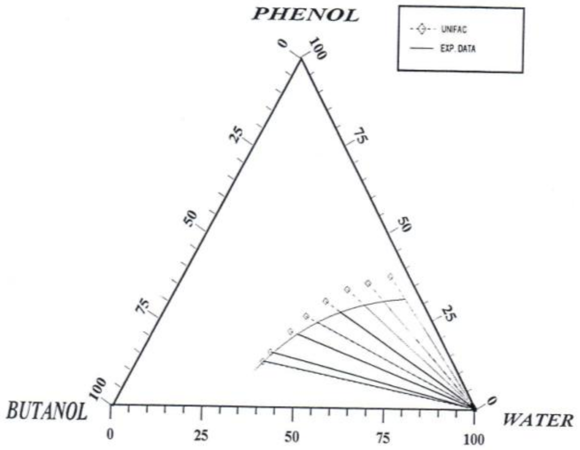

Fig.28. Representation of the Ternary System Water-Phenol-Butanol by UNIFAC Model with Parameters Obtained From LLE Data at 303 K.

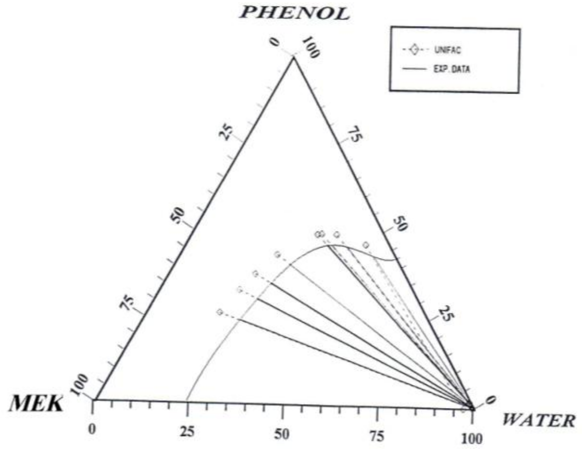

Fig.29. Representation of the Ternary System Water-Phenol-MEK by UNIFAC Model with Parameters Obtained from LLE Data at 303 K.

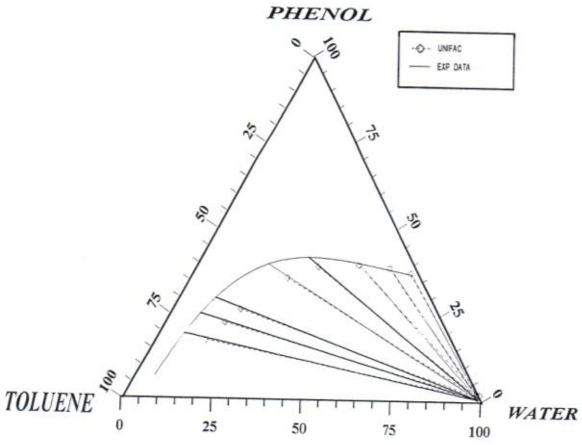

Fig.30. Representation of the Ternary System Water-Phenol-Toluene by UNIFAC Model with Parameters Obtained From LLE Data at 303K.

12. Correlation:

In liquid extraction studies experimental results obtained for low solute concentrations are most important. Table 5 shows the root mean square deviation between the experimental and calculated values for the tie-lines, as calculated from the formula

$$RMSD = F = 100 \times \left[\sum_{k=1}^{k} \min \sum_{j=1}^{N} \sum_{i=1}^{I} \left(\hat{x}_{ijk} - x_{ijk} \right)^2 \Big/ 6M \right]^{1/2} \quad ...(10)$$

and the average error in the distribution ratio for all tie-lines

$$\Delta\beta = 100 \times \left[\sum_{k} \left[\left(\hat{\beta}_k - \beta_k \right) \Big/ \beta_k \right]^2 \Big/ M \right]^{1/2} \qquad \ldots(11)$$

Table 5
Residuals for the six ternary Liquid-liquid equilibrium data set correlated by NRTL, UNIQUAC and UNIFAC at 303 K.

