JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Liquid−Liquid Equilibria for the Quaternary System Water (1) + Acrylic Acid (2) + Acetic Acid (3) + Cyclohexane (4) at (293.15, 303.15, and 313.15) K

Hongxun Zhang,* Yanwen Gong, Chen Li, Lei Zhang, and Chunshan Zhu

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, Henan 450001, China

ABSTRACT: Liquid−liquid equilibria (LLE) data for the quaternary system water + acrylic acid + acetic acid + cyclohexane at (293.15, 303.15, and 313.15) K have been measured at atmospheric pressure. The reliability of the experimental LLE data was ascertained through Othmer−Tobias and Bachman correlations. The pseudoternary phase diagrams at different temperatures for the quaternary system were given. The nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models were used to correlate the data of the quaternary system. The calculated values from both models agree well with the experimental values.

INTRODUCTION

Acrylic acid is a principal monomer and raw material of polymeric products in the modern organic chemical industry. Acrylic acid is the simplest unsaturated carboxylic acid which has a double bond and a carboxyl group at C3 one molecule with the formula $CH_2{=}CHCOOH$. The vinyl group is attached to the carbonyl carbon directly. Acrylic acid has two reaction points or functional groups required for the polymerization process. Glacial acrylic acid is a clear, colorless liquid with a characteristic acrid odor and is miscible with water. The major use of acrylic acid, and its esters, is in the production of surface coatings, textiles, adhesives, paper treatment, polishes, leather, fibers, detergents, and superabsorbent materials.[1−3]

Acrylic acid is conventionally produced from petrochemicals. At present, most commercial acrylic acid is produced by oxidation of propylene. Production of acrylic acid by a bioroute is becoming the hot research point because it has been proven to be environmentally friendly and uses renewable resources. Acetic acid is a staple byproduct in the production of acrylic acid by either oxidation of propylene or in a bioroute. Both acrylic acid and acetic acid can form a hydrogen-bonded associated complex with water. The system of water and mixed acid of acrylic acid and acetic acid has a very small separation factor. Therefore, the separation of the mixed acid and water by simple distillation is ruled out. The integration of liquid−liquid extraction and heterogeneous azeotropic distillation is considered to be a comparatively effective method because of a low energy cost.[4−19] The key to this method is to find a kind of appropriate solvent which is used as the extractant.

Cyclohexane can form an azeotrope with both water and acetic acid, is insoluble in water, and has a low latent heat of vaporization and toxicity. In this work, we measured the LLE data of the quaternary system of water + acrylic acid + acetic acid + cyclohexane at (293.15, 303.15, and 313.15) K.

EXPERIMENTAL SECTION

Chemicals. Acrylic acid ($w \geq 99.5$ %) and cyclohexane ($w \geq 99.5$ %) were purchased from the Sinopharm Chemical Reagent Co., Ltd.; acetic acid ($w \geq 99.5$ %) was supplied by the Tianjin Kermel Chemical Reagent Co., Ltd. Double-distilled water was prepared in our laboratory. All of the liquid chemicals were checked with chromatographic analysis and used without further purification.

Apparatus and Procedure. The experimental apparatus included a jacketed glass cell (internal volume about 50 cm^3), a thermostatically controlled bath, and a magnetic agitator. The circulating water from the thermostatically controlled bath was introduced into the jacket to keep the temperature of the liquid mixture essentially constant. The temperature fluctuation was controlled within ± 0.05 K. The LLE data for the system of interest were measured at atmospheric pressure. Before the experiment, water, the mixed acid of acrylic acid and acetic acid, and cyclohexane were added into the cell by mass at known ratios. Considering the actual situation in the industry production, the mixed acid was prepared in a 10:1 mass ratio. The weights of these reagents were determined by an electronic balance (AUY220, ± 0.1 mg). According to results from preliminary tests, the heterogeneous mixtures were stirred for at least 2 h with a magnetic stirrer at constant temperature and allowed to settle for a minimum of 4 h to reach complete phase separation. Samples were carefully withdrawn from each phase in equilibrium by using different samplers simultaneously. A series of liquid−liquid equilibrium measurements over a temperature range of (293.15 to 313.15) K were performed.

