JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Ternary Liquid−Liquid Equilibria of Water + Prop-2-enoic Acid + Isobutyl Ethanoate at Different Temperatures

Hongxun Zhang,* Yingming Zhang, Lei Zhang, Chen Li, and Chunshan Zhu

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

ABSTRACT: To screen the proper solvent for separating prop-2-enoic acid aqueous solution by the method of extraction followed by heterogeneous azeotropic distillation, the liquid−liquid equilibria (LLE) data for the ternary system water + prop-2-enoic acid + isobutyl ethanoate at (293.15, 303.15, and 313.15) K were measured at atmospheric pressure. The reliability of the experimental LLE data was ascertained through Othmer−Tobias and Hand correlations. The LLE phase diagrams at different temperatures for the ternary system were given. Distribution coefficients and separation factors were calculated from the LLE data. The thermodynamic models of nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) were used to correlate the data of the ternay system. The calculated values from both models agree well with the experimental values.

INTRODUCTION

Prop-2-enoic acid and the acrylates monomer may be the most attractive monomers of synthetic polymers. Production of prop-2-enoic acid through gas-phase catalytic oxidation of propylene and/or acrolein has been industrially widely practiced. This method normally consists of an oxidation step to catalytically oxidize propylene and/or acrolein using molecular oxygen in the gaseous phase, a collection step to collect an prop-2-enoic acid resulting from the oxidation step with water, and a recovery step to isolate and recover prop-2-enoic acid from the aqueous solution of the prop-2-enoic acid.[1] The economics of the process are largely dependent on how the water is separated. Similar to acetic acid, prop-2-enoic acid is difficult to separate from water by conventional distillation because there is a tangent pinch on the pure water end in their binary vapor−liquid equilibrium diagram at 1 atm. Therefore, the separation of the prop-2-enoic acid and water by conventional distillation is ruled out because of its high energy consumption. It is more customary to use the method of liquid−liquid extraction followed by heterogeneous azeotropic distillation.[2−12] The key to this method is to find a kind of appropriate solvent which is used as both extractant in the extraction process and entrainer in the azeotropic distillation process.

Isobutyl ethanoate is a colorless solvent with medium volatility and a characteristic fruity ester odor. It is highly miscible with all common organic solvents but only slightly miscible in water. Compared to toluene and 4-methyl-2-pentanone, isobutyl ethanoate has less toxicity. Isobutyl ethanoate is an economical replacement for 4-methyl-2-pentanone or toluene in many formulations.[13,14] Isobutyl ethanoate can form an azeotrope rich with water. This means that this entrainer is more capable of carrying water to the top of the column, and thus less entrainer is needed in the azeotropic distillation process. In this work, we measured the liquid−liquid equilibria (LLE) data of the ternary system of water + prop-2-enoic acid + isobutyl ethanoate at (293.15, 303.15, and 313.15) K.

EXPERIMENTAL SECTION

Chemicals. Prop-2-enoic acid and isobutyl ethanoate with a minimum mass fraction purity of 0.995 were purchased from the Sinopharm 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. The purities of the chemicals are listed in Table 1.

Apparatus and Procedure. The LLE data of the ternary systems investigated were measured at atmospheric pressure by an experimental apparatus including 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 (501A type, Shanghai, China) was introduced into the jacket to keep the temperature of the liquid mixture essentially constant. The temperature fluctuation was controlled within ± 0.05 K. Before the experiment, water, prop-2-enoic acid, and isobutyl ethanoate were added into the cell by mass at known ratios. The weights of these reagents were determined with an AUY220 electronic balance (standard uncertainty of 0.0001 g). To determine stirring and static placing time at a constant temperature, the preliminary tests of LLE have been made with different stirring time and static placing time. The static placing time was fixed when the stirring time was changed and vice versa. The stirring and static placing time can be determined when the composition of solvent-rich phase and water-rich phase remain largely unchanged. 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. A sample of each phase was taken by using different sampler simultaneously and placed in a vial with a certain amount of *n*-propanol. The addition of *n*-propanol prevents phase separation effects because of the variation of temperature after sampling from the cell.