Data Set No.	Residuals	NRTL		UNIQUAC			UNIFAC
		S_a	S_k	S_a	$S_{a'}$	S_k	S_k
1	F	0.342	1.4704	1.092	1.73	1.859	1.4996
	□ □	117.98	15.284	96.84	17.38	16.165	19.318
2	F	0.432	0.7267	1.021	0.405	0.501	0.5649
	□ □	65.76	12.645	97.787	15.359	15.757	19.106
3	F	0.543	1.788	0.7411	2.697	1.287	2.445
	□ □	32.944	9.005	68.856	29.725	31.369	21.054
4	F	0.2496	0.9316	0.412	2.729	2.731	2.482
	□ □	13.975	1.9572	152.02	5.608	5.608	8.803
5	F	1.122	1.867	1.058	2.475	2.058	2.703
	□ □	73.989	4.75	51.828	14.146	19.201	14.948
6	F	1.234	1.832	1.949	2.308	1.93	2.843
	□ □	129.28	1.54	172.92	6.173	9.895	46.86
Average	F	0.9775	1.436	1.045	2.057	1.727	2.089
	□ □	73.634	1.13	106.71	14.732	16.332	21.685

An analysis of table 5, shows that for all data sets the binodal curves are well reproduced by the regression criteria S_a for both models NRTL and UNIQUAC model but give a high residuals of the phenol distribution ratios for almost all the system as indicated by the residual □ □. The overall fit measured by F is worse when both S_a' and S_k were applied to UNIQUAC model but a large improvement in the values of □ □ is obtained as compared with the results of the regression criteria S_a. Using the UNIFAC equation, the correlation residuals does not improve the results. The NRTL models results using the regression criteria S_k can be more accurate than the UNIQUAC equation and give good improvement in F and the values of □ □. Table 5 verifies the results of the above figures. The disagreement between the experimental and calculated results, expressed in terms of solute distribution ratios, is more easily visualized in figures 31, 32, 33, 34, 35 and 36.

Figure 31, shows the experimental phenol distribution ratio at 30 ^{o}C together with those calculated by using the NRTL (S_a and S_k, which gave the best NRTL results), UNIQUAC (S_a, S_a' and S_k) and UNIFAC (S_k). The NRTL results can be seen to be more accurate with the objective function S_k than the other models with the different objective function. The results for the other five systems, figures 32, 33, 34, 35 and 36 are similar to that of figure 31.

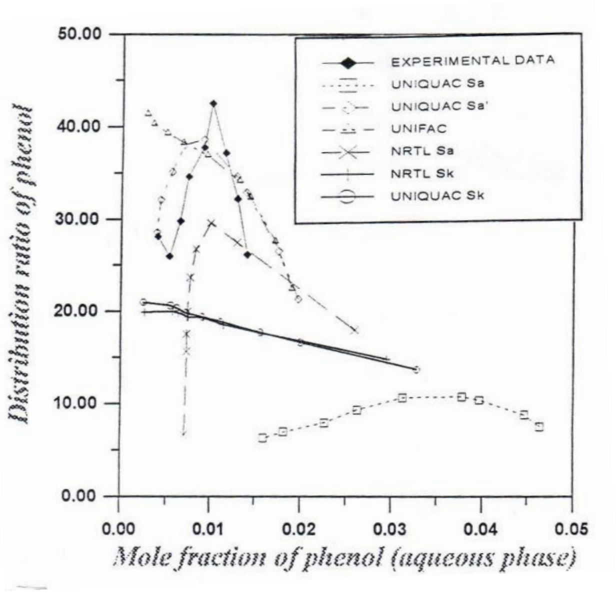

Fig.31. Experimental and Calculated Distribution Ratio of Water-Phenol- Benzene at 303 K.

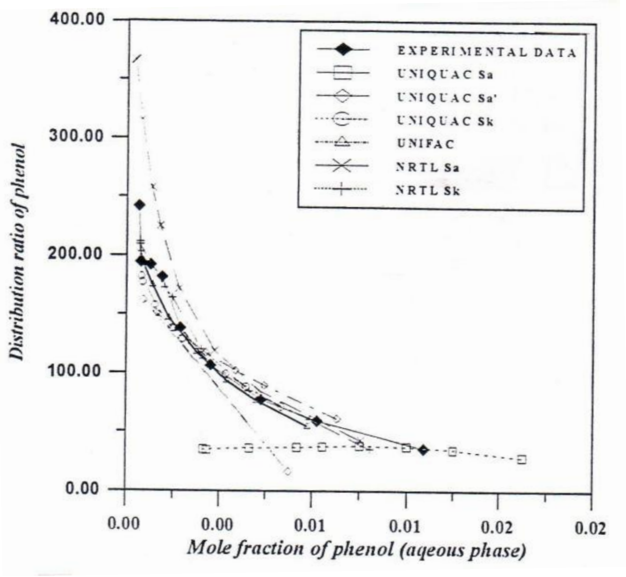

Fig.33. Experimental and Calculated Distribution Ratio of Water-Phenol-Isobutyle Acetate at 303K.