Sample Analysis. A gas chromatograph (model GC-122, Shanghai Precision Instrument Co. Ltd., China), equipped with a thermal conductivity detector (TCD), was used to analyze the compositions. A 2 m × 3 mm inner diameter (i.d.) stainless steel column packed with a GDX-103 80/100 was used for the chromatographic analysis. The temperatures of the oven, injection port, and detector were held at (483.15, 513.15, and 513.15) K, respectively. The injection volume was 0.2 μL. The bridge

Received: December 11, 2010
Accepted: March 31, 2011
Published: April 11, 2011

Table 1. LLE Data (Mole Fraction) for the Water (1) + Acrylic Acid (2) + Acetic Acid (3) + Cyclohexane (4) System at (293.15, 303.15, and 313.15) K

solvent-rich phase			water-rich phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
		T/K = 293.15			
0.0022	0.0000	0.0000	0.9995	0.0000	0.0000
0.0056	0.0138	0.0015	0.9750	0.0197	0.0045
0.0069	0.0318	0.0032	0.9350	0.0539	0.0095
0.0078	0.0451	0.0044	0.9023	0.0806	0.0145
0.0096	0.0626	0.0076	0.8539	0.1215	0.0204
0.0110	0.0816	0.0094	0.8191	0.1485	0.0268
0.0154	0.1087	0.0126	0.7835	0.1754	0.0334
0.0175	0.1473	0.0155	0.7253	0.2164	0.0464
		T/K = 303.15			
0.0074	0.0000	0.0000	0.9994	0.0000	0.0000
0.0170	0.0128	0.0010	0.9739	0.0222	0.0030
0.0219	0.0366	0.0037	0.9335	0.0558	0.0094
0.0267	0.0576	0.0042	0.8920	0.0916	0.0144
0.0349	0.0890	0.0086	0.8165	0.1530	0.0262
0.0451	0.1071	0.0110	0.7668	0.1957	0.0313
0.0557	0.1438	0.0172	0.6824	0.2659	0.0405
0.0779	0.1793	0.0246	0.6020	0.3265	0.0497
		T/K = 313.15			
0.0139	0.0000	0.0000	0.9989	0.0000	0.0000
0.0219	0.0411	0.0037	0.9327	0.0564	0.0090
0.0297	0.0759	0.0054	0.8556	0.1204	0.0200
0.0349	0.0890	0.0086	0.8225	0.1499	0.0230
0.0451	0.1071	0.0110	0.7793	0.1863	0.0288
0.0558	0.1322	0.0146	0.7154	0.2410	0.0357
0.0633	0.1637	0.0176	0.6751	0.2709	0.0410
0.0780	0.1800	0.0195	0.6296	0.3042	0.0464

current of the TCD was 150 mA. The flow rate of the carrier gas, hydrogen, was kept at 56 mL·min^{-1}. Very good peak separation was achieved under the above-mentioned chromatographic conditions. The external standard method was used to analyze the content of the three components.

RESULTS AND DISCUSSION

Experimental Results. The LLE data of the quaternary system of water + acrylic acid + acetic acid + cyclohexane at (293.15, 303.15, and 313.15) K were measured and are listed in Table 1. All concentrations are expressed in mole fraction.

To estimate the capability of the solvent to separate acrylic acid and acetic acid from water, the distribution ratio, D_i for acrylic acid (i = 2) and acetic acid (i = 3), and the separation factor, S_2 for acrylic acid and S_3 for acetic acid, at the investigated temperatures can be calculated from Table 1. The D_i and S_i were determined as follows:

$$D_i = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} \tag{1}$$

$$S_i = \frac{D_{\mathrm{i}}}{D_1} \tag{2}$$

Table 2. Constants of the Othmer−Tobias and Bachman Equation for the Water (1) + Acrylic Acid (2) + Acetic Acid (3) + Cyclohexane (4) System at (293.15, 303.15, and 313.15) K

	Othmer−Tobias				Bachman			
T/K	a	b	R^2 [a]	SD[a]	m	n	R^2 [a]	SD[a]
293.15	−1.1133	0.6966	0.9858	0.1890	2.1908	−1.1969	0.9480	0.0148
303.15	−1.0021	0.5673	0.9647	0.2619	2.1979	−1.2417	0.9747	0.0162
313.15	−0.9579	0.5128	0.9594	0.2316	2.4791	−1.5280	0.9784	0.0141

[a] R^2 is the linear correlation coefficient; SD is the standard deviation.

where x is the mole fraction; the superscript I represents the solvent-rich phase and II the water-rich phase.