Sample Analysis. A gas chromatograph (model GC-122, Shanghai Precision Instrument Co. Ltd., China), equipped with a thermal conductivity detector, was used to analyze the

Received: April 27, 2011
Accepted: June 27, 2011
Published: July 07, 2011

ACS Publications © 2011 American Chemical Society

dx.doi.org/10.1021/je2003226 | *J. Chem. Eng. Data* 2011, 56, 3411–3415

Table 1. Purity and UNIQUAC Parameters of Chemicals Used in This Work

	GC analysis	minimum purity[a]	UNIQUAC parameters[b]	
chemical	(mass percent)	(mass percent)	r	q
water	99.88	-	0.9200	1.4000
prop-2-enoic acid	99.62	99.5	2.6467	2.4000
isobutyl ethanoate	99.53	99.5	4.8266	4.1920

[a] Stated by supplier. [b] Taken from Aspen Plus simulator.

Table 2. Experimental (Liquid + Liquid) Equilibrium Mass Fraction w (Tie-Line Data), Distribution Ratio (D_1, D_2), and Separation Factor (S) for the System Water (1) + Prop-2-enoic Acid (2) + Isobutyl Ethanoate (3) System at (293.15, 303.15, and 313.15) K and Atmospheric Pressure[a]

	solvent-rich phase	water-rich phase					
T/K	w_1^{I}	w_2^{I}	w_1^{II}	w_2^{II}	D_1	D_2	S
293.15	0.0439	0.0000	0.9937	0.0000			
	0.0737	0.0648	0.9824	0.0104	0.0750	6.231	83.05
	0.1055	0.1216	0.9699	0.0218	0.1088	5.578	51.28
	0.1636	0.2076	0.9466	0.0415	0.1728	5.002	28.94
	0.1956	0.2405	0.9203	0.0651	0.2125	3.694	17.38
	0.2212	0.2638	0.9037	0.0784	0.2448	3.365	13.75
	0.2702	0.3033	0.8765	0.1044	0.3083	2.905	9.424
	0.3290	0.3419	0.8198	0.1484	0.4013	2.304	5.741
	0.4041	0.3642	0.7621	0.1884	0.5302	1.933	3.646
303.15	0.0586	0.0000	0.9885	0.0000			
	0.0853	0.0664	0.9769	0.0098	0.0873	6.776	77.60
	0.1268	0.1325	0.9623	0.0225	0.1318	5.889	44.69
	0.1703	0.1776	0.9465	0.0366	0.1799	4.852	26.97
	0.2083	0.2235	0.9205	0.0584	0.2263	3.827	16.91
	0.2389	0.2514	0.8996	0.0757	0.2656	3.321	12.51
	0.2911	0.2880	0.8643	0.1042	0.3368	2.764	8.206
	0.3769	0.3185	0.8087	0.1476	0.4661	2.158	4.630
	0.4336	0.3337	0.7455	0.1893	0.5816	1.763	3.031
313.15	0.0925	0.0000	0.9853	0.0000			
	0.1475	0.0796	0.9712	0.0102	0.1519	7.804	51.38
	0.1673	0.1176	0.9628	0.0175	0.1738	6.720	38.67
	0.2087	0.1745	0.9433	0.0354	0.2212	4.929	22.28
	0.2491	0.2261	0.9167	0.0585	0.2717	3.865	14.22
	0.2689	0.2465	0.8951	0.0768	0.3004	3.210	10.68
	0.3554	0.2815	0.8424	0.1193	0.4219	2.360	5.593
	0.4165	0.2932	0.7949	0.1546	0.5240	1.897	3.620
	0.4701	0.3055	0.7312	0.2005	0.6429	1.524	2.370

[a] Standard uncertainties u are $u(T)$ = 0.05 K, $u(p)$ = 2.4 kPa, and $u(w)$ = 0.0058.

