

Liquid-Liquid Equilibrium for the Ternary Systems of Solvents+Water+Propionic Acid at 25 °C and Atmospheric Pressure

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Abstract—Liquid-liquid equilibrium data for the ternary systems of toluene+water+propionic acid, o-xylene+water+propionic acid, methyl isobutyl ketone+water+propionic acid, ethyl acetate+water+propionic acid, and 1-butanol+water+propionic acid were measured at 25 °C and atmospheric pressure. The reliability of the experimental tie-line data was ascertained by means of the Othmer-Tobias, Bachman-Brown, and Hand correlations. For the extraction effectiveness of solvents, the distribution and selectivity curves were plotted. In addition, these experimental tie-line data were also correlated with NRTL and UNIQUAC models.

Key words: Liquid-Liquid Equilibrium, Ternary, NRTL, UNIQUAC, Propionic Acid

INTRODUCTION

With an increase in demand for environmentally friendly material, the recovery of organic acids from dilute solutions resulting from fermentation processes has become of interest. Economics of the process, however, depends on the development of an effective recovery method for the organic acids from the broth [Roychoudhury et al., 1995]. Solvent extraction processes as a promising recovery technique have been proposed as an alternative to the conventional precipitation process [Hartl and Marr, 1993], and many solvents have been tried to improve such recovery [Dramur and Tatli, 1993; Briones et al., 1994; Arce et al., 1995; Fahim and Al-Muhtaseb, 1996; Fahim et al., 1997]. Propionic acid is being used as a cellulosic solvent in pharmaceutical industries and also can be used to provide propionates, which are used as fungicides [Kirk and Othmer, 1947]. It is also used in the electroplating industry and to prepare perfume esters. Multicomponent multiphase liquid-liquid equilibrium data are of fundamental importance in the design and/or in the optimal operation of chemical processes. However, in reality, the reliable experimental data themselves are not sufficient to be used for the complete requirements of process engineering [Kim et al., 1996].

The purpose of this work is to determine LLE data of toluene+water+propionic acid, o-xylene+water+propionic acid, methyl isobutyl ketone+water+propionic acid, ethyl acetate+water+propionic acid, and 1-butanol+water+propionic acid, and the LLE data for the ternary systems were measured at 25 °C and atmospheric pressure. The selection of the optimum solvent to separate propionic acid from aqueous solution was investigated. In addition, The LLE data for these ternary systems were correlated by UNIQUAC [Abrams and Prausnitz, 1975] and NRTL [Renon and Prausnitz, 1968].

EXPERIMENTAL SECTION

1. Materials

Toluene, o-xylene, methyl isobutyl ketone, ethyl acetate, 1-butanol and propionic acid used in this work were supplied by Aldrich with a started purity of over 99.0%, 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 >99.0 mass fraction purities for toluene, o-xylene, methyl isobutyl ketone, ethyl acetate, 1-butanol and propionic acid. They were used without further purification.

2. Ternary Equilibrium Data Determination

According to Treybal's classification [Sorensen and Arlt, 1980], the all ternary systems in this study were formed type 1 having a plait point.

The mutual solubility (binodal curve) data were determined at 25 °C and atmospheric pressure by the cloud-point method as described by Othmer et al. [1941]. The mutual solubility data were determined in an equilibrium cell equipped with magnetic stirrer and isothermal fluid jacket. The cell was kept in a constant-temperature bath maintained at (25±0.1) °C. The cell was filled with homogeneous water+propionic acid mixtures prepared by weighing. The solvent was titrated into the cell from a microburet with an uncertainty of ±0.01 cm³. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient to provide the aqueous-rich side of the curves. The data for organic-rich side of the curves were therefore obtained by titrating homogeneous solvent+propionic acid binaries with water until the turbidity had appeared.

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 syringe from the upper and lower mixtures.

The mixtures of aqueous and organic phase were analyzed on an HP 5890 Series II gas chromatograph, equipped with a thermal conductivity detector (TCD). A 6 ft×1/8 in. column packed with Porapak Q was used. The injector and detector temperatures were maintained at 200 °C. The column temperature was programmed

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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 helium carrier gas was 30 ml/min. The uncertainty of the mass fraction measurements for the overall composition determination was ± 0.002 .

RESULTS AND DISCUSSION

The preliminary experiment of Butyl acetate+Water+Acetic acid system was compared with reference [Jang and Park, 2000] under the same conditions in order to ascertain the reliability of the apparatus. The binodal curve and tie-line of preliminary experiments were relatively agreed with those of the reference and are shown in Fig. 1.