The reliability of the experimental data can be ascertained by applying the Othmer−Tobias equation or Bachman equation.[20−25] The equations are represented, respectively, as follows:

$$\ln\left(\frac{1 - x_4^{\mathrm{I}}}{x_4^{\mathrm{I}}}\right) = a + b \ln\left(\frac{1 - x_1^{\mathrm{II}}}{x_1^{\mathrm{II}}}\right) \tag{3}$$

$$x_4^{\mathrm{I}} = m + n\left(\frac{x_4^{\mathrm{I}}}{x_1^{\mathrm{I}}}\right) \tag{4}$$

where x_4^{I} is the mole fraction of cyclohexane in the solvent-rich phase; x_1^{II} is the mole fraction of water in the water-rich phase; the letters a and b and m and n are constants of the equations of Othmer−Tobias and Bachman, respectively.

The parameters of the Othmer−Tobias and Bachman equations are listed in Table 2. All of the squares of the linear correlation coefficients (R^2) are greater than 0.948. The standard deviations (SDs) are less than 0.262. These results suggest that it is reasonable to accept the LLE data of the considered systems as reliable.

LLE Calculations. The relationship of liquid−liquid equilibrium can be represented with an activity coefficient model. In this model, the basic relationships for every component i in two coexistent liquid phases of a system at equilibrium are

$$x_i^{\mathrm{I}} r_i^{\mathrm{I}} = x_i^{\mathrm{II}} r_i^{\mathrm{II}} \tag{5}$$

$$\sum x_i^{\mathrm{I}} = 1 \tag{6}$$

$$\sum x_i^{\mathrm{II}} = 1 \tag{7}$$

where x_i^{I} and x_i^{II} are the mole fractions of component i in phases I and II and r_i^{I} and r_i^{II} are the activity coefficients of component i in phases I and II. The key to solve the equations is to calculate the activity coefficients. The LLE experimental data are used to correlate the interaction parameters between water, acrylic acid, acetic acid, and cyclohexane; these in turn are used to determine the activity coefficients from the nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) equations.[26,27] The adjustable parameters of the NRTL and UNQUAC models are defined, respectively, as follows:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{8}$$

$$\tau_{ij} = \exp^{(a_{ij} + b_{ij}/T)} \tag{9}$$

Table 3. UNIQUAC Structural Parameters of the Used Pure Component

component	r_i	q_i
water	0.9200	1.4000
acrylic acid	2.6467	2.4000
acetic acid	2.2024	2.0720
cyclohexane	4.0475	3.2400

Table 4. Values of the NRTL and UNIQUAC Binary Parameters Regressed from LLE Data and rsmd for the Water (1) + Acrylic Acid (2) + Acetic Acid (3) + Cyclohexane (4) System at (293.15, 303.15, and 313.15) K

	component	NRTL			UNIQUAC		
T/K	i−j	b_{ij}/K	b_{ji}/K	rmsd	b_{ij}/K	b_{ji}/K	rmsd
293.15	1−2	174.91	164.65	0.0049	106.04	−66.45	0.0043
	1−3	2152.60	26.33		−237.53	−87.65	
	1−4	1872.04	1447.38		−184.39	−1012.54	
	2−3	−9238.48	−222.95		−3017.36	−2413.46	
	2−4	479.29	163.93		29.62	−172.85	
	3−4	1187.99	1000.52		−547.59	−346.69	
303.15	1−2	625.97	−86.23	0.0061	−152.84	172.15	0.0070
	1−3	−1026.07	−235.81		−295.17	−2.16	
	1−4	1893.37	1164.80		−215.14	−767.48	
	2−3	−4530.69	1037.26		−379.11	−2089.35	
	2−4	667.53	252.41		−381.19	84.76	
	3−4	2077.61	3.95		−1746.31	−308.34	
313.15	1−2	486.52	−74.78	0.0072	48.37	59.67	0.0081
	1−3	3496.58	239.77		−963.19	290.86	
	1−4	1781.30	1110.00		−180.87	−738.09	
	2−3	435.49	−212.94		−3303.93	−2416.18	
	2−4	696.36	137.30		−1656.45	207.63	
	3−4	5106.07	3672.10		67.25	−842.09	

where a_{ij} and b_{ij} are the binary parameters and T is temperature. These parameters were determined by minimizing the deviation between the experimental data and the model calculated values.

The binary interaction parameters of both models were calculated using Aspen Plus software. The regression method was the least-squares method based on maximum likelihood principles. The Britt−Luecke algorithm was employed to obtain the model parameters with the Deming initialization method. In the process of regression calculations, the parameter of those two models in eqs 8 and 9, a_{ij}, was set to zero. The value of the nonrandomness parameter of the NRTL model, α, was fixed at 0.3. For the UNIQUAC model, the pure component structural parameters (r, q) are listed in the Table 3. The values of the binary parmeter b_{ij} are listed in Table 4.

