1066 *J. Chem. Eng. Data* **2006,** *51,* 1066−1069

Measurements of Quaternary Liquid−Liquid Equilibrium for Water + Acetic Acid + Propionic Acid + Solvent (Butyronitrile, Benzyl Acetate, or Methyl Isobutyl Ketone) at 298.15 K

Mehmet Bilgin*

Istanbul University, Engineering Faculty, Department of Chemical Engineering 34320 Avcilar, Istanbul, Turkey

---

Liquid−liquid equilibrium data of water + acetic acid + propionic acid + solvent (butyronitrile, benzyl acetate, and methyl isobutyl ketone (MIBK)) quaternary systems were measured. Complete phase diagrams were obtained by determining solubility curves and tie-line data at 298.15 K. The experimental data were compared with predicted values obtained from the UNIFAC method. Selectivity values for solvent separation efficiency were derived from the tie-line data. A comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients, separation factors, and solvent-free selectivity bases. The reliability of the data was ascertained from Othmer−Tobias plots. We conclude that the performance of the solvents increases in the order of butyronitrile, MIBK, and benzyl acetate.

Introduction

Acetic and propionic acids are the most important carboxylic acids that are widely used in industry, which makes the biotechnological production of these acids of interest. Liquid−liquid equilibrium (LLE) data are needed for the design of efficient and productive separation equipment. These data also provide valuable information about the molecular interactions and macroscopic behavior of fluid mixtures and can be used to test and improve thermodynamic models for calculating and predicting fluid-phase equilibria.

The solvent used for extraction should have high selectivity for the solute, high capacity, the capability to form two phases at reasonable temperatures and rapid phase separation (high density and low viscosity), noncorrosive and nonreactive properties, and good thermal stability. Butyronitrile, benzyl acetate, and methyl isobutyl ketone (MIBK), chosen as the solvents for this study, have many of these properties.

Although many studies for the recovery of acetic and propionic acids from aqueous solutions are performed in ternary bases, the quaternary LLE data on related acids is scarce in the literature.[1−3] Ternary LLE data for (water + acetic acid + butyronitrile) and (water + propionic acid + butyronitrile)[4] and for (water + acetic acid + MIBK),[5] (water + propionic acid + MIBK),[6] and (water + propionic acid + benzyl acetate)[7] have been presented previously. Quaternary LLE data of water + acetic acid + propionic acid + solvent (amyl alcohol, cyclohexyl acetate, and toluene) systems are also presented.[8] In this study, the LLE data of water + acetic acid + propionic acid + solvent (butyronitrile, benzyl acetate, and MIBK) quaternary systems were determined at 298.15 K, and the trend in the distribution coefficients and separation factors for these systems were shown because no such data are available in the literature. The phase equilibrium data were also used to analyze the applicability of the UNIFAC group contribution method.[9]

Experimental Section

Chemicals. Acetic acid (100 %), propionic acid (99.99 %), butyronitrile (>99 %), benzyl acetate (>99 %), and MIBK (>99 %) were supplied by Merck and used without further purification. GC analysis did not detect any appreciable impurity peaks. Deionized water was used during the experiments. The purity of the chemicals was checked on the basis of their refractive indexes and densities at (293 ± 0.20) K and their boiling points at (101.33 ± 0.27) kPa. Refractive indexes were measured with an Abbé−Hilger refractometer to ± 0.0005 accuracy. Densities were obtained with an Anton Paar (model DMA 4500) density meter. Boiling points were measured with a Fischer boiling-point apparatus. Estimations of the uncertainties in density and boiling-points measurements are ± 0.0001 g cm^{-3} and ± 0.1 K, respectively. The physical properties measured are in good agreement with published values, and they are listed in Table 1 along with literature values[10] for comparison.

