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Liquid−Liquid Equilibrium for the Quaternary System Toluene + Water + Propionic Acid + Ethyl Acetate at 25 °C and Atmospheric Pressure

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The liquid−liquid equilibrium for the quaternary system toluene + water + propionic acid + ethyl acetate was measured at 25 °C and atmospheric pressure. Binodal curves, tie lines, a distribution curve, and a selectivity curve for the quaternary system have been determined in order to investigate the effect of using binary solvents toluene and ethyl acetate on extracting propionic acid from aqueous solution. In addition, these experimental tie-line data were also compared with the values predicted by the UNIFAC model. It was shown that the UNIFAC model was capable of predicting the compositions of these quaternary systems within an average rmsd of 3.21 mol %.

Introduction

With an increase in demand for environmentally friendly materials, the recovery of organic acids from dilute solutions resulting from fermentation processes has become of interest. The economics of the process, however, depends on the development of an effective recovery method for organic acids from the broth.[1] Solvent extraction processes as a promising recovery technique have been proposed as an alternative to the conventional precipitation process,[2] and many solvents have been tried to improve such recovery.[3−7] Propionic acid is being used as a cellulosic solvent in the pharmaceutical industry and also can be used to provide propionates, which are used as fungicides.[8] It is also used in the electroplating industry and to prepare perfume esters.

The purpose of this work is to determine LLE data of toluene + water + propionic acid + ethyl acetate. The LLE data for the quaternary system were measured at 25 °C and atmospheric pressure. The effect of the mixed solvents to separate propionic acid 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 type 1 systems toluene + water + propionic acid and ethyl acetate + water + propionic acid and the type 2 system toluene + ethyl acetate + water. LLE data have also been predicted with the UNIFAC method,[9−11] and they are compared with the experimental data at 25 °C.

Experimental Section

Materials. The toluene, ethyl acetate, and propionic acid used in this work were supplied by Aldrich with a started purity of 99.5%, 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 >99.5 mass fraction purities for toluene, ethyl acetate, and propionic acid. They were used without further purification.

Quaternary Equilibrium Data Determination. According to the Prausnitz classification,[12] the quaternary system in this study was formed 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.[13] The study of the quaternary solubility surface was carried out for a system made up of water, propionic acid, and mixtures of toluene and ethyl acetate in ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 (pseudoternary systems) in mass fraction with the following analytical method. Figure 3 shows the method schematically, where R is the ratio of the solvents. The binodal curves of liquid−liquid equilibrium for four components were described by Prausnitz and Anderson.[14]

The mutual solubility (binodal curve) in toluene + water + propionic acid + ethyl acetate was determined at 25 °C and atmospheric pressure by the cloud-point method as described by Othmer et al.[15] For the determination of mutual solubility data, an accurately known mass of a homogeneous mixture of two compounds was placed in a thermostated glass-stoppered bottle, one of the nonconsolute compounds was titrated into the bottle from a microburet with an uncertainty of ±0.01 cm^3 until the solution became turbid, and 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. The end point has been confirmed by adding the consolute component until the turbidity disappears. The procedure was repeated to obtain the phase-boundary curve.

For the tie-line measurement, an equilibrium cell was immersed in a thermostat controlled at the desired temperature (±0.1 °C). The pure components were added, 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 upper and lower mixtures. The mixtures of aqueous and organic phases 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. The column temperature

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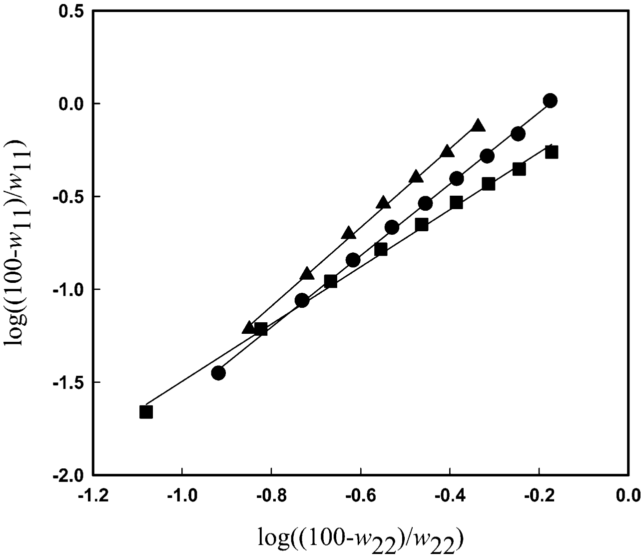