The root-mean-square deviation (rmsd) is a measure of agreement between experimental and calculated data. The values of the rmsd's of both models at each temperature are listed in Table 4. The rmsd is defined as

$$\text{rmsd} = \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(\frac{(x_{ijk}^{\text{calcd}} - x_{ijk}^{\text{exptl}})^2}{8n} \right) \right)^{1/2} \tag{10}$$

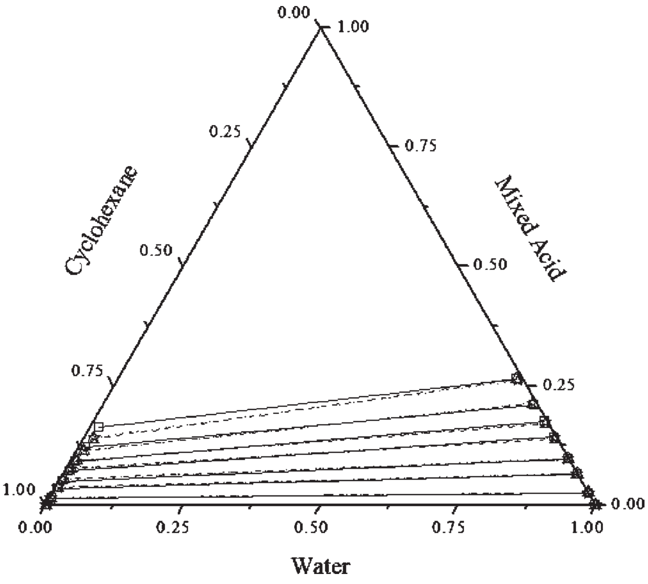

Figure 1. Pseudoternary LLE phase diagram for the water (1) + acrylic acid (2) + acetic acid (3) + cyclohexane (4) system at 293.15 K (in mole fraction): □, solid lines, experimental data tie lines; △, dash lines, tie lines calculated from NRTL; ☆, dot lines, tie lines calculated from UNIQUAC.

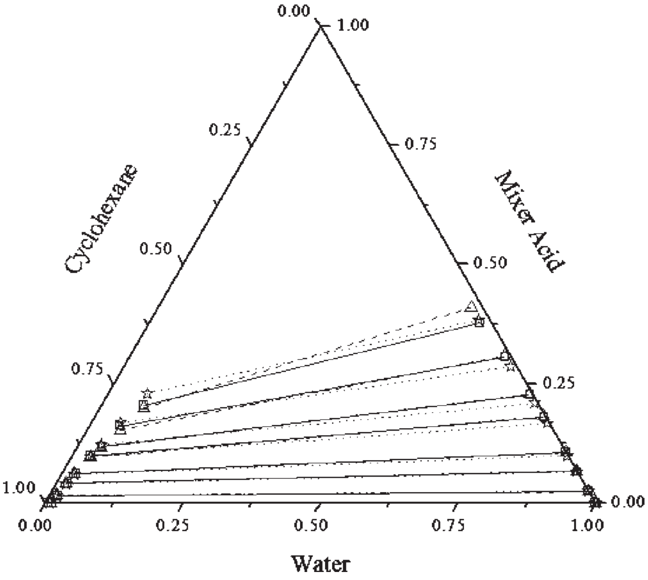

Figure 2. Pseudoternary LLE phase diagram for the water (1) + acrylic acid (2) + acetic acid (3) + cyclohexane (4) system at 303.15 K (in mole fraction): □, solid lines, experimental data tie lines; △, dash lines, tie lines calculated from NRTL; ☆, dot lines, tie lines calculated from UNIQUAC.

where x_{ijk}^{calcd} and x_{ijk}^{exptl} are the calculated and the experimental mole fractions of component i in phase j on tie-line k, and n is the number of tie-lines.