Table 1. Refractive Indexes n_D and Densities ρ at 20 °C and Boiling Points t_b at 101.33 kPa of Chemicals

	n_D		ρ/(g·cm^{-3})		t_b/°C	
compound	measd	lit	measd	lit	measd	lit
acetic acid	1.3721	1.3720	1.0443^{25}	1.0446^{25}	117.70	117.90
propionic acid	1.3811	1.3809	0.9880^{25}	0.9882^{25}	140.90	141.15
butyronitrile	1.3840	1.3842	0.7937	0.7936	117.40	117.60
benzyl acetate	1.5235	1.5232	1.0552	1.0550	213.10	213.00
MIBK	1.3959	1.3962	0.7962^{25}	0.7965^{25}	116.30	116.50

Apparatus and Procedure. Solubility data for the quaternary systems were determined by the cloud-point method. The LLE apparatus and experimental procedure were previously described in detail.[8]

The mutual solubilities of water and solvent were determined by applying a synthetic method. A mass amount of the first substance was introduced into the cell; the other was added until a permanent heterogeneity had been observed. An ultra-accurate titrator with an accuracy of ± 0.001 cm^3 was used.

The tie lines were obtained by preparing quaternary mixtures of known overall compositions lying within the two-phase region, and after being shaken thoroughly at constant temperature and allowed to reach equilibrium, samples were carefully taken from each phase and analyzed.

The analysis for the determination of acetic acid, propionic acid, and solvent content of the two layers was performed with

---

* E-mail: mbilgin@istanbul.edu.tr. Fax: +90-212-5911997.

10.1021/je050527x CCC: $33.50

Table 2. Solubility Data for Water (1) + Acetic Acid (2) + Propionic Acid (3) + Solvent (4) Quaternary Systems at 298.15 K

w_1	w_2	w_3	w_1	w_2	w_3
		Butyronitrile			
0.9659	0.0000	0.0000	0.2730	0.1570	0.1567
0.9144	0.0253	0.0251	0.2138	0.1469	0.1466
0.8456	0.0569	0.0568	0.1747	0.1355	0.1352
0.7401	0.0960	0.0958	0.1349	0.1155	0.1153
0.6625	0.1192	0.1191	0.0943	0.0865	0.0864
0.5805	0.1367	0.1364	0.0601	0.0501	0.0499
0.4910	0.1487	0.1485	0.0436	0.0286	0.0284
0.4133	0.1562	0.1560	0.0271	0.0000	0.0000
0.3410	0.1591	0.1588			
		Benzyl Acetate			
0.9995	0.0000	0.0000	0.3167	0.2138	0.2134
0.9409	0.0281	0.0279	0.2106	0.1981	0.1978
0.8942	0.0511	0.0510	0.1426	0.1750	0.1747
0.8104	0.0921	0.0920	0.1019	0.1500	0.1498
0.7403	0.1253	0.1251	0.0674	0.1182	0.1181
0.6462	0.1637	0.1634	0.0463	0.0885	0.0883
0.5570	0.1922	0.1918	0.0223	0.0540	0.0539
0.4579	0.2083	0.2080	0.0106	0.0276	0.0274
0.2566	0.2084	0.2081	0.0011	0.0000	0.0000
		MIBK			
0.9804	0.0000	0.0000	0.3135	0.1831	0.1829
0.9140	0.0327	0.0325	0.1991	0.1679	0.1676
0.8760	0.0516	0.0514	0.1256	0.1409	0.1407
0.7807	0.0931	0.0930	0.0875	0.1157	0.1156
0.7120	0.1218	0.1217	0.0724	0.0891	0.0889
0.5754	0.1602	0.1599	0.0479	0.0484	0.0483
0.4338	0.1797	0.1794	0.0220	0.0000	0.0000

a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) for the quantitative determination. A 30 m HP-Innowax poly(ethylene glycol) capillary column (320 μm diameter with a 50 μm film thickness) was used with temperature-programmed analysis. The standard compound for the analysis was ethanol. The following parameters were used: column temperature, 343.15 K to 493.15 K at 20 K•min^{-1}, at 493.15 K (3 min) injection mode, split ratio 100:1; injector and detector temperature, 523.15 K; carrier gas, nitrogen 1 cm^3•min^{-1}; injected volume of 0.3 μL of liquid sample. Water was analyzed by Karl Fischer titration (Mettler Toledo DL38). The uncertainty of the mass fraction measurements for the overall composition determination was ± 0.002.

Results and Discussion

The experimental solubility curve data and the experimental mutual solubilities for the water (1) + acetic acid (2) + propionic acid (3) + solvent (4) quaternary systems are reported in Table 2. The tie-line compositions for the systems are given in Table 3.