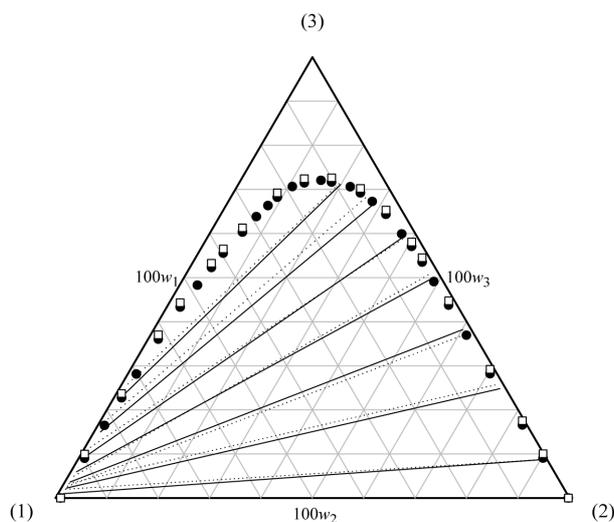


Fig. 1. Liquid-liquid equilibrium data for butyl acetate (1)+water (2)+acetic acid (3) system at 25 °C compared to the reference [Jang and Park, 2000]; ●, Binodal curve Ref. Data, □, Binodal curve Exp. Data, —, Tie-line Ref. Data, ----, Tie-line Exp. Data.

Liquid-liquid equilibrium data for the ternary systems of toluene+water+propionic acid, o-xylene+water+propionic acid, methyl isobutyl ketone+water+propionic acid, ethyl acetate+water+propionic acid, and 1-butanol+water+propionic acid are shown in Tables 1 and 2, and Fig. 2, respectively. It is evident from Fig. 2 that the area of heterogeneity increased for the systems studied in the order 1-butanol, ethyl acetate, methyl isobutyl ketone, toluene, and o-xylene. This is because of higher mutual solubilities of water and 1-butanol when compared with those for water and ethyl acetate, water and methyl isobutyl ketone, water and toluene, and water and o-xylene.

Othmer-Tobias [Othmer and Tobias, 1942], Hand [Hand, 1930],

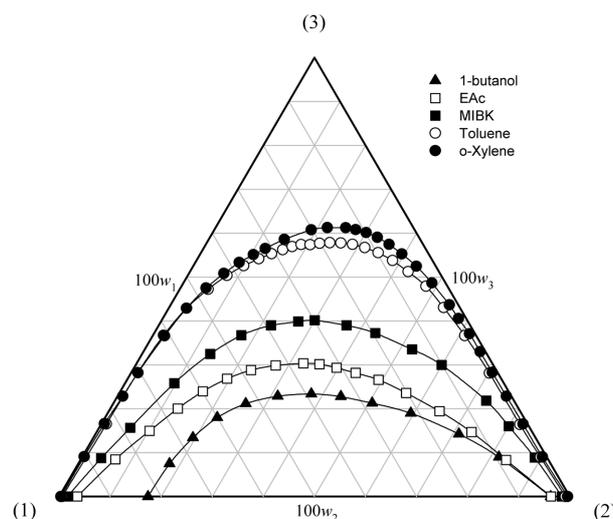


Fig. 2. Comparison of the binodal curves for the ternary systems of 1-butanol (1)+water (2)+propionic acid (3), ethyl acetate (1)+water (2)+propionic acid (3), methyl isobutyl ketone (1)+water (2)+propionic acid (3), toluene (1)+water (2)+propionic acid (3), and o-xylene (1)+water (2)+propionic acid (3) at 25 °C.

Table 1. Binodal curve data for ternary systems of 1-butanol (1)+water (2)+propionic acid (3), ethyl acetate (1)+water (2)+propionic acid (3), methyl isobutyl ketone (1)+water (2)+propionic acid (3), toluene (1)+water (2)+propionic acid (3), and o-xylene (1)+water (2)+propionic acid (3)

$t/^{\circ}\text{C}$	1-Butanol (1)+Water (2)+Propionic acid (3)			Ethyl acetate (1)+Water (2)+Propionic acid (3)			Methyl isobutyl ketone (1)+Water (2)+Propionic acid (3)			Toluene (1)+Water (2)+Propionic acid (3)			o-Xylene (1)+Water (2)+Propionic acid (3)		
	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
25	82.59	17.41	0.00	96.43	3.57	0.00	98.41	1.59	0.00	99.40	0.60	0.00	99.64	0.36	0.00
	74.65	17.89	7.46	84.75	6.78	8.47	87.40	3.86	8.74	82.49	1.01	16.50	82.85	0.58	16.57
	67.08	19.50	13.42	74.81	10.23	14.96	78.25	6.10	15.65	70.52	1.28	28.20	70.48	1.33	28.19
	60.02	21.97	18.01	66.76	13.21	20.03	64.55	9.63	25.82	61.21	2.07	36.72	53.61	3.50	42.89
	52.90	25.94	21.16	59.88	16.17	23.95	54.16	13.35	32.49	47.23	5.54	47.73	42.35	6.84	50.81
	45.75	31.38	22.87	48.02	23.17	28.81	45.93	17.32	36.75	37.56	9.86	52.58	31.39	12.11	56.50
	38.91	37.71	23.38	37.01	32.65	30.34	39.00	22.00	39.00	28.11	15.68	56.21	26.63	14.80	58.57
	33.44	43.79	22.77	27.85	43.99	28.16	29.88	29.97	40.15	18.08	24.09	57.83	13.26	25.51	61.23
	28.06	50.66	21.28	24.15	49.25	26.60	19.48	43.29	37.23	9.78	34.70	55.52	9.81	30.06	60.13
	21.62	59.38	19.00	15.79	64.78	19.43	10.09	59.94	29.97	4.20	47.90	47.90	3.80	43.73	52.47
	14.59	71.17	14.24	11.89	73.43	14.68	5.43	72.75	21.82	2.21	61.12	36.67	1.10	61.81	37.09
	9.40	81.62	8.98	8.30	83.36	8.34	2.40	88.73	8.87	1.27	89.75	8.98	1.05	70.68	28.27
	3.74	96.26	0.00	3.66	96.34	0.00	1.54	98.46	0.00	0.87	99.13	0.00	0.42	99.58	0.00