For the convenience of data processing, the mixed acid of acrylic acid and acetic acid was considered to be one component. The phase equilibria behavior of the quaternary system can be described by a pseudoternary LLE phase diagram. The pseudoternary LLE phase diagrams for the water + acrylic acid + acetic

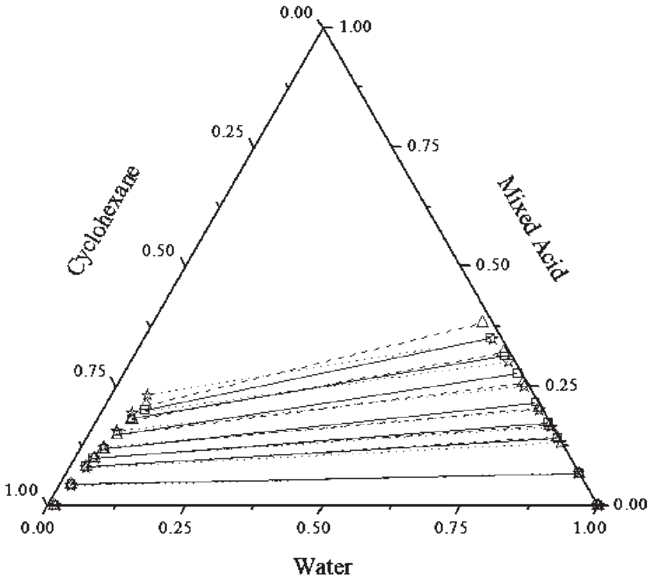

Figure 3. Pseudoternary LLE phase diagram for the water (1) + acrylic acid (2) + acetic acid (3) + cyclohexane (4) system at 313.15 K (in mole fraction): □, solid lines, experimental data tie lines; △, dash lines, tie lines calculated from NRTL; ☆, dot lines, tie lines calculated from UNIQUAC.

acid + cyclohexane system at (293.15, 303.15, and 313.15) K are shown in Figures 1 to 3, respectively. These pseudoternary LLE diagrams compare the experimental results with the calculated binodal locus and tie-lines from the NRTL and UNIQUAC models.

■ CONCLUSIONS

LLE data for the quaternary system of water + acrylic acid + acetic acid + cyclohexane at (293.15, 303.15, and 313.15) K at atmospheric pressure were measured. The reliability of the LLE data of the investigated system was inspected by the Othmer–Tobias and Bachman equations. The results are reliable. The distribution ratio of acrylic acid and acetic acid between water and cyclohexane and separation factor of cyclohexane to extract the mixed acid from water were given. The experimental data show that cyclohexane is a good solvent for extracting the mixed acid from aqueous solutions.

The NRTL and UNIQUAC models were used to correlate the experimental data. The rmsd is less than 0.0081. The results show that the LLE of the investigated system could be correlated well with both models.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86 371 67756725. Fax:+86 371 67756718. E-mail: ztonghy@163.com.

■ REFERENCES

(1) Aşçı, Y. S.; İncı, İ. Extraction Equilibria of Acrylic Acid from Aqueous Solutions by Amberlite LA-2 in Various Diluents. *J. Chem. Eng. Data* **2010**, *55*, 2385–2389.

(2) Keshav, A.; Chand, S.; Wasewar, K. L. Reactive Extraction of Acrylic Acid Using Tri-*n*-butyl Phosphate in Different Diluents. *J. Chem. Eng. Data* **2009**, *54*, 1782–1786.

(3) Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of acrylic, propionic, and butyric acid using Aliquat 336 in oleyl alcohol: Equilibria and effect of temperature. *Ind. Eng. Chem. Res.* **2009**, *48*, 888–893.

(4) Wu, Y. Y; Zhu, J. W.; Chen, K.; Wu, B.; Shen, Y. L. Liquid–Liquid Equilibria of Water + 2,3-Butanediol + Butyl Acetate at T = 298.15 K, T = 308.15 K, and T = 318.15 K. *J. Chem. Eng. Data* **2008**, *53*, 559–563.

(5) Narasigadu, C.; Raal, J. D.; Naidoo, P.; Ramjugernath, D. Ternary Liquid-Liquid Equilibria of Acetonitrile and Water with Heptanoic Acid and Nonanol at 323.15 K and 1 atm. *J. Chem. Eng. Data* **2009**, *54*, 735–738.

(6) Domańska, U.; Żołek-Tryznowska, Z.; Tshibangu, M. M.; Ramjugernath, D.; Letcher, T. M. Separation of an Alcohol and a Tetrahydrofuran, Methyl *tert*-Butyl Ether, or Ethyl *tert*-Butyl Ether by Solvent Extraction with a Hyperbranched Polymer at T = 298.15 K. *J. Chem. Eng. Data* **2010**, *55*, 2879–2885.

(7) Cháfer, A.; Lladosa, E.; Montón, J. B.; Burguet, M. Liquid–Liquid Equilibria for the System 1-Methyl Propyl Ethanoate (1) + Acetic Acid (2) + Water (3) at (283.15 and 323.15) K. *J. Chem. Eng. Data* **2010**, *55*, 523–525.

