36 *J. Chem. Eng. Data* **2008,** *53,* 36–40

Liquid–Liquid Equilibrium for the Quaternary System Water + Tetrahydrofuran + Toluene + 1-Butanol Mixture at 25 °C and Atmospheric Pressure

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Liquid–liquid equilibria (LLE) for the quaternary system water + tetrahydrofuran + toluene + 1-butanol mixture were measured at 25 °C and atmospheric pressure. Binodal curves, tie-lines, distribution, and selectivity for the quaternary system have been determined to investigate the effect of using binary solvents, toluene, and 1-butanol, on extracting tetrahydrofuran from aqueous solution. In addition, these experimental tie-line data were also compared with the values predicted by the UNIFAC model. It is found that the UNIFAC group interaction parameters used for LLE could not provide a good prediction.

Introduction

Liquid–liquid extraction has grown in importance in recent years because of the growing demand for temperature-sensitive products, higher-purity requirements, more efficient equipment, and availability of solvents with higher selectivity.[1] Considerable data of a physical-chemical nature are necessary for the development of liquid–liquid extraction processes and the design of equipment for them.[2] And liquid–liquid extraction is often more acceptable than distillation as a technique for separating liquids because it does not involve a heating process.[3]

The efficient separation of ring-containing compounds (e.g., cyclic ethers and cyclic alcohols) from aqueous solutions is important in the chemical industry, where many solvents have been tested to improve such recovery.[4–10]

Tetrahydrofuran (THF) is an organic solvent, an important organic raw material, and the precursor of polymers. Due to its proton-accepting nature, it is used as a solvent in many chemical industries. Many chemical and pharmaceutical industries encounter problems in separating THF from aqueous waste streams because their mixture forms azeotropes at low compositions of water.[11]

The purpose of this work is to determine liquid–liquid equilibrium (LLE) data of the water + THF + toluene + 1-butanol mixture, and the LLE data for the quaternary system were measured at 25 °C and atmospheric pressure. The effect of the mixed solvents to separate THF from aqueous solution was investigated. The system studied was a type C quaternary system, and the ternary systems relevant to the quaternary mixtures at 25 °C have been reported for the type 1 systems water + THF + toluene and water + THF + 1-butanol and type 2 system water + toluene + 1-butanol. LLE data have also been predicted with the UNIFAC method,[12–14] and they are compared with the experimental data at 25 °C.

Experimental Section

Materials. Toluene, 1-butanol, and THF used in this work were purchased from Aldrich and were of 99.9 % purity, and ordinary bidistilled water was used. The purity of each of the components was checked by gas chromatography. The GC analysis did not show any appreciable peaks of impurities for all the components and determined > 99.9 % purities for toluene, 1-butanol, and THF. They were used without further purification.

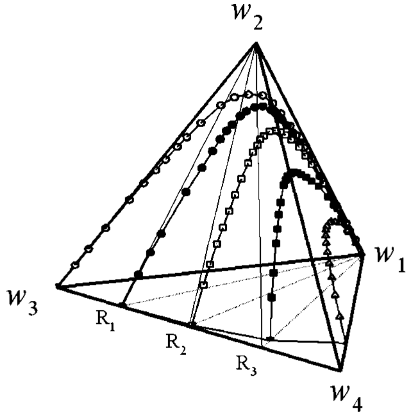

Figure 1. Phase equilibrium of the water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C. R_1, R_2, and R_3 denote quaternary sectional planes: ○, w_3/w_4 (100/0); •, w_3/w_4 (75/25); □, w_3/w_4 (50/50); ■, w_3/w_4 (25/75); △, w_3/w_4 (0/100).