Table 2. Liquid-Liquid Equilibrium Compositions for the ternary systems of 1-butanol (1)+water (2)+propionic acid (3), ethyl acetate (1)+water (2)+propionic acid (3), methyl isobutyl ketone (1)+water (2)+propionic acid (3), toluene (1)+water (2)+propionic acid (3), and o-xylene (1)+water (2)+propionic acid (3)

1-Butanol (1)+Water (2)+Propionic acid (3)						
t/°C	Organic phase			Aqueous phase		
	100x ₁	100x ₂	100x ₃	100x ₁	100x ₂	100x ₃
25	48.75	47.03	4.22	1.35	97.87	0.78
	42.86	49.35	7.79	1.94	96.43	1.63
	35.60	53.71	10.69	2.74	94.60	2.66
	25.79	62.57	11.64	4.24	91.56	4.20
Ethyl acetate (1)+Water (2)+Propionic acid (3)						
t/°C	Organic phase			Aqueous phase		
	100x ₁	100x ₂	100x ₃	100x ₁	100x ₂	100x ₃
25	70.46	23.03	6.51	1.21	97.88	0.91
	56.63	32.09	11.28	1.63	96.62	1.75
	44.50	40.61	14.89	2.12	95.15	2.73
	34.95	47.80	17.25	2.72	93.35	3.93
	25.43	56.89	17.68	3.85	90.39	5.76
	Methyl isobutyl ketone (1)+Water (2)+Propionic acid (3)					
t/°C	Organic phase			Aqueous phase		
	100x ₁	100x ₂	100x ₃	100x ₁	100x ₂	100x ₃
25	75.42	15.83	8.75	0.36	99.12	0.52
	61.15	23.80	15.05	0.38	98.54	1.08
	49.84	30.34	19.82	0.39	97.85	1.76
	40.57	36.11	23.32	0.45	97.15	2.40
	32.25	42.38	25.37	0.61	96.33	3.06
	25.08	48.93	25.99	0.74	95.31	3.95
Toluene (1)+Water (2)+Propionic acid (3)						
t/°C	Organic phase			Aqueous phase		
	100x ₁	100x ₂	100x ₃	100x ₁	100x ₂	100x ₃
25	90.77	4.35	4.88	0.21	98.27	1.52
	80.12	4.77	15.11	0.38	94.86	4.76
	69.80	4.98	25.22	0.47	91.07	8.46
	58.85	6.74	34.41	0.71	85.95	13.34
	45.94	12.47	41.59	1.45	78.86	19.69
	o-Xylene (1)+Water (2)+Propionic acid (3)					
t/°C	Organic phase			Aqueous phase		
	100x ₁	100x ₂	100x ₃	100x ₁	100x ₂	100x ₃
25	88.67	2.47	8.86	0.18	96.14	3.68
	76.13	2.96	20.91	0.21	92.63	7.16
	64.07	5.05	30.88	0.24	88.37	11.39
	50.75	9.84	39.41	0.52	82.68	16.80
	36.72	16.95	46.33	1.45	74.61	23.94

and Bachman-Brown [Brown, 1948] correlations were used to ascertain the reliability of the experimental results for each system.

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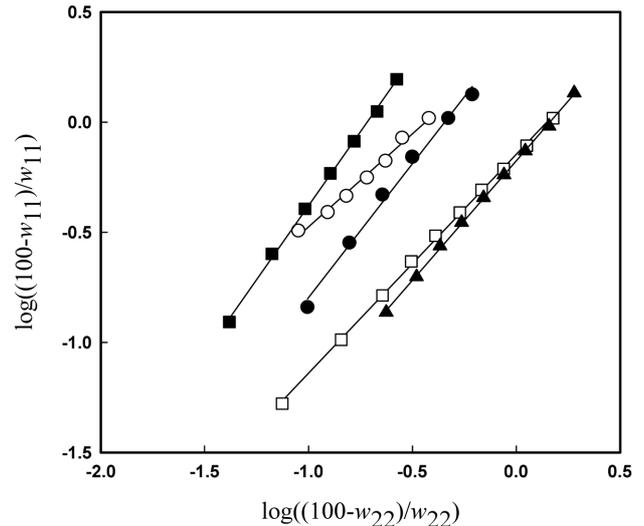


Fig. 3. Othmer-Tobias correlation for solvents (1)+water (2)+propionic acid (3) systems at 25 °C; ○, 1-butanol; ●, ethyl acetate; ■, methyl isobutyl ketone, □, toluene, ▲, o-xylene.