Figure 1. Othmer−Tobias plots of toluene (1) + water (2) + propionic acid (3) + ethyl acetate (4) at 25 °C: ▲, toluene/ethyl acetate (25/75); ●, toluene/ethyl acetate (50/50); ■, toluene/ethyl acetate (25/75).

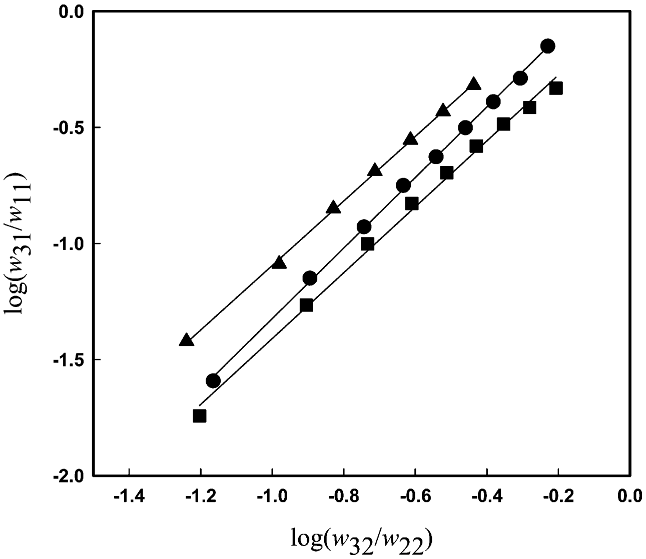

Figure 2. Hand plots of toluene (1) + water (2) + propionic acid (3) + ethyl acetate (4) at 25 °C: ▲, toluene/ethyl acetate (25/75); ●, toluene/ethyl acetate (50/50); ■, toluene/ethyl acetate (25/75).

was programmed for an initial temperature of 130 °C and a final temperature of 250 °C. The heating rate was 50 °C/min, and the flow rate of the helium carrier gas was 30 mL/min. The uncertainty of the mass fraction measurements for the overall composition determination was ±0.002.

The reliability of measured tie-line compositions was ascertained by making Othmer−Tobias[16] and Hand[17] plots for the quaternary system. The plots are presented in Figures 1 and 2. The linear correlation coefficients for the system in ratios of 75/25, 50/50, and 25/75 in mass fraction as mixed solvents are 0.9992, 0.9995, and 0.9982 in Othmer−Tobias and 0.9997, 09996, and 0.9977 in Hand, respectively. The linearity of the plots (a correlation factor close to 1) indicates the degree of consistency of the related data.

Results and Discussion

The liquid−liquid equilibrium for the quaternary system toluene + water + propionic acid + ethyl acetate was measured at 25 °C and atmospheric pressure. The quaternary experimental data exhibited type C quaternary LLE behavior as shown in Figure 3 and are composed of two ternary LLE mixtures of type 1 having a plait point (toluene + water + propionic acid and ethyl acetate + water + propionic acid) and one ternary LLE mixture of type 2 having two immiscible binary pairs (toluene + ethyl acetate + water). Figure 4 shows the experimental results for the ternary mixtures constituting the quaternary mixtures toluene + water + propionic acid + ethyl acetate. The mutual solubility data and the equilibrium tie-line compositions measured at 25 °C for the ternary mixtures of toluene + water + propionic acid, ethyl acetate + water + propionic acid, and toluene + ethyl acetate + water are shown in Tables 1 and 2. Quaternary solubility data concerning planes R$_1$(75/25), R$_2$(50/50), and R$_3$(25/75) are given in Table 3, and the tie-line results of the quaternary mixtures for the toluene + water + propionic acid + ethyl acetate system at 25 °C are given in Table 4. The effect of the mixing ratio on the binodal curves for the quaternary system at 25 °C is shown in Figure 5. As shown in Figure 5, the heterogeneous zone of ethyl acetate was increased with the addition of toluene, but mixed solvents toluene and ethyl acetate in ratios of 75/25, 50/50, and 25/75 were