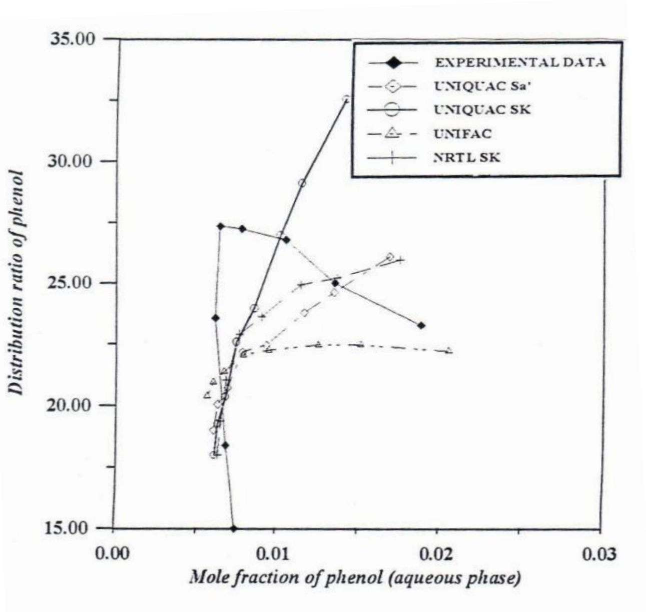

Fig.32. Experimental and Calculated Distribution Ratio of Water-Phenol-Chloroform at 303 K.

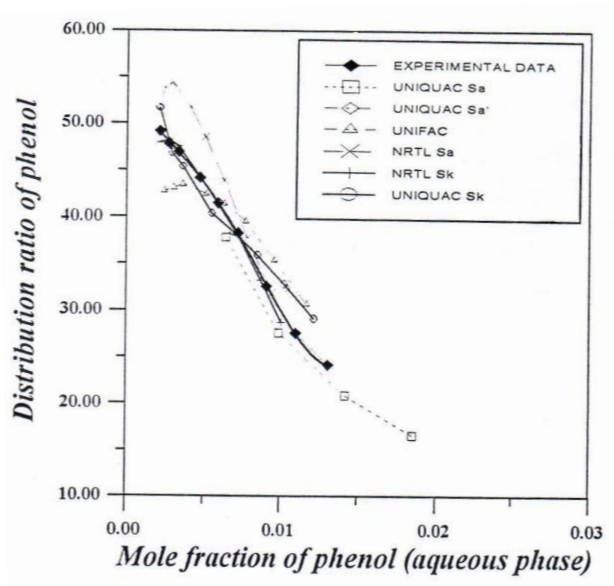

Fig.34. Experimental and Calculated Distribution Ratio of Water-Phenol- Butanol at 303 K.

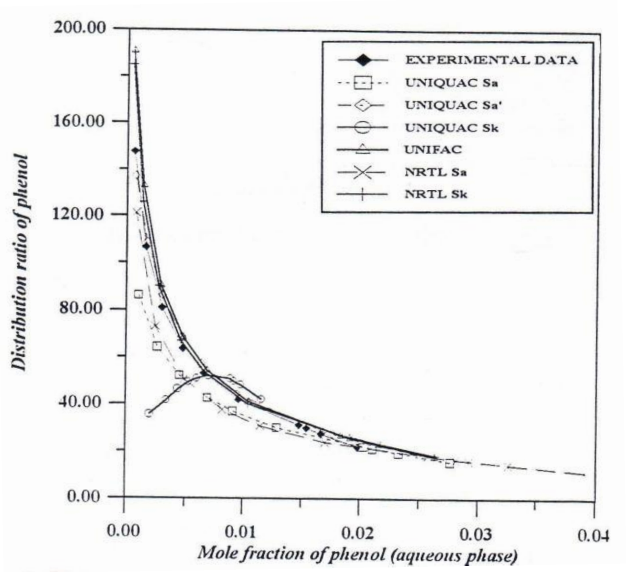

Fig.35. Experimental and Calculated Distribution Ratio of Water-Phenol- MEK at 303 K.