The correlations are given in Figs. 3-5, and the constants of the correlations are also given in Table 3. The Othmer-Tobias correlation is

$$\log\left(\frac{100-w_{11}}{w_{11}}\right) = M \log\left(\frac{w_{32}}{w_{22}}\right) + N \quad (1)$$

The Hand correlation is

$$\log\left(\frac{w_{31}}{w_{11}}\right) = M \log\left(\frac{w_{32}}{w_{22}}\right) + N \quad (2)$$

The Bachman-Brown correlation is

$$\frac{w_{11}}{w_{22}} = M w_{11} + N \quad (3)$$

The plait-point data determined by Treybal's method [Treybal et al., 1946] on Hand's coordinates, are summarized in Table 4 and the plait-point of o-xylene (1)+water (2)+propionic acid (3) system is representatively shown in Fig. 6.

As the most important in liquid-liquid extraction is the selectivity of solvent, the solvents having 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 importance is distribution and selectivity. They are shown in the following equations.

$$D = \frac{\text{propionic acid mol \% in solvent layer}}{\text{propionic acid mol \% in water layer}} = \frac{x_{31}}{x_{32}} \quad (4)$$

$$S = \frac{\text{propionic acid mol \% in solvent - free solvent layer}}{\text{propionic acid mol \% in water - free solvent layer}} = \frac{x_{31}/(x_{31}+x_{21})}{x_{32}/(x_{32}+x_{22})} \quad (5)$$

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

The distribution and selectivity curves were plotted in Figs. 12

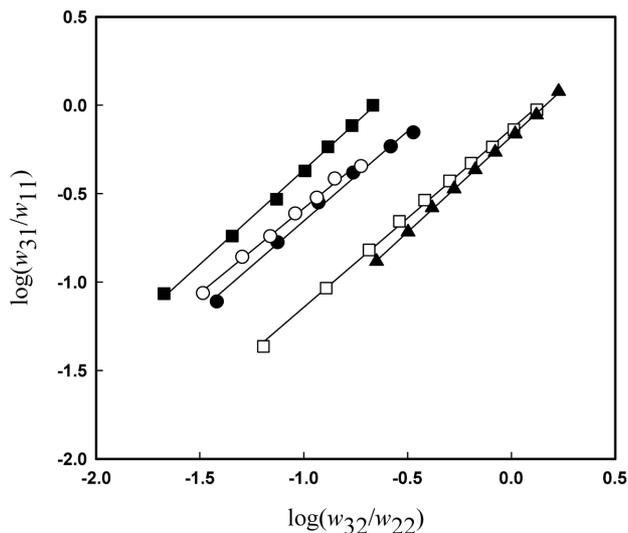


Fig. 4. Hand correlation for solvents (1)+water (2)+propionic acid (3) systems at 25 °C; ●, ethyl acetate; ■, methyl isobutyl ketone, □; toluene, ▲, o-xylene.

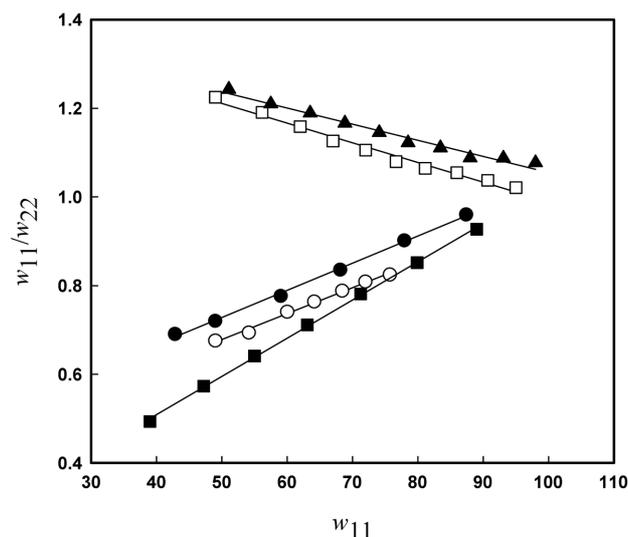


Fig. 5. Bachman-Brown correlation for solvents (1)+water (2)+propionic acid (3) systems at 25 °C; ●, ethyl acetate; ■, methyl isobutyl ketone, □; toluene, ▲, o-xylene.

and 13 to ascertain which of the solvents as extractant are better. As seen from the distribution curves and selectivity curves, propionic acid prefers solvent phase in all systems. With regard to the distribution curves and selectivity curves, the order of solvents studied is o-xylene, toluene, methyl isobutyl ketone, ethyl acetate, and 1-butanol. o-Xylene can be used for the extraction of propionic acid because it is more available and at a cheaper rate when compared to the other solvents.