Quaternary Equilibrium Data Determination. According to the Prausnitz classification,[15] the quaternary system in this study was type C, which contains two ternary LLE mixtures of type 1 having a plait point and one ternary LLE mixture of type 2 having two pairs of partially miscible compounds in the Treybal classification.[16] The study of the quaternary solubility surface was carried out for the system made up of the water, THF, and toluene/1-butanol mixture in 100/0, 75/25, 50/50, 25/75, and 0/100 mass ratios (pseudoternary systems). Figure 1 shows the method schematically, where R is the mass fraction of the solvents. The binodal curves of liquid–liquid equilibrium for four components have been described by Prausnitz and Anderson.[17]

The binodal (solubility) curves in the water + THF + toluene + 1-butanol mixture were determined at 25 °C and atmospheric pressure by the cloud-point method as described by Othmer et al.[2] For the determination of the mutual solubility data, accurately known masses of the solvent mixture (toluene + 1-butanol) were placed in a thermostatted glass-stoppered bottle, and water was titrated into the bottle from a microburet with

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10.1021/je700289p CCC: $40.75

Table 1. Binodal Curve Data for the Ternary Systems at 25 °C: Water (1) + THF (2) + Toluene (3), Water (1) + THF (2) + 1-Butanol (4), and Water (1) + Toluene (3) + 1-Butanol (4)

	water (1) + THF (2) + toluene (3)		water (1) + THF (2) + 1-butanol (4)		water (1) + toluene (3) + 1-butanol (4)	
T/°C	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_3
25	0.03	0.00	19.83	0.00	0.00	99.86
	0.57	44.95	21.10	7.84	0.35	91.53
	1.13	50.20	22.71	13.97	0.69	82.61
	3.17	68.96	26.82	22.41	1.40	74.09
	7.20	78.59	30.86	27.54	2.19	66.21
	15.61	78.51	33.46	28.99	3.06	58.90
	20.98	74.86	36.43	29.80	4.13	52.32
	32.93	64.62	39.95	29.92	5.21	46.31
	43.78	54.67	46.36	28.94	6.48	39.81
	51.95	46.85	50.26	28.02	7.31	34.93
	62.00	37.00	57.51	25.64	8.72	29.44
	73.20	26.00	66.00	22.46	10.07	25.69
	82.60	17.00	77.23	16.24	12.84	18.01
	91.80	8.00	88.57	7.86	15.44	10.78
	99.95	0.00	92.94	0.00	19.27	0.00

an uncertainty of ± 0.01 cm^3 until the solution became turbid. The amount titrated was recorded. The bottle was kept in a constant-temperature bath. The temperature of the bath was maintained at (25 ± 0.1) °C. To determine points on the water side, the same procedure is followed, starting with an initial measured quantity of water in the bottle. The solvent mixture (toluene + 1-butanol) was added in the bottle from the microburet until the solution became turbid.

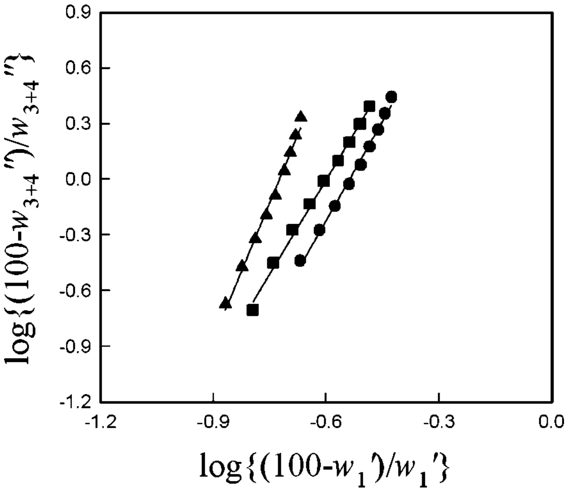

Figure 2. Othmer−Tobias plots of the water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C: ■, w_3/w_4 (75/25); •, w_3/w_4 (50/50); ▲, w_3/w_4 (25/75).