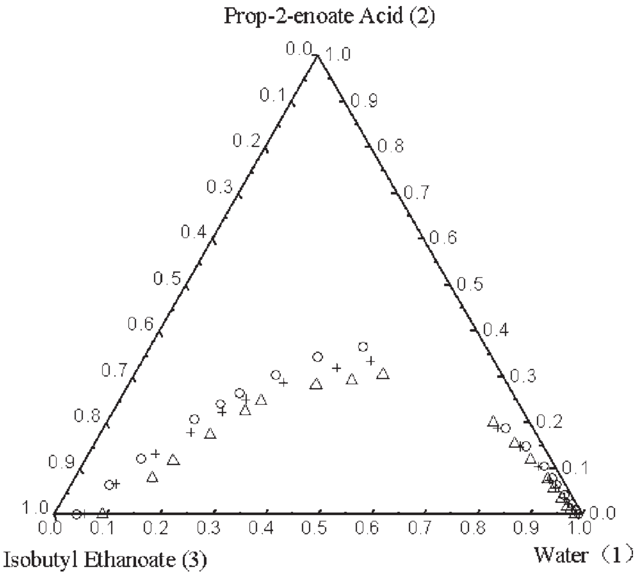

Figure 1. Ternary LLE phase diagram for the water (1) + prop-2-enoic acid (2) + isobutyl ethanoate (3) system at different temperatures: ○, T = 293.15 K; +, T = 303.15 K; △, T = 313.15 K.

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 (488.15, 513.15, and 513.15) K, respectively. The injection volume was 0.2 mm^3. The bridge current of the TCD was 150 mA. The flow rate of the carrier gas, hydrogen, was kept at 0.9333 cm^3·s^{-1}. Very good peak separation was achieved under the chromatographic conditions. The external standard method was used to analyze the content of the four components including *n*-propanol. All measurements were carried out in triplicate. Considering the stability of the composition during the measurements, the uncertainty in calibration, and the repeatability and reproducibility of gas chromatography, we estimated the uncertainty of composition measurements to be within 0.0058 for the mass fraction of each component in the both liquid phases.

■ RESULTS AND DISCUSSION

Experimental LLE Data. The experimental LLE compositions of the ternary system water + prop-2-enoic acid + isobutyl ethanoate at (293.15, 303.15, and 313.15) K were measured and are listed in Table 2 and shown in Figure 1. All concentrations are expressed in mass fraction.

As it can be seen in Figure 1, the two-phase region of the ternary system investigated becomes smaller when the temperature increases. It can also be found that the solubility curves in the side of the solvent-rich phase has more significant variation with increasing temperature compared with those in the water-rich phase.

The reliability of the experimental data can be ascertained by applying the Othmer−Tobias equation or Hand equation.[15−19] The equations are represented, respectively, as follows:

$$\ln\left(\frac{1-w_3{}^{\mathrm{I}}}{w_3{}^{\mathrm{I}}}\right) = a + b\ln\left(\frac{1-w_1{}^{\mathrm{II}}}{w_1{}^{\mathrm{II}}}\right) \tag{1}$$

$$\ln\left(\frac{w_2{}^{\mathrm{I}}}{w_3{}^{\mathrm{I}}}\right) = m + n\ln\left(\frac{w_2{}^{\mathrm{II}}}{w_1{}^{\mathrm{II}}}\right) \tag{2}$$

where $w_3{}^{\mathrm{I}}$ is the mass fraction of isobutyl ethanoate in the solvent-rich phase; $w_1{}^{\mathrm{II}}$ is the mass fraction of water in the

Table 3. Constants of the Othmer−Tobias and Hand Equations

	Othmer−Tobias				Hand			
T/K	*a*	*b*	R^{2a}	SD^a	*m*	*n*	R^{2a}	SD^a
293.15	2.3930	1.0627	0.9964	0.0850	1.6732	0.9314	0.9949	0.0764
303.15	2.4813	1.1356	0.9922	0.1183	1.5246	0.8797	0.9979	0.0466
313.15	2.3437	1.0437	0.9889	0.1250	1.2839	0.7779	0.9991	0.0289