1. Data Correlation

NRTL and UNIQUAC models were used to correlate and predict the LLE data in the present work.

1-1. NRTL Model

The activity coefficient of the *i*th component in a multicomponent system is expressed as follows:

$$\frac{G^E}{RT} = \sum_i x_i \cdot \frac{\sum_j x_j \tau_{ij} g_{ji}}{\sum_j x_j g_{ji}} \quad (6)$$

$$\ln \gamma_k = \frac{\sum_{j=1}^N x_j \tau_{jk} g_{jk}}{\sum_{l=1}^N x_l g_{lk}} + \sum_{j=1}^N \frac{x_j g_{kj}}{\sum_{l=1}^N x_l g_{lj}} \left(\tau_{kj} - \frac{\sum_{r=1}^N x_r \tau_{rj} g_{rj}}{\sum_{l=1}^N x_l g_{lj}} \right) \quad (7)$$

where

$$\tau_{ij} = \frac{g_{ij} - g_{ii}}{RT} \quad g_i = g_{ij} \quad (8)$$

and

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad \alpha_{ii} = \alpha_{ij} \quad (9)$$

1-2. UNIQUAC Model

The equations for UNIQUAC model are given below:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (10)$$

$$\ln \gamma_i = \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{2}{z} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^N x_j l_j$$

Table 3. Correlation of LLE equilibrium data for the ternary systems of 1-butanol (1)+water (2)+propionic acid (3), ethyl acetate (1)+water (2)+propionic acid (3), methyl isobutyl ketone (1)+water (2)+propionic acid (3), toluene (1)+water (2)+propionic acid (3), and o-xylene (1)+water (2)+propionic acid (3) at 25 °C

Solvent		1-butanol	EAc	MIBK	Toluene	o-Xylene	
Correlation	Othmer-Tobias	M=	0.8436	1.2164	1.3436	0.9931	1.0871
		N=	0.3678	0.4197	0.9639	-0.1468	-0.1759
		r=	0.9954	0.9962	0.9995	0.9997	0.9997
Hand		M=	0.9602	1.0182	1.0652	1.0087	1.0827
		N=	0.3768	0.3626	0.6980	-0.1352	-0.1771
		r=	0.9978	0.9967	0.9992	0.9994	0.9998
Bachman-Brown		M=	0.0058	0.0061	0.0086	-0.0045	-0.0036
		N=	0.3866	0.4214	0.1638	1.4339	1.4183
		r=	0.9965	0.9989	0.9997	-0.9918	-0.9889

Table 4. Estimated plait point data for the ternary systems of 1-butanol (1)+water (2)+propionic acid (3), ethyl acetate (1)+water (2)+propionic acid (3), methyl isobutyl ketone (1)+water (2)+propionic acid (3), toluene (1)+water (2)+propionic acid (3), and o-xylene (1)+water (2)+propionic acid (3) at 25 °C

Solvent	Hand correlation		
	100w ₁	100w ₂	100w ₃
1-Butanol	21.62	59.55	18.83
Ethyl acetate	22.93	51.34	25.73
Methyl isobutyl ketone	11.92	56.38	31.70
Toluene	24.16	18.54	57.30
o-Xylene	23.19	17.19	59.61

$$+q_i \left[1 - \ln \left(\frac{\sum_{j=1}^N \theta_j \tau_{ji}^*}{\sum_{k=1}^N \theta_k \tau_{kj}^*} \right) \right] \quad (11)$$

where

$$l_i = \frac{2}{z} (r_i - q_i) - (r_i - 1) \quad z=10 \quad (12)$$

$$\Phi_i = \frac{r_i x_i}{\sum_l (r_l x_l)} \quad (13)$$

$$\theta_i = \frac{q_i x_i}{\sum_l (q_l x_l)} \quad (14)$$

$$\tau_{ji}^* = \exp \left(\frac{U_{ji} - U_{ii}}{RT} \right) \quad (15)$$

r and q are structural size parameters and structural area parameters, and are cited from Prausnitz et al. [1980].