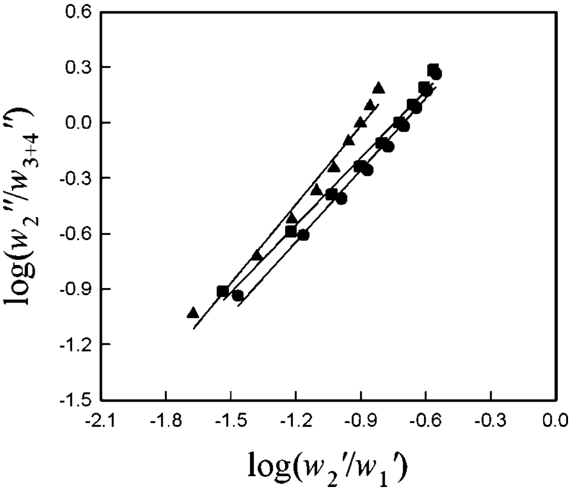

Figure 3. Hand plots of the water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C: ■, w_3/w_4 (75/25); •, w_3/w_4 (50/50); ▲, w_3/w_4 (25/75).

The end point (the major central part of the solubility curves) had been confirmed by adding solvent (to determine solubility curve of solvent side) or water (to determine solubility curve of water side) until the turbidity disappears.[18] The transition point between the homogeneous and heterogeneous zones was determined visually.

For the tie-line measurement, an equilibrium cell was immersed in a thermostat at the desired temperature (± 0.1 °C). Mixtures of known masses of water, THF, and solvents lying within the heterogeneous gap were introduced into the equilibrium cell, and the mixture was stirred for at least 1 h with a magnetic stirrer. The two-phase mixture was allowed to settle for at least 24 h. Samples were taken by a syringe from the aqueous layer and organic layer. The mixtures of aqueous and organic layers were analyzed on an HP 5890 Series II gas chromatograph, equipped with a thermal conductivity detector (TCD). A 1.8 m × 3.2 mm column packed with Porapack Q was used. The injector and detector temperatures were maintained at 200 °C and 230 °C, respectively. The column

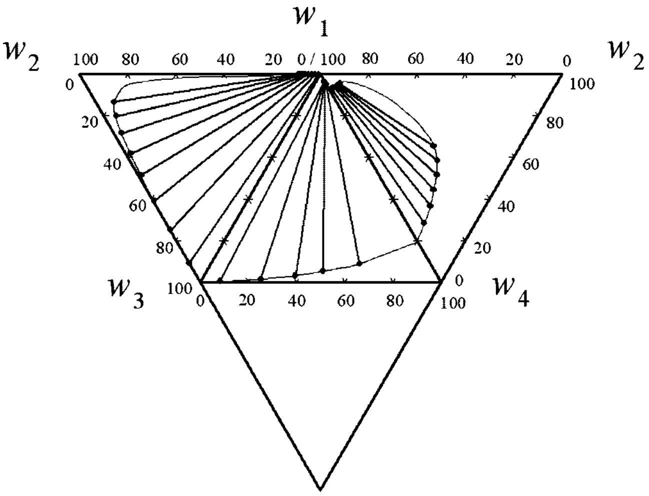

Figure 4. Binodal curves and tie-lines of three ternary mixtures making up the water (1) + THF (2) + toluene (3), water (1) + THF (2) + 1-butanol (4), and water (1) + toluene (3) + 1-butanol (4) mixtures at 25 °C, respectively.

Table 2. Tie-Line Data for the Ternary Systems at 25 °C: Water (1) + THF (2) + Toluene (3), Water (1) + THF (2) + 1-Butanol (4), and Water (1) + Toluene (3) + 1-Butanol (4)

	organic layer (100 w''_i)		aqueous layer (100 w'_i)	
T/°C	100 w_1''	100 w_2''	100 w_1'	100 w_2'
	Water (1) + THF (2) + Toluene (3)			
25	0.16	8.95	99.23	0.72
	0.27	24.78	97.75	2.20
	0.57	38.51	96.29	3.66
	1.45	49.98	94.94	5.01
	2.25	59.61	93.66	6.29
	3.31	68.24	92.58	7.37
	5.21	74.61	91.77	8.19
	7.65	78.99	90.89	9.06
	Water (1) + THF (2) + 1-Butanol (4)			
	21.15	7.24	91.92	1.24
	22.67	13.88	91.30	2.6
	25.24	19.15	90.75	3.35
	27.54	24.01	90.21	4.34
	30.91	27.59	89.85	5.14
	35.67	29.70	89.52	5.90
	Water (1) + Toluene (3) + 1-Butanol (4)			
	0.35	91.53	96.38	0.10
	1.40	74.09	96.44	0.20
	3.06	58.90	96.23	0.29
	5.21	46.31	94.91	0.54
	8.71	29.44	95.15	0.05

temperature was programmed for an initial temperature of 150 °C and a final temperature of 200 °C. The heating rate was 2 °C·min^{-1}, and the flow rate of helium carrier gas was 30 mL·min^{-1}.