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

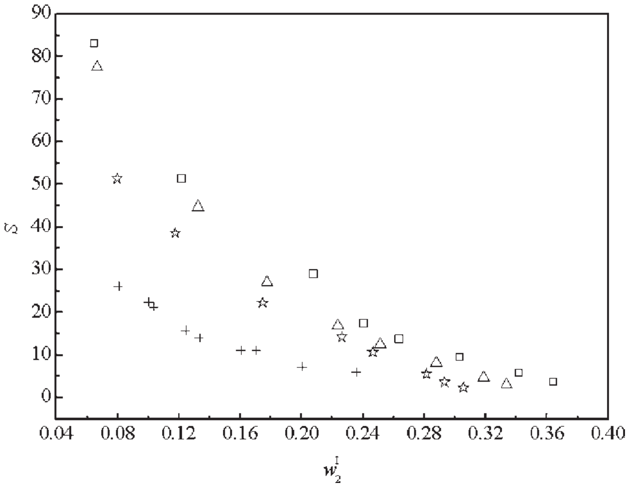

Figure 2. Separation factor (*S*) for the water (1) + prop-2-enoic acid (2) + isobutyl ethanoate (3) system at (□, *T* = 293.15; △, *T* = 303.15; ☆, *T* = 313.15) K and the water (1) + prop-2-enoic acid (2) + 4-methyl-2-pentanone (3) system at +, *T* = 298.15 K.[10]

water-rich phase; the letters *a* and *b* and *m* and *n* are constants of the equations of Othmer−Tobias and Hand, respectively.

The parameters of the Othmer−Tobias and Hand equations are listed in Table 3. All of the linear correlation coefficients (R^2) are greater than 0.9889. The standard deviations (SDs) are less than 0.125. These results suggest that it is reasonable to accept the LLE data of the considered systems as reliable.

The feasibility of using the isobutyl ethanoate as a solvent to separate prop-2-enoic acid from water was evaluated by the distribution ratio of water (D_1) and prop-2-enoic acid (D_2) and the separation factor of isobutyl ethanoate (*S*), calculated from experimental data as follows

$$D_i = \frac{w_i^{\mathrm{I}}}{w_i^{\mathrm{II}}} \tag{3}$$

$$S = \frac{D_2}{D_1} \tag{4}$$

where *w* is the mass fraction; the superscript I represents the solvent-rich phase and II the water-rich phase. The values of D_1, D_2, and *S* at different temperatures are listed in Table 1, together with the experimental LLE data.

The variety of *S* values at each temperature with the composition of prop-2-enoic acid in the solvent-rich phase (w_2^{I}) are shown in Figure 2. A comparison with the separation factor of 4-methyl-2-pentanone calculated from the data in the literature[10] for the ternary system water + prop-2-enoic acid + 4-methyl-2-pentanone at 298.15 K is also made. As can be seen from Figure 2, the *S* values decrease with increasing temperature and w_2^{I}. The *S* values of isobutyl ethanoate are larger than those of 4-methyl-2-pentanone at the same w_2^{I} value.

Table 4. NRTL and UNIQUAC Parameters for the Water (1) + Prop-2-enoic Acid (2) + Isobutyl Ethanoate (3) System at (293.15, 303.15, and 313.15) K as well as the Root-Mean-Square Deviation (rmsd)

	component	NRTL				UNIQUAC		
T/K	*i*−*j*	τ_{ij}	τ_{ji}	α	rmsd	τ_{ij}	τ_{ji}	rmsd
293.15	1−2	2.1547	−0.0971	0.47	0.0072	0.1113	3.2112	0.0070
	1−3	5.9254	1.2012	0.30		0.4370	0.5545	
	2−3	−1.9387	3.4171	0.35		1.5012	1.5421	
303.15	1−2	2.2831	−0.4107	0.47	0.0062	0.0688	3.0773	0.0044
	1−3	5.4297	0.8696	0.30		0.4924	0.5945	
	2−3	−2.0531	3.5088	0.35		1.4902	0.7639	
313.15	1−2	2.5759	−0.7667	0.47	0.0045	0.0402	3.1467	0.0046
	1−3	5.3984	0.3265	0.30		0.3986	0.8938	
	2−3	−1.9963	8.2936	0.35		2.5113	0.0080	