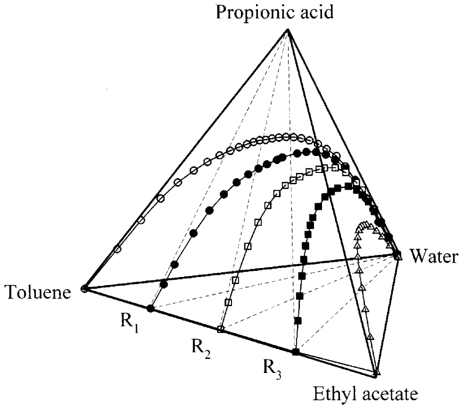

Figure 3. Phase equilibrium of toluene (1) + water (2) + propionic acid (3) + ethyl acetate (4). R$_1$, R$_2$, and R$_3$ denote quaternary sectional planes.

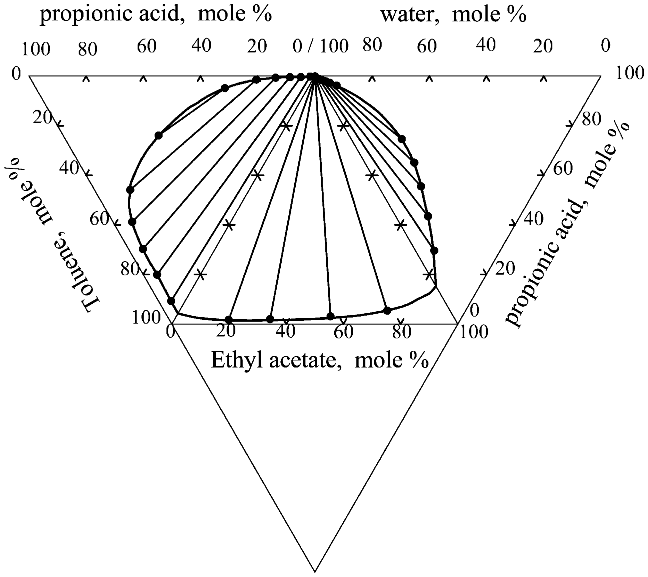

Figure 4. Binodal curves and tie lines of three ternary mixtures making up toluene (1) + water (2) + propionic acid (3), ethyl acetate (1) + water (2) + propionic acid (3), and toluene (1) + ethyl acetate (2) + water (3) at 25 °C.

Table 1. Binodal Curve Data for the Ternary Systems Toluene (1) + Water (2) + Propionic Acid (3), Ethyl Acetate (1) + Water (2) + Propionic Acid (3), and Toluene (1) + Ethyl Acetate (2) + Water (3)

	toluene (1) + water (2) + propionic acid (3)			ethyl acetate (1) + water (2) + propionic acid (3)			toluene (1) + ethyl acetate (2) + water (3)		
t/°C	$100x_1$	$100x_2$	$100x_3$	$100x_1$	$100x_2$	$100x_3$	$100x_1$	$100x_2$	$100x_3$
25	84.67	15.33	0.00	97.01	2.99	0.00	95.70	0.00	4.30
	66.22	25.91	7.87	76.25	4.78	18.97	89.95	7.5	2.55
	52.45	35.08	12.47	62.88	5.84	31.28	70.59	28.00	1.41
	43.02	41.63	15.35	52.11	9.01	38.88	32.46	64.02	3.52
	35.76	47.23	17.01	35.00	21.00	44.00	16.13	76.90	6.97
	24.55	57.93	17.52	24.49	32.88	42.63	9.74	80.64	9.62
	15.90	68.60	15.50	15.77	45.00	39.23	0.00	84.68	15.32
	10.07	77.81	12.11	8.48	57.79	33.73			
	8.14	81.19	10.66	3.82	69.24	26.94	0.17	0.00	99.83
	4.44	89.06	6.50	1.36	79.34	19.30	0.01	0.13	99.86
	3.06	92.44	4.49	0.61	86.73	12.66	0.01	0.32	99.66
	1.95	95.72	2.33	0.27	97.36	2.37	0.02	0.43	99.55
	0.77	99.23	0.00	0.17	99.83	0.00	0.00	0.77	99.23