Results and Discussion

LLE for the quaternary system water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture were measured at 25 °C and atmospheric pressure. The compositions of mixtures are expressed as w'_i and w'_{ii} which denote the mass fraction of the ith component in the aqueous and organic layer, respectively. The quaternary experimental data exhibit type C quaternary LLE behavior as shown in Figure 1 and are composed of two ternary LLE mixtures of type 1 having a plait point, the water + THF + toluene and water + THF + 1-butanol systems, and one ternary LLE mixture of type 2 having two immiscible binary pairs, the water + toluene + 1-butanol system. The reliability of measured tie-line compositions was ascertained by making Othmer–Tobias[19] and Hand[20] plots for the quaternary system. The plots are presented in Figures 2 and 3. The linear correlation coefficients for the system in 75/25, 50/50, and 25/75 mass ratios as mixed solvents are 0.9980, 0.9964, and 0.9960 in Othmer–

Table 4. Calculated and Experimental Tie-Line Compositions for the Water (1) + THF (2) + Toluene (3) + 1-Butanol (4) Quaternary System at 25 °C

	organic layer (w'')			aqueous layer (w')		
	100 w''_1	100 w''_2	100 w''_3	100 w'_1	100 w'_2	100 w'_3
	$w_3/w_4 = 75/25$					
exptl	6.27	10.25	61.19	86.17	2.51	0.46
calcd	1.39	9.08	69.24	96.24	0.70	0.10
exptl	7.96	26.80	47.56	83.02	7.68	0.22
calcd	1.85	24.88	56.40	95.21	2.20	0.05
exptl	10.13	39.30	36.64	80.15	12.63	0.22
calcd	2.46	38.16	45.47	94.23	3.71	0.05
exptl	12.69	48.67	27.81	77.53	16.93	0.21
calcd	3.22	49.41	36.09	93.30	5.09	0.05
exptl	15.61	55.55	20.67	75.33	20.44	0.21
calcd	4.14	58.93	28.02	92.48	6.27	0.05
exptl	18.84	60.32	14.88	73.52	23.47	0.20
calcd	5.22	66.90	21.09	91.78	7.32	0.05
exptl	22.40	63.28	10.18	71.97	25.85	0.20
calcd	6.50	73.48	15.09	91.15	8.18	0.05
	$w_3/w_4 = 50/50$					
exptl	18.18	8.52	34.20	82.35	2.81	0.44
calcd	4.68	8.78	45.07	95.05	0.81	0.10
exptl	19.15	22.65	27.03	79.03	8.12	0.22
calcd	5.09	24.08	36.75	93.90	2.41	0.05
exptl	20.71	33.78	20.98	76.32	12.82	0.21
calcd	5.69	37.12	29.47	92.90	3.90	0.05
exptl	22.53	42.31	16.10	74.31	16.89	0.21
calcd	6.39	48.03	23.35	92.12	5.23	0.05
exptl	24.58	48.86	12.09	72.73	20.39	0.20
calcd	7.20	57.27	18.09	91.50	6.41	0.05
exptl	26.71	53.79	8.80	71.49	23.24	0.20
calcd	8.07	65.03	13.61	90.99	7.39	0.05
exptl	28.92	57.44	6.13	70.43	25.69	0.20
calcd	9.01	71.60	9.76	90.55	8.25	0.05
	$w_3/w_4 = 25/75$					
exptl	9.86	7.63	20.51	88.06	1.86	0.09
calcd	10.96	8.17	21.19	93.89	0.95	0.05
exptl	11.95	20.34	16.67	86.00	5.19	0.09
calcd	11.30	22.64	17.18	92.75	2.69	0.05
exptl	13.79	31.22	13.38	84.44	7.99	0.09
calcd	11.57	34.94	13.84	91.88	4.17	0.05
exptl	16.62	41.54	10.35	83.23	10.39	0.09
calcd	11.82	45.40	10.98	91.09	5.56	0.05
exptl	19.78	48.40	7.83	82.35	12.50	0.09
calcd	12.03	54.41	8.55	90.69	6.59	0.05