The objective function, F, was used to minimize the difference between the experimental and calculated mole fraction:

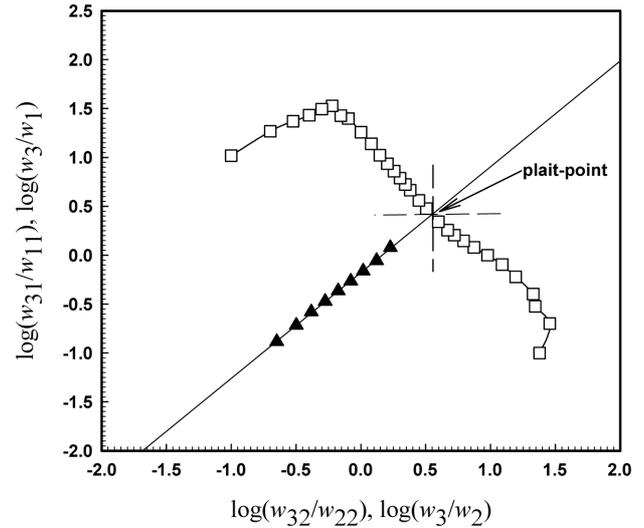


Fig. 6. Determination of plait point for o-xylene (1)+water (2)+propionic acid (3) system at 25 °C; ▲, Tie-line data, □; Binodal curve data.

$$F = \sum_i^n \sum_j^3 \sum_k^2 [x_{jk}^{exp}(i) - x_{jk}^{cal}(i)]^2 \quad (16)$$

$x_{jk}^{exp}(i)$ is the experimental mole fraction, $x_{jk}^{cal}(i)$ is the calculated mole fraction, and n is the number of the experimental tie-lines. The values of the parameters that minimized this objective function were sought, using both NRTL and UNIQUAC models. Applying the method of Varhegyi and Eon [1977], the value of U_{11} was set, and the values of the five parameters for UNIQUAC model were calculated.

$$U_{22}, U_{33}, U_{12}, U_{13}, U_{23} \text{ (J}\cdot\text{mol}^{-1}\text{)} \quad (17)$$

The values of g_{11} were set, and the values of the eight parameters for NRTL model for the ternary liquid-liquid system were calculated by using Hooke and Jeeves' direct search method [Hooke and Jeeves, 1961].

$$g_{22}, g_{33}, g_{12}, g_{13}, g_{23}, \alpha_{12}, \alpha_{13}, \alpha_{23} \text{ (J}\cdot\text{mol}^{-1}\text{)} \quad (18)$$

Table 5. The NRTL Parameters (g_{ij}) and Root-Mean-Square-Deviation (RMSD) Values for the solvents at 25 °C

Solvent	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
1-Butanol	1000.0	1184.9	3351.4	3321.3	1122.3	1995.4	0.396	0.891	0.001	0.2465
EAc	1000.0	2160.4	3032.5	3263.5	1374.5	2456.4	0.373	0.983	0.139	0.3555
MIBK	1000.0	3030.6	3978.6	4289.0	1865.2	3261.5	0.328	0.942	0.019	0.1820
Toluene	1000.0	1698.8	2211.6	4008.0	1826.7	2607.1	0.365	0.598	0.570	0.6612
o-Xylene	1000.0	2104.4	2279.6	4841.0	1665.1	2563.0	0.294	0.385	0.639	0.6380

Table 6. The UNIQUAC Parameters (U_{ij}) and Root-Mean-Square-Deviation (RMSD) Values for the solvents at 25 °C

Solvent	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
1-butanol	1000.0	217.9	2853.2	3854.2	2087.3	2468.0	0.9071
EAc	1000.0	2289.0	3583.4	4995.3	1130.4	637.31	0.9954
MIBK	1000.0	2145.8	4749.9	3211.2	1987.4	-916.8	0.5922
Toluene	1000.0	-1258.3	432.6	1492.5	786.7	-42.2	0.7470
o-Xylene	1000.0	1401.4	3590.6	4998.3	754.7	1002.6	1.0880

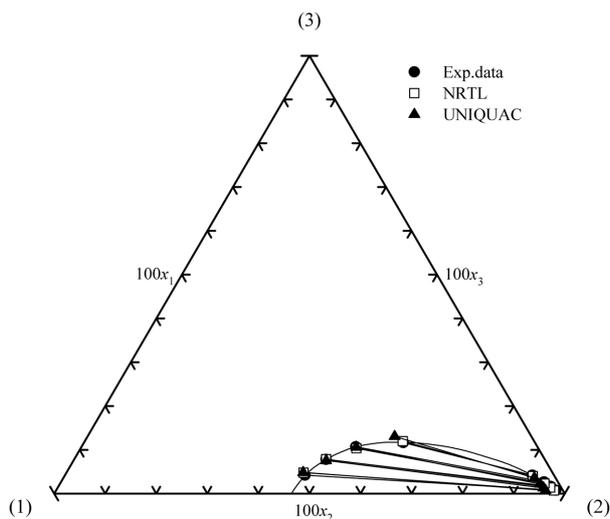


Fig. 7. Comparison of the experimental data and values calculated by NRTL and UNIQUAC models for 1-butanol (1)+water (2)+propionic acid (3) system at 25 °C.