Data Correlation. The nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models[20,21] were used to correlate the experimental LLE data of the systems discussed here. The adjustable parameters of those two models are defined as follows, respectively

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{5}$$

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T) \tag{6}$$

The binary parameters, a_{ij} and b_{ij}, in eqs 5 and 6 were obtained by using the data regression of the Aspen Plus software. These parameters were determined by minimizing the deviation between the experimental data and the model calculated values. The object function (OF) used is

$$\mathrm{OF} = \min \sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} (w_{ijk}^{\mathrm{calcd}} - w_{ijk}^{\mathrm{exptl}})^2 \tag{7}$$

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

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. For the NRTL model, the value of the nonrandomness parameter, α, was fixed at α = 0.47 for the water−prop-2-enoic acid pair, α = 0.3 for the water−isobutyl ethanoate pair, and α = 0.35 for the prop-2-enoic acid−isobutyl ethanoate pair. For the UNIQUAC model, the pure component structural parameters (*r*, *q*) were obtained from Aspen Plus database and listed in the Table 1. The values of the adjustable parameters of the both models, τ_{ij}, are listed in Table 4.

The root-mean-square deviation (rmsd) is a measure of agreement between experimental and calculated data. The

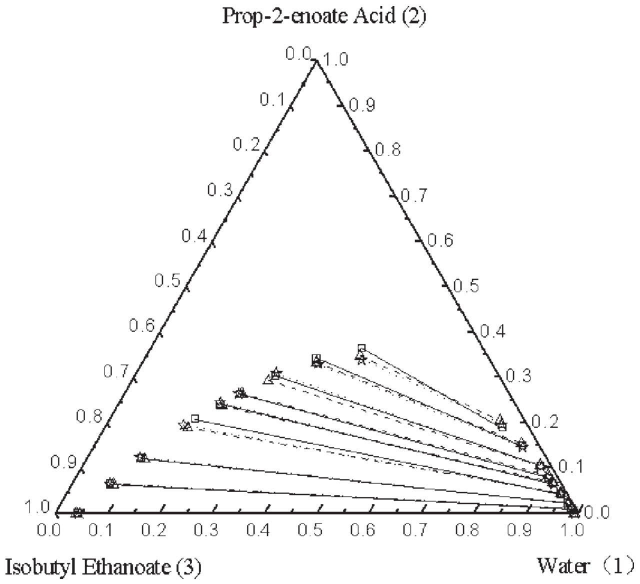

Figure 3. Ternary LLE phase diagram for the water (1) + prop-2-enoic acid (2) + isobutyl ethanoate (3) system at 293.15 K: □, solid lines, experimental data tie lines; △, dashed lines, tie lines calculated from NRTL; ☆, dotted lines, tie lines calculated from UNIQUAC.

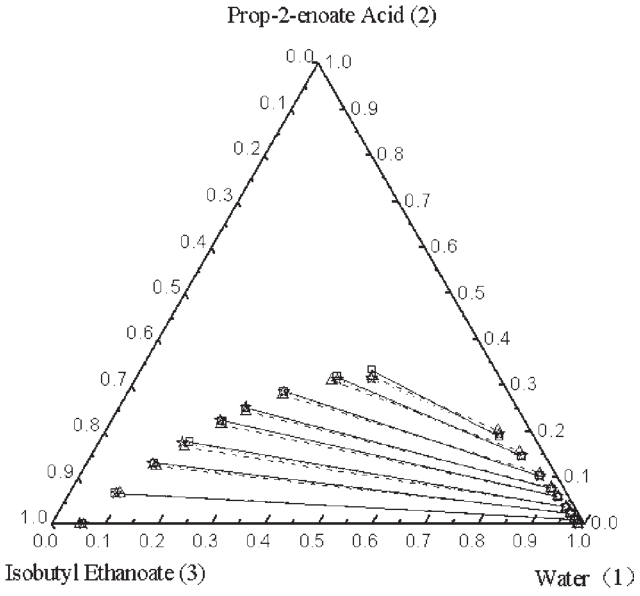

Figure 4. Ternary LLE phase diagram for the water (1) + prop-2-enoic acid (2) + isobutyl ethanoate (3) system at 303.15 K: □, solid lines, experimental data tie lines; △, dashed lines, tie lines calculated from NRTL; ☆, dotted lines, tie lines calculated from UNIQUAC.