Table 2. Liquid−Liquid Equilibrium Compositions for the Ternary Systems; Toluene (1) + Water (2) + Propionic Acid (3), Ethyl Acetate (1) + Water (2) + Propionic Acid (3), and Toluene (1) + Ethyl Acetate (2) + Water (3)

Toluene (1) + Water (2) + Propionic Acid (3)

	organic phase			aqueous phase		
t/°C	$100x_1$	$100x_2$	$100x_3$	$100x_1$	$100x_2$	$100x_3$
25	90.7700	4.3500	4.8800	0.2100	98.2700	1.5200
	80.1200	4.7700	15.1100	0.3800	94.8600	4.7600
	69.8000	4.9800	25.2200	0.4700	91.0700	8.4600
	58.8500	6.7400	34.4100	0.7100	85.9500	13.3400
	45.9400	12.4700	41.5900	1.4500	78.8600	19.6900
	23.9600	33.4200	42.6200	4.8600	66.1000	29.0400

Ethyl Acetate (1) + Water (2) + Propionic Acid (3)

	organic phase			aqueous phase		
t/°C	$100x_1$	$100x_2$	$100x_3$	$100x_1$	$100x_2$	$100x_3$
25	70.4600	23.0300	6.5100	1.2100	97.8800	0.9100
	56.6300	32.0900	11.2800	1.6300	96.6200	1.7500
	44.5000	40.6100	14.8900	2.1200	95.1500	2.7300
	34.9500	47.8000	17.2500	2.7200	93.3500	3.9300
	25.4300	56.8900	17.6800	3.8500	90.3900	5.7600

Toluene (1) + Ethyl Acetate (2) + Water (3)

	organic phase			aqueous phase		
t/°C	$100x_1$	$100x_2$	$100x_3$	$100x_1$	$100x_2$	$100x_3$
25	79.3000	19.0100	1.6900	0.0110	0.1320	99.8570
	64.5000	33.3900	1.9100	0.0130	0.2150	99.7720
	42.8900	53.9600	3.0800	0.0147	0.3210	99.6643
	22.0300	72.6500	5.3200	0.0152	0.4330	99.5518

not better than pure solvent toluene as an extraction solvent.

Because the most important factor in liquid−liquid extraction is the selectivity of the solvent, solvents having a higher distribution and selectivity for the solute should be selected after considering the recovery, chemical stability, boiling and freezing points, corrosion, density, and so forth. For this property, the most important factors are distribution and selectivity. They are shown in the following equations.

$$D = \frac{\text{propionic acid mol \% in solvent layer}}{\text{propionic acid mol \% in water layer}} = \frac{x_{31}}{x_{32}} \quad (1)$$

$$S = \frac{\text{propionic acid mol \% in solvent − free solvent layer}}{\text{propionic acid mol \% in solvent − free water layer}} = \frac{x_{31}/(x_{31} + x_{21})}{x_{32}/(x_{32} + x_{22})} \quad (2)$$

Compositions are expressed in mole fraction x_{CL}, where the first index refers to the component (2 = water, 3 = propionic acid) and the second index refers to the phase (1 = upper layer, 2 = lower layer).