The experimental data were compared with the value predicted by the UNIFAC method. The structural and interaction parameters between CH, CH_2, CH_3, COOH, CH_3COO, CH_3CO, ACH, $ACCH_2$, CH_2CN, and H_2O were taken from the literature.[11] The root-mean-square deviations (rmsd's) are calculated from the difference between the experimental data and the predictions of the UNIFAC model according to the following equation

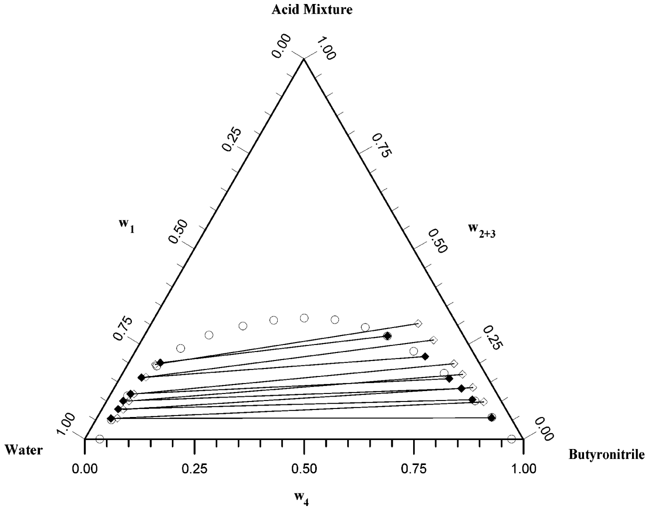

Figure 1. Phase equilibrium of a water (1) + acid mixture (2 + 3) + butyronitrile (4) system at 298.15 K: ○, solubility data; ◆, experimental tie-line data; ◇, UNIFAC tie-line data.

$$\mathrm{rmsd} = \left[\frac{\sum_k^N \left[\sum_j \sum_i (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2\right]}{6N}\right]^{1/2} \tag{1}$$

where x_{ijk} is the composition of component i in phase j on tie line k. N is the number of tie lines.

The experimental tie-line compositions and solubility values of the water + acid mixture + butyronitrile, water + acid mixture + benzyl acetate, and water + acid mixture + MIBK systems are plotted in Figures 1 to 3, respectively, along with the UNIFAC-predicted tie-line data. The concentrations in phase diagrams were given in mass fraction (w). The UNIFAC method correlated the experimental data for butyronitrile, benzyl acetate, and MIBK with rmsd values of 0.0249, 0.0221, and 0.0507, respectively. As seen from the Figures, all solvents show low solubility against water and can be used to extract the acid mixture from dilute aqueous solutions. The results indicate that the solubility of the solvents is high enough in the acid mixture. The tetrahedral representation of the solubility surface of the quaternary system obtained from the experimental data is shown in Figure 4.

Table 3. Tie-Line Compositions for Water (1) + Acetic Acid (2) + Propionic Acid (3) + Solvent (4) Quaternary Systems at 298.15 K

aqueous phase						solvent phase					
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
						Butyronitrile					
0.9134	0.0349	0.0194	0.8363	0.0792	0.0396	0.0448	0.0221	0.0339	0.0897	0.0678	0.0912
0.8847	0.0523	0.0264	0.7899	0.1060	0.0559	0.0651	0.0416	0.0620	0.1155	0.0969	0.1203
0.8626	0.0653	0.0348	0.7275	0.1313	0.0695	0.0749	0.0537	0.0793	0.1746	0.1244	0.1468
						Benzyl Acetate					
0.9240	0.0436	0.0295	0.6886	0.1719	0.1256	0.0162	0.0157	0.0332	0.0698	0.0874	0.1400
0.8360	0.0958	0.0636	0.5969	0.2071	0.1506	0.0266	0.0369	0.0701	0.0842	0.1150	0.1639
0.7735	0.1333	0.0889	0.5287	0.2267	0.1704	0.0356	0.0583	0.1008	0.1234	0.1428	0.1886
						MIBK					
0.9379	0.0246	0.0149	0.7854	0.1237	0.0581	0.0293	0.0107	0.0212	0.0774	0.0906	0.1099
0.9087	0.0452	0.0225	0.7426	0.1420	0.0723	0.0372	0.0239	0.0404	0.0945	0.1075	0.1346
0.8630	0.0762	0.0359	0.6898	0.1711	0.0848	0.0530	0.0432	0.0677	0.1195	0.1297	0.1602
0.8263	0.0943	0.0454				0.0587	0.0589	0.0847			