values of the rmsd's of both models at each temperature are listed in Table 4. The rmsd is defined as

$$\text{rmsd} = \left(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(\frac{(w_{ijk}^{\text{calcd}} - w_{ijk}^{\text{exptl}})^2}{6n}\right)\right)^{1/2} \quad (8)$$

The ternary LLE phase diagrams for the water + prop-2-enoic acid + isobutyl ethanoate system at (293.15, 303.15, and 313.15) K are shown in Figures 3 to 5, respectively. These LLE phase diagrams compare the experimental results with the calculated binodal curve and tie-lines from the NRTL and UNIQUAC models. As can be seen, the results are good.

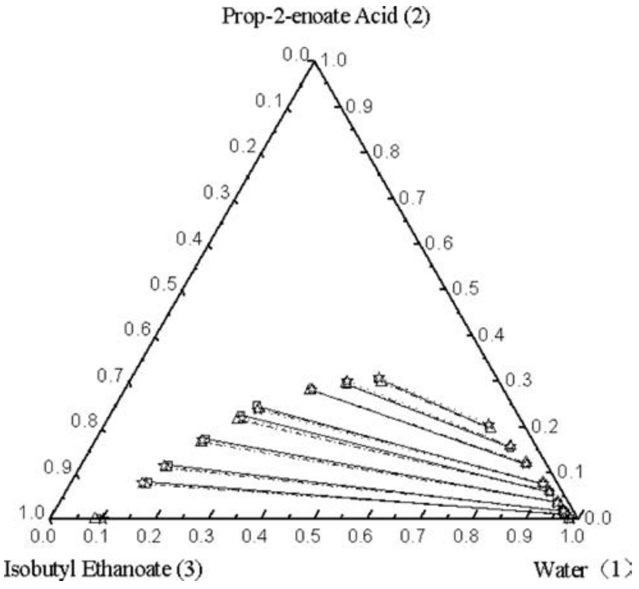

Figure 5. Ternary LLE phase diagram for the water (1) + prop-2-enoic acid (2) + isobutyl ethanoate (3) system at 313.15 K: □, solid lines, experimental data tie lines; △, dashed lines, tie lines calculated from NRTL; ☆, dotted lines, tie lines calculated from UNIQUAC.

■ CONCLUSIONS

LLE data for the ternary system of water + prop-2-enoic acid + isobutyl ethanoate at (293.15, 303.15, and 313.15) K at atmospheric pressure were measured. If all of the R^2 values of the Othmer–Tobias and Hand equations are no less than 0.9889, the values of standard deviation are all no more than 0.125. The reliability of the LLE data is acceptable. The LLE data and the separation factors of isobutyl ethanoate at different temperatures were compared. It is concluded that isobutyl ethanoate may serve as a feasible solvent to separate prop-2-enoic acid from aqueous solutions and a better extracting effect was obtained at lower temperatures.

The NRTL and UNIQUAC models were used to correlate the experimental data, and the interaction parameters of the models were obtained. The results show that those two models give a satisfactory representation of the tie-line values of the investigated system at different temperatures.

■ AUTHOR INFORMATION

Corresponding Author

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

■ REFERENCES

(1) Tao, Z. B. *Acrylic Acid and Acrylic Esters Production and Application*; Chemical Industry Press: Beijing, 2007.

(2) Chien, I. L.; Kuo, C. L. Investigating the need of a pre-concentrator column for acetic acid dehydration system via heterogeneous azeotropic distillation. *Chem. Eng. Sci.* **2006**, *61* (2), 569–585.

(3) Tolsma, J. E.; Barton, P. I. Computation of heteroazeotropes. Part I: Theory. *Chem. Eng. Sci.* **2000**, 55 (18), 3817–3834.