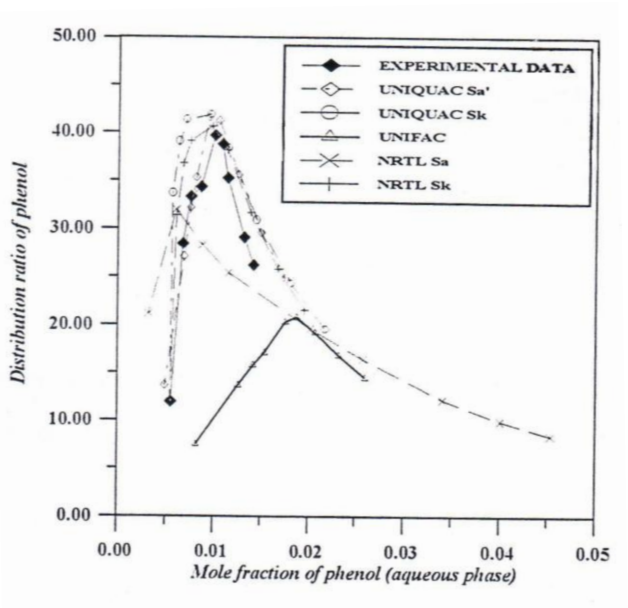

Fig.36. Experimental and Calculated Distribution Ratio of Water-Phenol-Toluene at 303 K.

Table 6
Fitting Accuracy of Ternary LLE Data

No.	NRTL				UNIQUAC						UNIFAC	
	S_a		S_k		S_a		$S_{a'}$		S_k		S_k	
	□ x		□ x		□ x		□ x		□ x		□ x	
	I	II	I	II	I	II	I	II	I	II	I	II
1	15.1	16.9	18.8	1.66	13.8	16.3	23.8	2.01	4.8	7.20	28.4	1.98
2	0.76	0.76	9.76	0.64	11.8	6.51	5.28	0.83	22.1	1.25	7.52	0.98
3	6.51	1.06	22.1	0.47	8.93	12.1	35.3	1.01	17.1	1.53	32.6	1.27
4	3.15	0.62	11.7	0.39	3.49	4.28	36.8	0.76	36.8	0.78	32.7	0.48
5	5.55	14.2	24.2	2.11	13.2	5.33	48.3	1.38	27.3	0.72	38.1	2.12
6	7.13	0.56	22.0	0.41	9.63	13.2	33.2	1.54	29.1	1.79	25.6	2.16
Av.	7.49	6.69	18.1	0.95	10.2	29.2	30.5	1.25	22.8	2.13	27.5	1.53

13. Comparison of Fitting Accuracy:

The fitting accuracy of six set of ternary LLE data applying NRTL with two regression criteria, UNIQUAC with three regression criteria and UNIFAC with one regression criteria are listed in Table 6, it can be seen from the table that correlation is improved by applying the NRTL model with regression criteria S_k .

14. Conclusions:

1. Of the six solvents used to extract phenol from an aqueous phenol solution, both iso-butyle acetate and Etyl methyl keton have the highest selectivity and capacity because the iso-butyle acetate hydrogen bonds and ethyl methyl keton hydrogen bond preferentially with phenol. And due to the greatest differences between the boiling point and specific gravity of the ethyl methyl keton and those of phenol. It is therefore considered an excellent

solvent for extracting phenol from phenol-water solutions.

2. The consistency of experimental tie-line data for the ternary system water-phenol-solvent at 30 ^oC was confirmed for six different solvents, and the data can then be used to calculate the values of the parameters and the tie-lines in the NRTL, UNIQUAC and UNIFAC models.
3. The NRTL model for the activity coefficients of ternary liquid systems gives a good representation of liquid-liquid equilibria for the systems under study. This fact helps for calculations required in the design of extraction unit to reach the optimum use of the solvent.
4. The root mean-square deviation F between the calculated and the experimental tie-lines lays within the range of 1.867-0.726 for the NRTL model for the objective function F2 and in terms of the error □ □ the range is lays within 15.284-9.005.
5. The NRTL equation gives F values slightly lower than those of the UNIQUAC equation but the difference is not significant it is 1.2-1.1 times larger than the NRTL model.
6. The NRTL equation gives the best □ □ results, in which case it proves to be more accurate than the UNIQUAC equation at all objective functions, it is 1.5 times larger than the NRTL model.
7. The UNIFAC equation gives F values slightly lower than those of the UNIQUAC equation for the system containing an alcohol component but the difference is not significant.