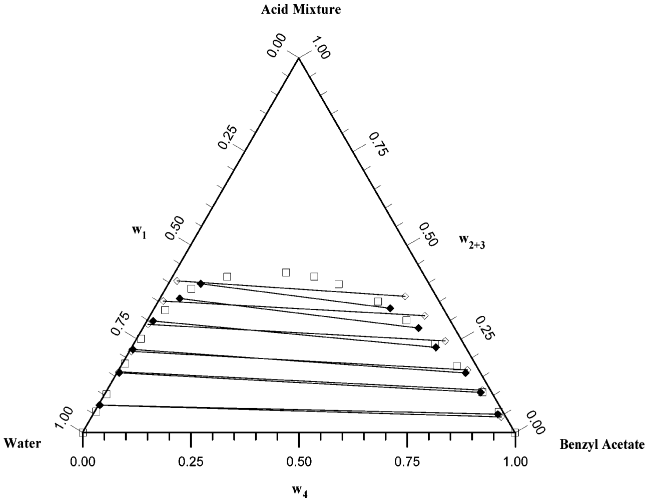

Figure 2. Phase equilibrium of a water (1) + acid mixture (2 + 3) + benzyl acetate (4) system at 298.15 K: □, solubility data; ◆, experimental tie-line data; ◇, UNIFAC tie-line data.

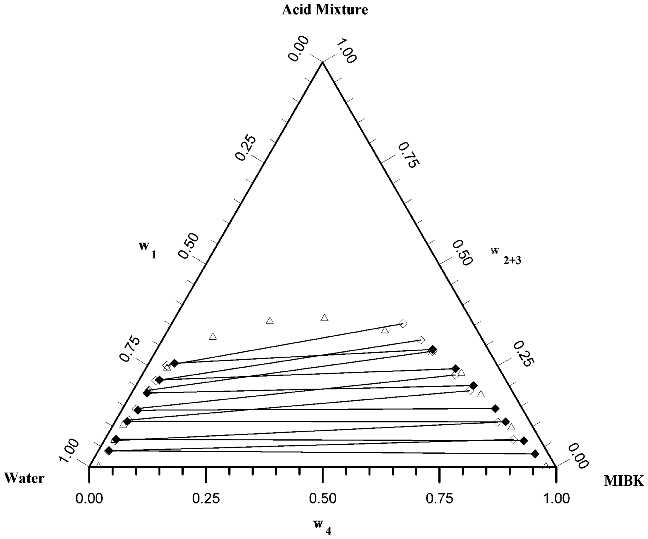

Figure 3. Phase equilibrium of a water (1) + acid mixture (2 + 3) + MIBK (4) system at 298.15 K: △, solubility data; ◆, experimental tie-line data; ◇, UNIFAC tie-line data.

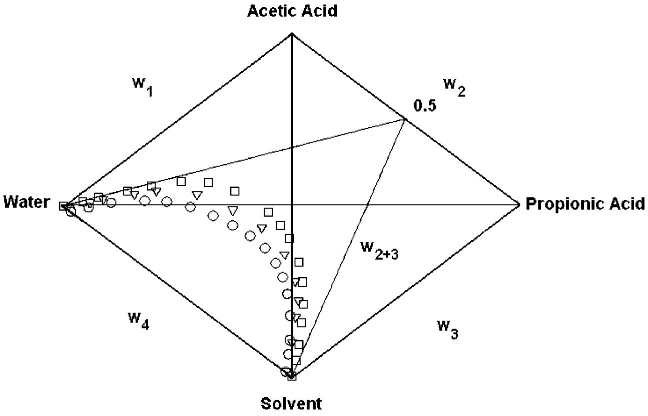

Figure 4. Tetrahedral representation of the solubility surface of a water (1) + acetic acid (2) + propionic acid (3) + solvent (4) quaternary system: ○, butyronitrile; □, benzyl acetate; ▽, MIBK.