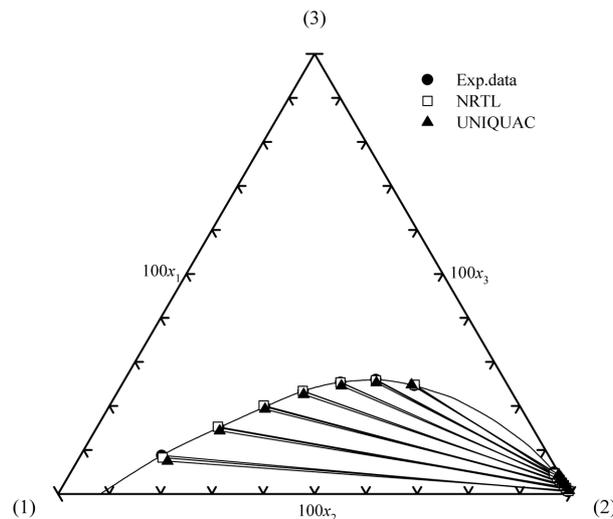


Fig. 9. Comparison of the experimental data and values calculated by NRTL and UNIQUAC models for methyl isobutyl ketone (1)+water (2)+propionic acid (3) system at 25 °C.

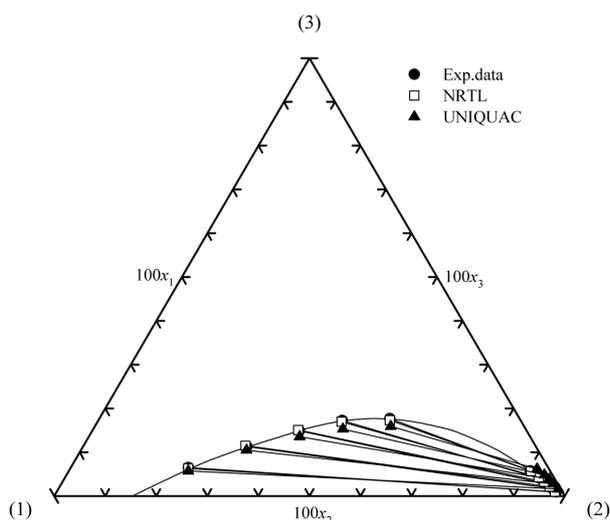


Fig. 8. Comparison of the experimental data and values calculated by NRTL and UNIQUAC models for ethyl acetate (1)+water (2)+propionic acid (3) system at 25 °C.

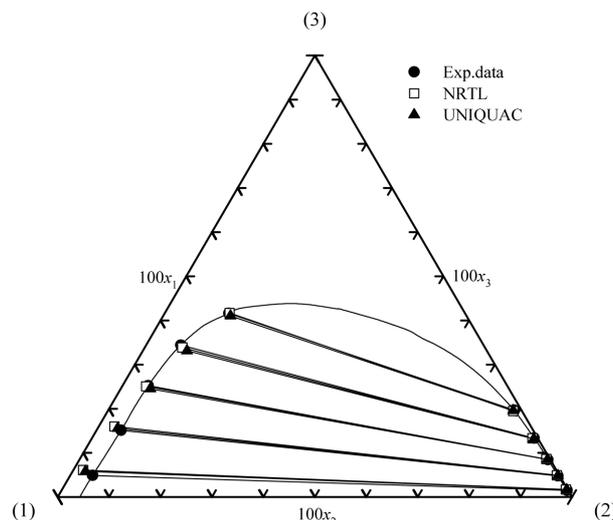


Fig. 10. Comparison of the experimental data and values calculated by NRTL and UNIQUAC models for toluene (1)+water (2)+propionic acid (3) system at 25 °C.

The parameters calculated in this way are shown in Tables 5 and 6. Also included in the tables is the root-mean-square-deviation (RMSD) defined as

$$\text{RMSD}_3 = 100 \left[\sum_{i=1}^N \sum_{j=1}^3 \sum_{k=1}^2 (x_{jk}^{\text{exp}}(i) - x_{jk}^{\text{cal}}(i))^2 / (6N) \right]^{1/2} \quad (19)$$

The RMSD is a measurement of the agreement between the experimental and calculated values. The calculated values using both UNIQUAC and NRTL models for the systems are presented in Figs. 7-11.

CONCLUSION

Liquid-liquid equilibrium data were determined for the ternary

systems of toluene+water+propionic acid, o-xylene+water+propionic acid, methyl isobutyl ketone+water+propionic acid, ethyl acetate+water+propionic acid, and 1-butanol+water+propionic acid at 25 °C and atmospheric pressure.

The tie-line data for all systems were satisfactorily correlated by the methods of Othmer-Tobias, Hand, Bachman-Brown.

Analyzing the distribution and selectivity curves, we concluded that o-xylene appeared to be a better solvent for extraction purposes than the other when propionic acid needs to be extracted from its aqueous solution.