Table 3. Binodal Curve Data for the Water (1) + THF (2) + Toluene (3) + 1-Butanol (4) Quaternary System at 25 °C

	$w_3/w_4 = 75/25$			$w_3/w_4 = 50/50$			$w_3/w_4 = 25/75$		
T/°C	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
25	0.47	0.00	74.65	1.48	0.00	49.26	6.87	0.00	23.28
	0.52	12.58	65.17	2.59	14.24	41.58	8.88	13.48	19.41
	0.82	21.25	58.44	4.70	28.49	33.41	10.87	21.13	17.00
	1.41	28.42	52.62	7.21	39.58	26.61	13.57	30.01	14.11
	2.74	44.36	39.68	8.47	45.12	23.21	14.91	34.46	12.66
	4.13	53.41	31.84	9.72	50.67	19.80	16.26	38.90	11.21
	5.55	63.95	22.88	11.47	55.81	16.36	18.19	42.56	9.81
	7.33	69.12	17.66	12.59	59.50	13.95	21.08	47.58	7.84
	10.34	73.68	11.98	15.23	63.50	10.64	27.90	49.76	5.58
	12.90	74.80	9.23	19.33	65.51	7.58	33.98	48.49	4.38
	22.28	71.52	4.65	29.13	62.34	4.26	41.82	44.76	3.35
	30.52	65.33	3.11	39.13	55.83	2.52	47.12	42.03	2.71
	40.20	57.37	1.83	49.61	47.07	1.66	53.86	38.43	1.93
	47.06	50.93	1.51	60.09	37.62	1.15	62.96	32.15	1.22
	57.40	40.85	1.31	66.70	31.35	0.98	68.86	27.51	0.91
	73.77	25.24	0.74	73.31	25.08	0.81	76.35	20.63	0.76
	85.27	13.84	0.66	86.53	12.54	0.47	83.90	13.76	0.59
	99.80	0.00	0.15	99.75	0.00	0.13	98.25	0.00	0.44

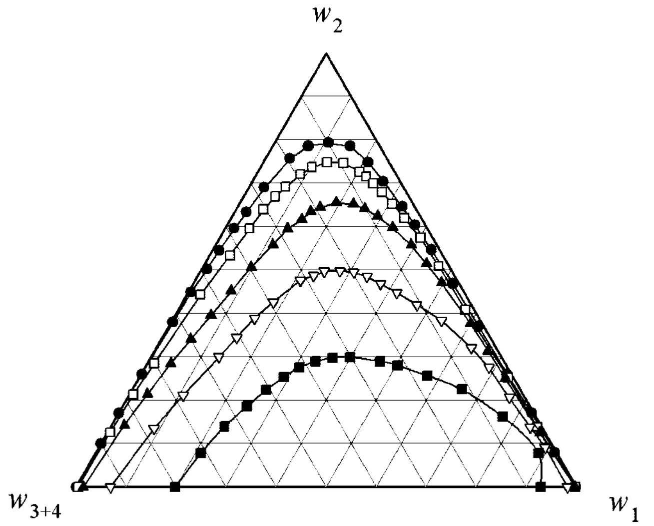

Figure 5. Effect of mixing ratio on binodal curves of the water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture for the quaternary system at 25 °C: •, w_3/w_4 (100/0); □, w_3/w_4 (75/25); ▲, w_3/w_4 (50/50); ▽, w_3/w_4 (25/75); ■, w_3/w_4 (0/100).