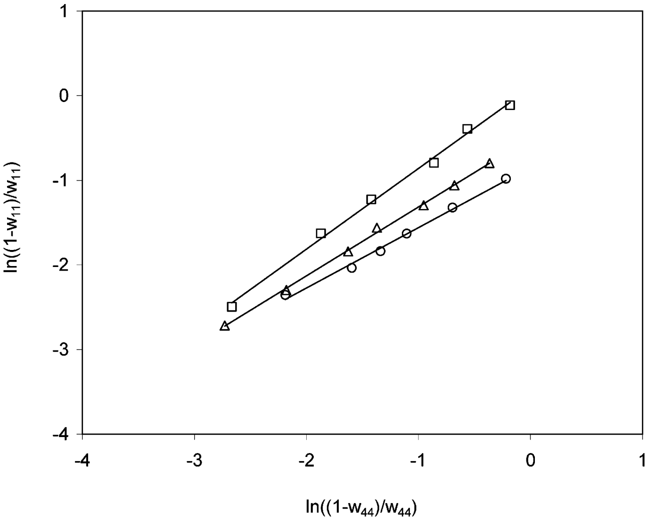

Figure 5. Othmer−Tobias plots of water (1) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K: ○, butyronitrile; □, benzyl acetate; △, MIBK.

Table 4. Experimental Distribution Coefficients D_i and Separation Factors S_i at 298.15 K

D_1	D_2	D_3	S_2	S_3	D_1	D_2	D_3	S_2	S_3
				Butyronitrile					
0.0490	0.6332	1.7474	12.91	35.63	0.1073	0.8561	2.3030	7.98	21.47
0.0736	0.7954	2.3485	10.81	31.92	0.1462	0.9142	2.1521	6.25	14.72
0.0868	0.8224	2.2787	9.47	26.24	0.2400	0.9474	2.1122	3.95	8.80
				Benzyl Acetate					
0.0175	0.3601	1.1254	20.54	64.19	0.1014	0.5084	1.1146	5.02	11.00
0.0318	0.3852	1.1022	12.11	34.64	0.1411	0.5553	1.0883	3.94	7.72
0.0460	0.4374	1.1339	9.50	24.64	0.2334	0.6299	1.1068	2.70	4.74
				MIBK					
0.0312	0.4350	1.4228	13.92	45.54	0.0985	0.7324	1.8916	7.43	19.19
0.0409	0.5288	1.7956	12.92	43.86	0.1273	0.7570	1.8617	5.95	14.63
0.0614	0.5669	1.8858	9.23	30.71	0.1732	0.7580	1.8892	4.38	10.90
0.0710	0.6246	1.8656	8.79	26.26					

The reliability of measured tie-line compositions was ascertained by making Othmer−Tobias plots[12] for each system. The plots are presented in Figure 5. The linear correlation coefficient and the standard deviation of the regression for the system with butyronitrile are 0.9938 and 0.0436; for the system with benzyl acetate, they are 0.9960 and 0.0620; and for the system with MIBK, they are 0.9984 and 0.0335, respectively. The linearity of the plots (a correlation factor close to 1) indicates the degree of consistency of the related data. The standard deviation for tie-line composition data was 0.0015.

To study the capacity and selectivity of the solvents used to extract the acid mixture, distribution coefficients D_i for acetic acid (i = 2) and propionic acid (i = 3) and the separation factors S_i are determined as follows

$$D_i = \frac{w_{i4}}{w_{i1}} \tag{2}$$

$$S_i = \frac{D_i}{D_1} \tag{3}$$

where w_{i4} and w_{i1} are the mass fractions of component i in the solvent and aqueous phase, respectively. The results for the water (1) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K are listed in Table 4. The results for the distribution values and the separation factors make the solvents good candidates for separating agents. Although the initial concentration of the acid mixture was in a 1:1 mass ratio, it is noticeable that all solvents show higher distribution coefficients and separation factors for propionic acid than acetic acid. To compare the selectivity advantages of butyronitrile, benzyl acetate, and MIBK, solvent-free-based selectivity diagrams are