Finally, the calculations based on both UNIQUAC and NRTL models gave a good representation of the tie-line data for the systems of toluene+water+propionic acid, o-xylene+water+propionic acid, methyl isobutyl ketone+water+propionic acid, ethyl acetate+wa-

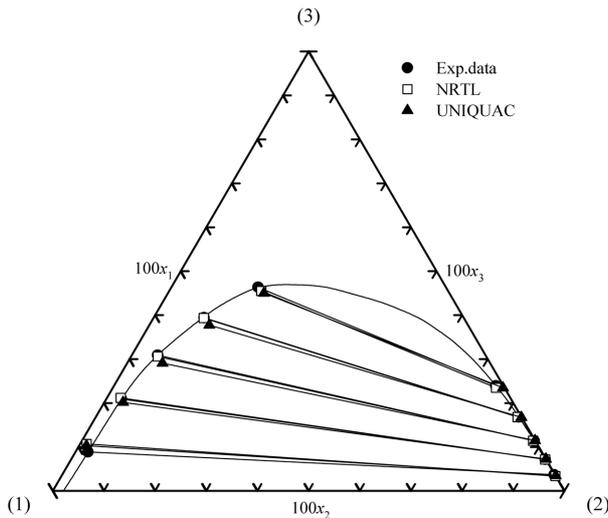


Fig. 11. Comparison of the experimental data and values calculated by NRTL and UNIQUAC models for o-xylene (1)+water (2)+propionic acid (3) system at 25 °C.

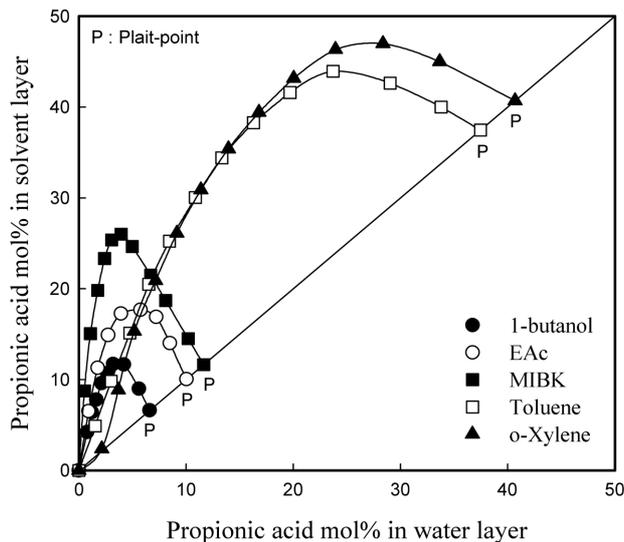


Fig. 12. Distribution of propionic acid between aqueous phase and organic phase at 25 °C.

ter+propionic acid, and 1-butanol+water+propionic acid. However, the NRTL model, fitted to the experimental data, was more accurate than the UNIQUAC model, as can be seen from the RMSD in Tables 5 and 6.

NOMENCLATURE

- g_{ji} : NRTL parameters between j-i components [cal/g-mol]
 l_k : pure-component constant defined in Eq. (10) [dimensionless]
 U_{ji} : UNIQUAC parameters between j-i components [cal/g-mol]
 q_i : molecular surface area parameter, for component i [dimensionless]
 r_i : molecular volume parameter, for component i [dimensionless]

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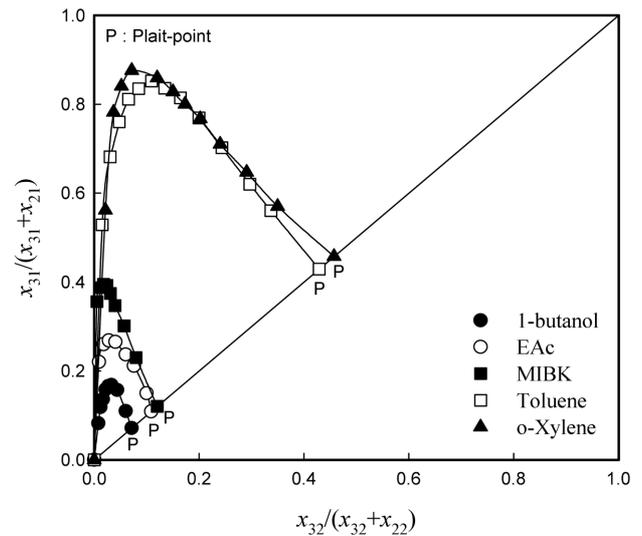


Fig. 13. Selectivity of propionic acid between aqueous phase and organic phase at 25 °C.

- x_i : mole fraction for component i [%]
 w_i : weight fraction for component i [%]
 z : lattice coordination number [dimensionless]

Greek Letters

- α_{ji} : nonrandomness parameter in NRTL model [dimensionless]
 γ_i : activity coefficient for component i [dimensionless]
 γ_i^C : activity coefficient, combinatorial part [dimensionless]
 γ_i^R : activity coefficient, residual part [dimensionless]
 θ_i : surface area fraction [dimensionless]
 θ_{ij} : surface area fraction, local for around j [dimensionless]
 Φ_i : volume fraction for component i in mixture [dimensionless]
 τ_{ji} : NRTL parameter between j-i components [dimensionless]
 τ_{ji}^* : UNIQUAC parameter between j-i components [dimensionless]

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