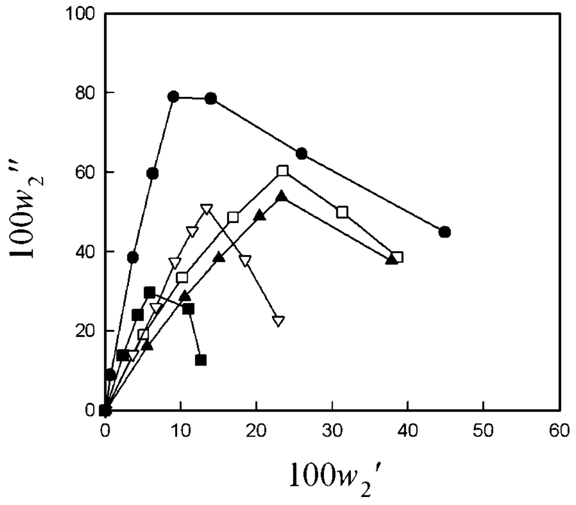

Figure 6. Distribution of THF mass fraction between the aqueous and organic layer for the quaternary system water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C: •, w_3/w_4 (100/0); □, w_3/w_4 (75/25); ▲, w_3/w_4 (50/50); ▽, w_3/w_4 (25/75); ■, w_3/w_4 (0/100).

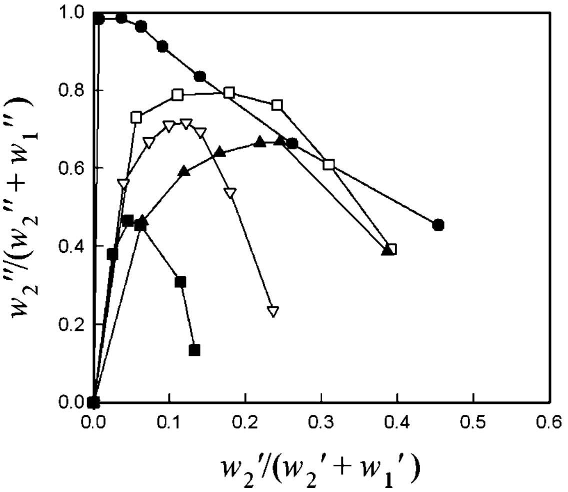

Figure 7. Selectivity of THF mass fraction between the aqueous and organic layer for the quaternary system water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C: •, w_3/w_4 (100/0); □, w_3/w_4 (75/25); ▲, w_3/w_4 (50/50); ▽, w_3/w_4 (25/75); ■, w_3/w_4 (0/100).

Tobias and 0.9945, 0.9941, and 0.9897 in Hand, respectively. The linearity of the plots (a correlation factor close to 1) indicates the degree of consistency of the related data. Figure 4 shows the experimental results for the ternary mixtures constituting the quaternary mixture water + THF + toluene + 1-butanol. The mutual solubility data and the equilibrium tie-line compositions measured at 25 °C of the ternary mixtures for water + THF + toluene, water + THF + 1-butanol, and water + toluene + 1-butanol are shown in Tables 1 and 2. The quaternary solubility data concerning the planes R_1 (75/25), R_2 (50/50), and R_3 (25/75) were shown in Table 3, and the tie-line results of the quaternary mixtures for the water + THF + toluene + 1-butanol mixture system at 25 °C are in Table 4. The effect of the mixing ratio on binodal curves for the quaternary system at 25 °C is shown in Figure 5. As shown in Figure 5, the heterogeneous zone of 1-butanol was increased with addition of toluene, but mixed solvents, toluene/1-butanol in 75/25, 50/50, and 25/75 mass ratios, were not better than the pure solvent, toluene, as an extractant solvent.

As the most important step in liquid–liquid extraction is the selectivity of the solvent, the solvents having a higher distribution and selectivity for solute should be selected after consideration for recovery, chemical stability, boiling and freezing point, corrosion and density, and so on. In this property, the most important is distribution and selectivity. Distribution (*D*) and selectivity (*S*) were calculated as following eqs 1 and 2.

$$D=\frac{w''_2}{w'_2} \tag{1}$$

$$S=\frac{w''_2/(w''_2+w''_1)}{w'_2/(w'_2+w'_1)} \tag{2}$$

Figures 6 and 7 illustrate the effect of the distribution and selectivity for the mixed solvents, toluene/1-butanol, in 75/25, 50/50, and 25/75 mass ratios. As for the binodal curves, they were also not better than the pure solvent, toluene, as an extractant solvent. Perhaps this is because of the higher mutual solubility of water and 1-butanol when compared with those for water and toluene. The results indicate that the solubility of THF is high enough in toluene.