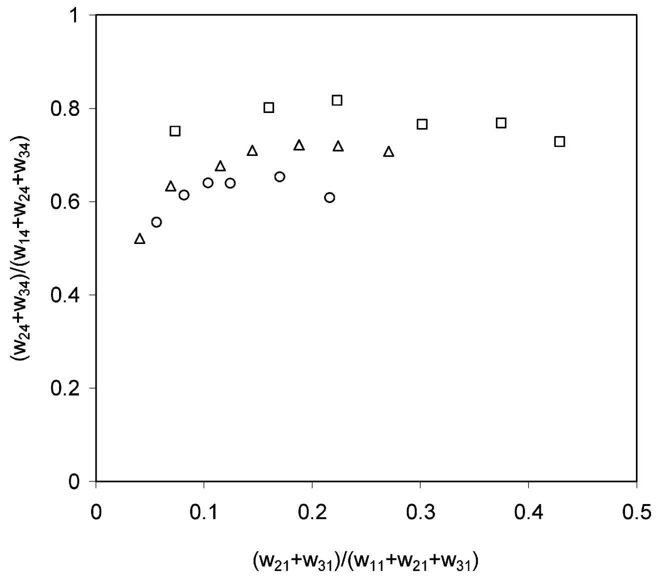

Figure 6. Selectivity diagrams of water (1) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K: ○, butyronitrile; □, benzyl acetate; △, MIBK.

plotted in Figure 6. The selectivity diagram indicated that the performance of the solvents increases in the order of butyronitrile, MIBK, and benzyl acetate. This order can be explained by the relationship of the polarity of acids and solvents. Whereas acetic and propionic acids are weak acids with low polarity, the extraction ability increases with decreasing solvent polarity.

Conclusions

LLE data of water + acetic acid + propionic acid + solvent (butyronitrile, benzyl acetate, and MIBK) quaternary systems at 298.15 K were measured, and the trends in the distribution coefficients and separation factors for these systems were calculated. The experimental tie lines of these systems were compared with the predicted data of the UNIFAC method. It is concluded that all solvents showing low solubility against water may serve as adequate solvents to extract acetic and propionic acid mixtures from their dilute aqueous solutions. It is observed that all solvents used in this study show higher distribution coefficients and separation factors for propionic acid than acetic acid.

Literature Cited

(1) Cehreli, S. Liquid−Liquid Equilibria of the Acetic Acid−Water−Mixed Solvent (Cyclohexyl Acetate-Cyclohexanol) System. *Braz. J. Chem. Eng.* **2002**, *19*, 45−53.
(2) Ruiz, F.; Prats, D. Quaternary Liquid Liquid Equilibria: Experimental Determination and Correlation of Equilibrium Data: Part I. System Water−Acetone−Acetic Acid−Chloroform. *Fluid Phase Equilib.* **1983**, *10*, 77−93.
(3) Ruiz, F.; Prats, D.; Gomis, V.; Varo, P. Quaternary Liquid Liquid Equilibrium Water−Acetic Acid−1,Butanol−*n*,Butyl Acetate at 25 °C. *Fluid Phase Equilib.* **1984**, *18*, 171−183.
(4) Letcher, T. M.; Redhi, G. G. Phase Equilibria for Liquid Mixtures of (Butanenitrile + a Carboxylic Acid + Water) at 298.15 K. *Fluid Phase Equilib.* **2002**, *193*, 123−133.
(5) Mišek, T. *Recommended Systems for Liquid Extraction Studies*; European Federation of Chemical Engineers−The Institution of Chemical Engineers: Rugby, Warwickshire, England, 1978.
(6) Kim, J. K.; Park, D. W. Liquid Liquid Equilibrium for the Ternary System of Solvents + Water + Propionic Acid at 25 °C and Atmospheric Pressure. *Korean J. Chem. Eng.* **2005**, *22*, 256−263.
(7) Cehreli, S. Application of the UNIFAC Model to Liquid−Liquid Equilibria of Water−Propionic Acid−Solvent Ternaries. *Pamukkale University, Engineering College, J. Eng. Sciences* **2003**, *9*, 125−128.
(8) Cehreli, S.; Bilgin, M. Quaternary Liquid−Liquid Equilibrium of Water + Acetic Acid + Propionic Acid + Solvent (Amyl Alcohol, Cyclohexyl Acetate or Toluene) Systems. *J. Chem. Eng. Data* **2004**, *49*, 1456−1459.
(9) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086−1099.
(10) Lide, D. R. *CRC Handbook of Chemistry and Physics*; Internet Version 2005, http://www.hbcpnetbase.com, CRC Press: Boca Raton, FL, 2005.
(11) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(12) Othmer, D. F.; Tobias, P. E. Tie Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693−696.

Received for review December 16, 2005. Accepted February 14, 2006.

JE050527X