Figures 6 and 7 illustrate the effect of the distribution and selectivity for the mixtures in ratios 75/25, 50/50, and

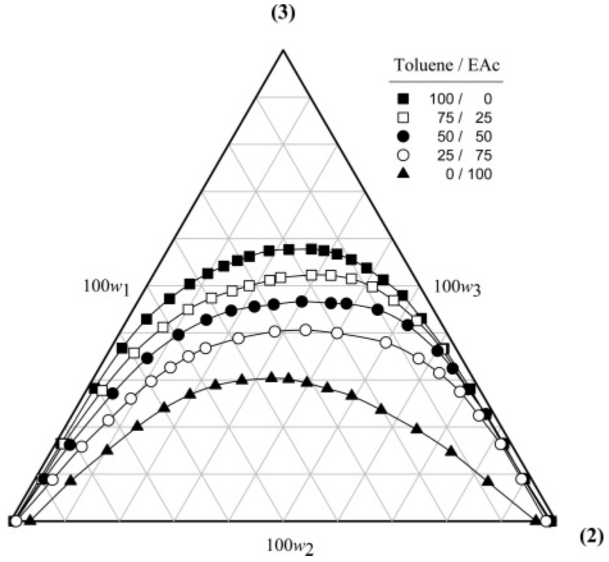

Figure 5. Effect of the mixing ratio on binodal curves of the toluene (1) + water (2) + propionic acid (3) + ethyl acetate (4) quaternary system at 25 °C.

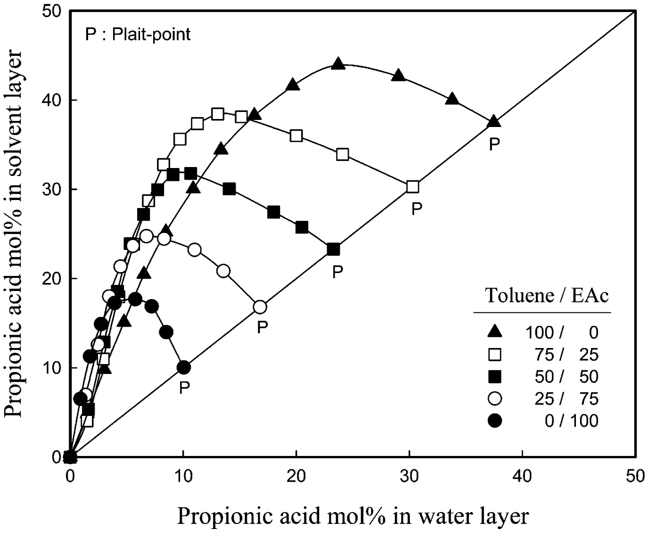

Figure 6. Distribution of propionic acid between aqueous and organic phases at 25 °C.

Table 3. Binodal Curve Data for the Toluene (1) + Water (2) + Propinic Acid (3) + Ethyl Acetate (4) Quaternary System

	$w(1)/w(4) = 75/25$				$w(1)/w(4) = 50/50$				$w(1)/w(4) = 25/75$			
t/°C	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
25	74.48	0.70	0.00	24.82	49.59	0.82	0.00	49.59	24.75	1.01	0.00	74.24
	67.33	1.27	8.98	22.42	44.69	1.68	8.94	44.69	21.98	3.27	8.79	65.96
	61.54	1.54	16.41	20.51	40.51	2.77	16.21	40.51	19.77	5.12	15.81	59.30
	52.01	2.91	27.74	17.34	33.87	5.16	27.10	33.87	17.84	7.24	21.41	53.51
	44.63	4.78	35.71	14.88	28.83	7.75	34.59	28.83	16.24	9.06	25.98	48.72
	38.60	7.35	41.17	12.88	24.72	11.00	39.56	24.72	14.85	10.92	29.69	44.54
	33.71	10.11	44.94	11.24	21.37	14.52	42.74	21.37	13.59	13.00	32.63	40.78
	29.61	13.14	47.38	9.87	18.61	18.11	44.67	18.61	12.48	15.14	34.94	37.44
	26.20	16.17	48.90	8.73	14.37	25.25	46.01	14.37	11.47	17.39	36.71	34.43
	20.18	21.95	51.13	6.74	11.65	30.08	46.62	11.65	7.86	28.31	40.25	23.58
	14.03	29.03	52.26	4.68	7.67	38.48	46.18	7.67	5.04	39.92	39.91	15.13
	8.83	36.76	51.46	2.95	5.12	44.88	44.88	5.12	3.06	49.87	37.90	9.17
	6.58	41.46	49.76	2.20	3.19	52.01	41.61	3.19	1.98	57.54	34.53	5.95
	3.18	53.20	42.56	1.06	1.84	60.20	36.12	1.84	0.96	68.68	27.48	2.88
	2.01	60.83	36.50	0.66	1.05	69.93	27.97	1.05	0.72	74.69	22.42	2.17
	1.13	75.77	22.73	0.37	0.74	75.79	22.73	0.74	0.49	81.69	16.34	1.48
	1.06	89.63	8.96	0.35	0.71	89.62	8.96	0.71	0.46	89.22	8.93	1.39
	0.80	98.93	0.00	0.27	0.57	98.86	0.00	0.57	0.45	98.17	0.00	1.38