(8) Suresh, K. R.; Ghosh, P.; Banerjee, T. Liquid–Liquid Equilibria of Nitrobenzene Inorganic Acid Systems at 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 1302–1307.

(9) Zhang, H.; Zhang, L.; Gong, Y.; Li, C.; Zhu, C. Liquid–Liquid Equilibria for the Ternary System Water (1) + Acetic Acid (2) + Diisopropyl Ether (3) at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **2010**, *55*, 5354–5358.

(10) Qin, W.; Zhang, Y.; Li, Z.; Dai, Y. Extraction Equilibria of Glycolic and Glyoxylic Acids with Trialkylphosphine Oxide and Trioctylamine as Extractant. *J. Chem. Eng. Data* **2003**, *48*, 430–434.

(11) Li, Y.; Wang, Y.; Li, Y.; Dai, Y. Extraction of Glyoxylic Acid, Glycolic Acid, Acrylic Acid, and Benzoic Acid with Trialkylphosphine Oxide. *J. Chem. Eng. Data* **2003**, *48*, 621–624.

(12) Pinto, G. M.; Machado, A. B.; Ardila, Y. C.; Aznar, M.; Wolf-Macie, M. R. Liquid–Liquid Equilibria of the Ternary System Water + Acrylic Acid + 4-Methyl-2-pentanone at 298.15 K. *J. Chem. Eng. Data* **2008**, *53*, 659–662.

(13) Wolf-Maciel, M. R. Progress in acrylic acid production from lactic acid. *Chem. Ind. Eng. Prog.* **2010**, *29*, 683–689.

(14) Gangadwala, J.; Radulescu, G.; Kienle, A.; Steyer, F.; Sundmacher, K. New processes for recovery of acetic acid from waste water. *Clean Technol. Environ. Policy* **2008**, *10*, 245–254.

(15) Bilgin, M. Measurements of Quaternary Liquid-Liquid Equilibrium for Water + Acetic Acid + Propionic Acid + Solvent (Butyronitrile, Benzyl Acetate, or Methyl Isobutyl Ketone) at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1066–1069.

(16) Xiao, X.; Wang, L.; Ding, G.; Li, X. Liquid-Liquid Equilibria for the Ternary System Water + Acetic Acid + Propyl Acetate. *J. Chem. Eng. Data* **2006**, *51*, 582–583.

(17) Wang, L.; Cheng, Y.; Xiao, X.; Li, X. Liquid-Liquid Equilibria for the Ternary Systems Acetic Acid + Water + Butyl Acetate and Acetic Acid + Water + 2-Methyl Propyl Acetate at 304.15 K, 332.15 K, and 366.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1255–1257.

(18) Miao, X.; Zhang, H.; Wang, T.; He, M. Liquid-Liquid Equilibria of the Ternary System Water + Acetic Acid + Methyl *tert*-Butyl Ether. *J. Chem. Eng. Data* **2007**, *52*, 789–793.

(19) Zhang, H.; Wang, T. Measurement and Correlation of Liquid-Liquid Equilibrium Data for Water + Acetic Acid + Methyl *tert*-Butyl Ether + NaCl. *J. Chem. Eng. Data* **2009**, *54*, 945–949.

(20) Othmer, D. F.; Tobias, P. E. Tie-line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–700.

(21) Hand, D. B. The Distribution of Consolute Liquid between Two Immiscible Liquids. *J. Phys. Chem.* **1930**, *34*, 1961–2000.

(22) Ince, E. Liquid–Liquid Equilibria of the Ternary System Water + Acetic Acid + Dimethyl Succinate. *Fluid Phase Equilib.* **2005**, *238*, 33–58.

(23) Wang, B.; Qiu, T.; Li, S. Liquid-Liquid Equilibrium for the System Water + 1,4-Dioxane + 2,6-Dimethyloct-7-en-2-ol over the

Temperature Range of (343.2 to 358.2) K. *J. Chem. Eng. Data* **2010**, *55*, 558–560.

(24) 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.

(25) Naydenov, D.; Bart, H. J. Ternary Liquid-Liquid Equilibria for Systems Containing Alcohol or Acetic Acid + Ester + 1-Ethyl-3-methylimidazolium Hydrogen Sulfate at 313.2 K Using Headspace Gas Chromatography. *J. Chem. Eng. Data* **2009**, *54*, 43–47.

(26) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

(27) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodinamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Party or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.