UNIFAC Predicted LLE Data. Because experimental data are often missing or of poor quality, group contribution methods have become increasingly valuable. The great advantage of the group contribution concept is that it is possible to predict a large

Table 5. UNIFAC Group Volume (R_k), Surface Area (Q_k), and Interaction Parameters (a_{nm})

	CH_3	CH_2	ACH	$ACCH_3$	OH	H_2O	FCH_2O	R_k	Q_k
CH_3	0.00	0.00	−114.80	−115.70	644.60	1300.00	662.10	0.9011	0.8480
CH_2	0.00	0.00	−114.80	−115.70	644.60	1300.00	662.10	0.6744	0.5400
ACH	156.50	156.50	0.00	167.00	703.90	859.40	32.14	0.5313	0.4000
$ACCH_3$	104.40	104.40	−146.80	0.00	4000.00	5695.00	213.10	1.2663	0.9680
OH	328.20	328.20	−9.21	1.27	0.00	27.73	262.50	1.0000	1.2000
H_2O	342.40	342.40	372.80	203.70	−122.40	0.00	64.42	0.9200	1.4000
FCH_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.9138	1.1000

number of systems using only a relatively small number of group interaction parameters. The most common group contribution method for the prediction of phase equilibrium is UNIFAC.[12–14]

This model requires two group interaction parameters (a_{mn} and a_{nm}) per pair of groups and group volume and surface areas of individual groups for estimation of the activity coefficient γ_i. The UNIFAC group volume, surface area, and interaction parameters used in this work were shown in Table 5.[21]

The experimental LLE data and tie-lines were compared with predictions obtained by the UNIFAC. The rmsd (root mean square deviation), deviation of the estimate by experimental compositions and the UNIFAC predictions, was obtained by eq 3 for the ternary system and by eq 4 for the quaternary system.

$$\mathrm{rmsd}_3 = \left[\sum_{i=1}^{N}\sum_{j=1}^{3}\sum_{k=1}^{2}(X_{jk}^{\mathrm{exptl}}(i) - X_{jk}^{\mathrm{calcd}}(i))^2/6N\right]^{1/2} \tag{3}$$

$$\mathrm{rmsd}_4 = \left[\sum_{i=1}^{N}\sum_{j=1}^{4}\sum_{k=1}^{2}(X_{jk}^{\mathrm{exptl}}(i) - X_{jk}^{\mathrm{calcd}}(i))^2/8N\right]^{1/2} \tag{4}$$

Conclusion

LLE data were determined for the quaternary system water (1) + THF (2) + toluene (3) + 1-butanol (4) mixture at 25 °C and atmospheric pressure. The variation of selectivity with mixtures of both solvents is of little significance, with toluene appearing as the better extractant solvent on account of the wide heterogeneous zone in the solubility diagram and distribution and selectivity. The usage of mixed solvents in 75/25, 50/50, and 25/75 mass ratios to improve the extraction of THF will only be advisable when both solvents show some favorable properties, such as distribution and/or selectivity, to take advantage of the synergistic effect of the mixture.

Finally, the experimental data were also compared with the predictions from the UNIFAC model. In the ternary system, the predictions for water + THF + toluene and water + THF + 1-butanol composed of type 1 were shown within an average rmsd of 0.28, and 3.8 %, and toluene + 1-butanol + water composed of type 2 was shown within 1.1 %. For the quaternary system, average root-mean-square deviations for the system in 75/25, 50/50, and 25/75 mass ratios as mixed solvents are (9.2, 10.5, and 4.0) %, respectively.

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Received for review May 24, 2007. Accepted October 12, 2007. This Paper was Supported by Dong-A University Research Fund in 2007.

JE700289P