(4) Xu, W.; Diwekar, U. M. Environmentally Friendly Heterogeneous Azeotropic Distillation System Design: Integration of EBS Selection and IPS Recycling. *Ind. Eng. Chem. Res.* **2005**, *44* (11), 4061–4067.

(5) Luyben, W. L. Control of the Heterogeneous Azeotropic n-Butanol/Water Distillation System. *Energy Fuels* **2008**, *22* (6), 4249–4258.

(6) Font, A.; Asensi, J. C.; Ruiz, F.; Gomis, V. Application of Isooctane to the Dehydration of Ethanol. Design of a Column Sequence to Obtain Absolute Ethanol by Heterogeneous Azeotropic Distillation. *Ind. Eng. Chem. Res.* **2003**, *42* (1), 140–144.

(7) Ivonne, R. D.; Vincent, G.; Xavier, J. Heterogeneous Entrainer Selection for the Separation of Azeotropic and Close Boiling Temperature Mixtures by Heterogeneous Batch Distillation. *Ind. Eng. Chem. Res.* **2001**, *40* (22), 4935–4950.

(8) Moussa, A. S.; Jiménez, L. Entrainer Selection and Systematic Design of Heterogeneous Azeotropic Distillation Flowsheets. *Ind. Eng. Chem. Res.* **2006**, *45* (12), 4304–4315.

(9) Szanyi, A.; Mizsey, P.; Fonyo, Z. Optimization of Nonideal Separation Structures Based on Extractive Heterogeneous Azeotropic Distillation. *Ind. Eng. Chem. Res.* **2004**, *43* (26), 8269–8274.

(10) 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* (3), 659–662.

(11) Hengstermann, A.; Cameretti, L. Solvent Screening and Measurement of Phase Diagrams for the Yield Maximization of an Acrylic acid Crystallization. *J. Chem. Eng. Data* **2010**, *55* (11), 4597–4606.

(12) Olson, J. D.; Morrison, R. E.; Wilson, L. C. Thermodynamics of Hydrogen-Bonding Mixtures. 5. GE, HE, and TSE and Zeotropy of Water + Acrylic acid. *Ind. Eng. Chem. Res.* **2008**, *47* (15), 5127–5131.

(13) Cháfer, A.; Lladosa, E.; de la Torre, J.; Burguet, M. C. Study of liquid—liquid equilibrium of the systems isobutyl ethanoate + acetic acid + water and isobutyl alcohol + acetic acid + water at different temperatures. *Fluid Phase Equilib.* **2008**, *271* (1—2), 76–81.

(14) Procházka, J.; Heyberger, A. Correlation of ternary liquid—liquid equilibria in system isobutyl ethanoate-acetic acid-water. *Chem. Eng. Sci.* **1996**, *51* (6), 893–903.

(15) Othmer, D. F.; Tobias, P. E. The Line Correlation. *Ind. Eng. Chem.* **1942**, *34* (6), 693–700.

(16) Chen, Y.; Meng, Y.; Zhang, S.; Zhang, Y.; Liu, X.; Yang, J. Liquid—Liquid Equilibria of Aqueous Biphasic Systems Composed of 1-Butyl-3-methyl Imidazolium Tetrafluoroborate + Sucrose/Maltose + Water. *J. Chem. Eng. Data* **2010**, *55* (9), 3612–3616.

(17) França, B. B.; Pinto, F. M.; Pessoa, F. L. P.; Uller, A. M. C. Liquid—Liquid Equilibria for Castor Oil Biodiesel + Glycerol + Alcohol. *J. Chem. Eng. Data* **2009**, *54* (9), 2359–2364.

(18) Chen, Y.; Xiong, Z.; Liu, X.; et al. Measurements and Correlation of Liquid—Liquid Equilibria Containing Dimethyl Carbonate and Diethyl Carbonate at T = 298.15 K. *J. Chem. Eng. Data* **2010**, *55* (6), 2133–2139.

(19) Hand, D. B. The Distribution of Consolute Liquid between Two Immiscible Liquids. *J. Phys. Chem.* **1930**, *34* (9), 1961–2000.

(20) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14* (1), 135–144.

(21) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Party or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116–128.