Table 4. Calculated and Experimental Liquid−Liquid Equilibrium Compositions for the Toluene (1) + Water (2) + Propionic Acid (3) + Ethyl Acetate (4) Quaternary System at 25 °C

	organic phase				aqueous phase			
	$100x_1$	$100x_2$	$100x_3$	$100x_4$	$100x_1$	$100x_2$	$100x_3$	$100x_4$
			$x(1)/x(4) = 75/25$					
exptl	70.35	3.51	4.07	22.07	0.02	98.30	1.50	0.19
calcd	69.27	1.43	6.02	23.28	0.02	98.53	1.27	0.18
exptl	62.83	5.72	10.99	20.46	0.02	96.82	2.93	0.23
calcd	63.77	2.47	12.49	21.27	0.02	97.27	2.49	0.22
exptl	55.68	7.90	17.97	18.45	0.03	95.42	4.29	0.26
calcd	57.76	4.03	19.05	19.16	0.03	96.07	3.65	0.25
exptl	49.80	10.33	23.82	16.05	0.03	94.07	5.62	0.28
calcd	51.42	6.24	25.35	16.99	0.04	94.90	4.79	0.27
exptl	44.45	12.77	28.71	14.07	0.04	92.73	6.93	0.30
calcd	44.96	9.17	31.03	14.84	0.05	93.74	5.92	0.29
			$x(1)/x(4) = 50/50$					
exptl	43.64	8.45	5.37	42.54	0.01	97.86	1.63	0.49
calcd	44.26	3.75	7.11	44.88	0.01	98.69	0.99	0.31
exptl	38.26	12.19	12.89	36.66	0.03	96.45	2.99	0.54
calcd	39.42	6.29	14.41	39.88	0.02	97.82	1.82	0.34
exptl	32.92	16.61	18.57	31.90	0.03	95.24	4.18	0.55
calcd	34.39	9.57	21.23	34.81	0.02	97.07	2.56	0.35
exptl	28.10	20.82	23.90	27.18	0.03	94.09	5.32	0.56
calcd	29.61	13.35	27.05	29.99	0.02	96.35	3.27	0.36
exptl	24.22	25.45	27.19	23.14	0.04	92.92	6.49	0.54
calcd	25.19	17.50	31.78	25.53	0.03	95.61	4.01	0.35
			$x(1)/x(4) = 25/75$					
exptl	19.11	17.54	6.95	56.40	0.02	97.81	1.37	0.80
calcd	20.60	8.65	7.77	62.98	0.01	98.85	0.72	0.42
exptl	16.00	23.96	12.59	47.45	0.02	96.71	2.46	0.81
calcd	17.70	13.20	14.98	54.12	0.01	98.26	1.30	0.43
exptl	13.28	29.66	17.99	39.07	0.02	95.71	3.45	0.83
calcd	15.03	17.94	21.02	46.01	0.01	97.72	1.83	0.44
exptl	10.82	35.81	21.33	32.04	0.02	94.70	4.46	0.82
calcd	12.69	22.58	25.87	38.86	0.01	97.17	2.38	0.44
exptl	8.78	41.51	23.65	26.06	0.04	93.61	5.54	0.82
calcd	10.67	27.02	29.60	32.71	0.02	96.57	2.97	0.44

25/75. As for the binodal curves, they were also not better than the pure solvent, toluene, as an extraction solvent. Perhaps this is because of the higher mutual solubility of water and ethyl acetate when compared with that for water and toluene. The results indicate that the solubility of toluene is high enough in propionic acid.