15. Nomenclature Abbreviations:

LLE	Liquid – Liquid Equilibrium
MEK	Methyl Ethyl Keton (Butanone)
NRTL	Non-Random Two Liquid Activity Coefficient model
RMSD	Root mean square deviation
UNIFAC	UNIQUAC Functional Group Activity Coefficients model
UNIQUAC	Universal Quasi-Chemical Activity Coefficient model

16. Symbols:

a_i	Activity of component i
F1	Objective function no. 1
F2	Objective function no. 2
G^E	Excess Gibbs function
K_i	Selectivity
m	slope of the line
M	No. of experimental points
M.wt.	Molecular weight
n	Intersect of the line
S_a	Classical regression criteria
S_K	Statistical regression criteria
S_{ij}	Distribution coefficient
x_i^I	mole fraction of component i in the I phase
x_i^{II}	mole fraction of component i in the II phase
X_{ss}	mole fraction of solvent in the solvent phase
X_{ww}	mole fraction of water in the water phase
Z_i	number of mole of component i in the system

17. Greek Litters:

□□	Average error
□	Activity coefficient

18. Superscript:

E	Excess Property
I	Phase I
II	Phase II
$\wedge$	Experimental value
i	component *i*
j	component *j*
ss	*solvent* in the *solvent* phase
ww	water in the water phase

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استخلاص الفينول من المياه الصناعية باستخدام مذيبات مختلفة

محمود عمر*   خالد فرهود   بشرى ياسين*****

*قسم الهندسة الكيمياوية / جامعة النهرين
**قسم الهندسة الكيمياوية / الجامعة التكنولوجية
***قسم الهندسة الكيمياوية / الجامعة المستنصرية

الخلاصة

تم تحليل و دراسة كفاءة استخلاص الفينول من المياه الصناعية باستخدام مذيبات مختلفة. بحسب المعلومات العملية المحدودة المتوفرة في النشرات والمجلات العلمية لتوازن سائل – سائل للأنظمة الثلاثية والتي تحوي على الثنائي الماء و الفينول ،فان الهدف من هذه الدراسة هو معرفة بيانات التوازن للأطوار لغرض إيجاد علاقات توازن السائل – السائل لأنظمة الماء و الفينول مع المذيبات المختلفة بضمنها مخطط الأطوار ، معامل التوزيع للفينول وبيانات خطوط التوازن وانتقائية افضل مذيب للفينول.

تم إيجاد بيانات مخططات التوازن للأنظمة الثلاثية التالية : ماء-فينول-بنزين ، ماء-فينول-كلوروفورم ، ماء-فينول-ايزوبيوتايل اسيتيت ، ماء-فينول-بيوتانول ، ماء-فينول-اثيل مثيل كيتون و ماء-فينول-تلوين عند درجة حرارة 303 كلفن وضغط جوي واحد .

تم حساب سعة وانتقائية كل من هذه المذيبات العضوية لكل من الأنظمة المذكورة أعلاه من بيانات توازن الأطوار . لقد وجد ان سعة الأيزوبيوتايل اسيتيت هي الأعلى مقارنة مع المذيبات الأخرى. كما إن انتقائية المذيب اعلاه هي الأعلى ، بينما كانت سعة و انتقائية مذيب الاثيل مثيل كيتون اقل من المذيب أعلاه والأعلى مقارنة مع المذيبات الأخرى . يمكن القول ان كل من مذيب الأيزوبيوتايل اسيتيت و مذيب الاثيل مثيل كيتون من المذيبات الانتقائية الجيدة ويمكن استخدامهم في استخلاص مادة الفينول من المياه الصناعية .

تم تطبيق النتائج العملية للأنظمة الثلاثية على معادلات NRTL, UNIQUAC and UNIFAC لمعامل الفعالية ، وذلك لمعرفة المعاملات الثنائية لتلك المعادلات . تم حساب التراكيز المتوقعة حسب تلك المعادلات و مقارنتها مع النتائج العملية ووجد ان معادلة NRTL مع الدوال الرياضية لتقليل نتائج الفرق بين القيم النظرية و العملية لمعامل التوزيع يعطي افضل النتائج حيث إن معدل الخطأ في مخطط قابلية الإذابة بحدود 1.436 % ومعدل الخطأ في نسبة التوزيع بحدود 10.776 % .