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 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.[9−11]

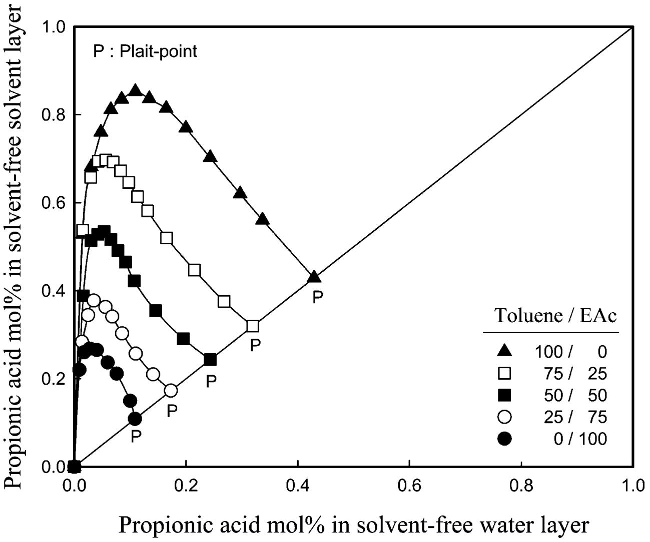

Figure 7. Selectivity of propionic acid between aqueous and organic phases at 25 °C.

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

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

	CH_3	CH_2	H_2O	COOH	CH_3COO	ACH	$ACCH_3$	R_k	Q_k
CH_3	0	0	1300.0	139.4	972.4	−114.8	−115.7	0.9011	0.8480
CH_2	0	0	1300.0	139.4	972.4	−114.8	−115.7	0.6744	0.5400
H_2O	342.4	342.4	0	−465.7	−6.320	372.8	203.7	0.9200	1.4000
COOH	1744.0	1744.0	652.3	0	−117.6	75.49	147.3	1.3013	1.2240
CH_3COO	−320.1	−320.1	385.9	1417.0	0	114.8	−170.0	1.9031	1.7280
ACH	156.5	156.5	859.4	461.8	6.0	0	167.0	0.5313	0.4000
$ACCH_3$	104.4	104.4	5695.0	339.1	5688.0	−146.8	0	1.2663	0.9680

shown in Table 5.[18]

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

$$\mathrm{rmsd}_3 = 100\left[\sum_{i=1}^{N}\sum_{j=1}^{3}\sum_{k=1}^{2}\frac{(X_{jk}^{\mathrm{exptl}}(i) - X_{jk}^{\mathrm{calcd}}(i))^2}{6N}\right]^{1/2} \tag{3}$$

$$\mathrm{rmsd}_4 = 100\left[\sum_{i=1}^{N}\sum_{j=1}^{4}\sum_{k=1}^{2}\frac{(X_{jk}^{\mathrm{exptl}}(i) - X_{jk}^{\mathrm{calcd}}(i))^2}{8N}\right]^{1/2} \tag{4}$$

Conclusions

Liquid−liquid equilibrium data were determined for the quaternary system toluene + water + propionic acid + ethyl acetate 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 extraction solvent on account of the wide heterogeneous zone in the solubility diagram and the distribution and selectivity curve. The use of mixed solvents in ratios of 75/25, 50/50, and 25/75 to improve the extraction of propionic acid will be advisable only when both solvents show some favorable properties, such as the distribution coefficient and/or selectivity, in order to take advantage of the synergistic effect of the mixture.

Finally, the experimental data were also compared with the values predicted by the UNIFAC model. In ternary system, the predictions for toluene + water + propionic acid and ethyl acetate + water + propionic acid composed of type 1 were shown within an average root-mean-square deviation of 3.39 mol %, and the prediction for toluene + ethyl acetate + water composed of type 2 was shown within 1.09 mol %. For the quaternary system, it was shown that the UNIFAC model was capable of predicting the compositions within an average root-mean-square deviation of 3.21 mol %.

Literature Cited

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