Liquid−Liquid Equilibria for the Ternary Systems Water + 2-Propanol + Methyl Methacrylate, + Butyl Methacrylate, and + Isobutyl Methacrylate

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Liquid−liquid equilibrium (LLE) data for the systems water + 2-propanol + methyl methacrylate, butyl methacrylate, and isobutyl methacrylate were determined at atmospheric pressure over temperatures of 288.15 K and 318.15 K. From these new LLE data, we can find that very small amounts of the organic compounds were found in the aqueous phase, and water dissolved appreciably in the organic-rich phase, especially near the plait point. The reliability of the experimental tie-line data was determined through the Othmer−Tobias and Bachman plots. The experimental data were also compared with the values correlated by the NRTL and UNIQUAC models. Good quantitative agreement was obtained with these models. In general, the average deviations from the NRTL model are slightly smaller than those from the UNIQUAC model.

Introduction

Short-chain alcohols are widely used as co-emulsifiers in the emulsion polymerization of many acrylic resins. It is well-known that the influences of the mutual solubility of co-emulsifiers and monomers in water on the results of emulsion polymerization are very large, including the critical micelle concentration (CMC) of emulsifiers, the emulsified nucleation mechanism, and the reaction kinetics, etc. In our laboratory, we are interested in investigating the fundamental solubility properties of those co-emulsifiers and methacrylic monomers in water for the acrylic emulsion polymerization application. The focus of this paper is on liquid−liquid equilibria (LLE) for the systems of water + 2-propanol with one of three methacrylic monomers: methyl methacrylate, butyl methacrylate, and isobutyl methacrylate. The phase compositions of the two coexistent liquid phases are measured at temperatures of 288.15 K and 318.15 K and near the plait point of these investigated systems. No literature data were found at comparable conditions. The experimental tie-line data were correlated to test consistency with the Othmer−Tobias[1] and Bachman[2] equations. These new LLE data are also correlated with the NRTL[3] and the UNIQUAC[4] solution models. Good quantitative agreement was obtained with these models.

Experimental Section

Liquid−liquid equilibrium data for the ternary systems were measured by an apparatus similar to that of Peschke and Sandler,[5] which included a jacketed glass cell, a thermostatically controlled bath, a magnetic agitator, and a gas chromatograph. In the jacketed equilibrium glass cell (internal volume of about 20 cm^3), the thermostatic water was circulated to control the temperature of the cell within ± 0.1 K. The cell temperature was measured by a precision thermometer (model-1506, Hart Scientific, USA) with a platinum RTD probe to an uncertainty of ± 0.03 K. The prepared mixtures were introduced into the equilibrium cell and were agitated vigorously for at least 3 h to sufficiently mix the compounds and then settled for at least 8 h for complete phase separation. The sample of the organic-rich phase was carefully taken from the top sampling port of the cell with a syringe, and that of the water-rich phase was taken from a bottom sampling port of the cell. This operating method avoids cross contamination by the other phase during the sampling procedure.

Table 1. Average Deviations of GC Calibration Curves

mixture	phase	average deviations[a]
water + methyl methacrylate	organic	0.0016
	aqueous	0.0002
water + butyl methacrylate	organic	0.0019
	aqueous	0.0002
water + isobutyl methacrylate	organic	0.0019
	aqueous	0.0002
2-propanol + methyl methacrylate	organic	0.0017
	aqueous	0.0017
2-propanol + butyl methacrylate	organic	0.0019
	aqueous	0.0019
2-propanol + isobutyl methacrylate	organic	0.0012
	aqueous	0.0012

[a] Average deviations = $(1/n_p)\sum_{j=1}^{n_p}|x_{act} - x_{calb}|_j$, where n_p is the number of calibration points and x is the minor constituent compound. The subscripts act and calb represent the actual values and calibrated values, respectively.

The composition of the sample was analyzed by a gas chromatograph (GC) (model: 9800, China Chromatography Co., Taiwan) with a thermal conductivity detector (TCD) and using high purity helium (99.99 %) as a carrier gas. A stainless steel column packed with 10 % Porapak Qs 60/80 (2 m × 1/8 in.) can clearly separate the constituent compounds of the samples. Five samples were replicated for each phase at a fixed experimental condition, and the area fraction was converted into mole fraction by the calibration equations. Two calibration lines were previously constructed according to the organic-rich or the water-rich phases for each binary system. The deviations of the calibration curves from the actual values are tabulated in Table 1. The experimental mole fractions for each phase were obtained by averaging the results from these five replications. The uncertainty of reported mole fractions was estimated to be less than ± 1 %. Because no literature LLE data were available

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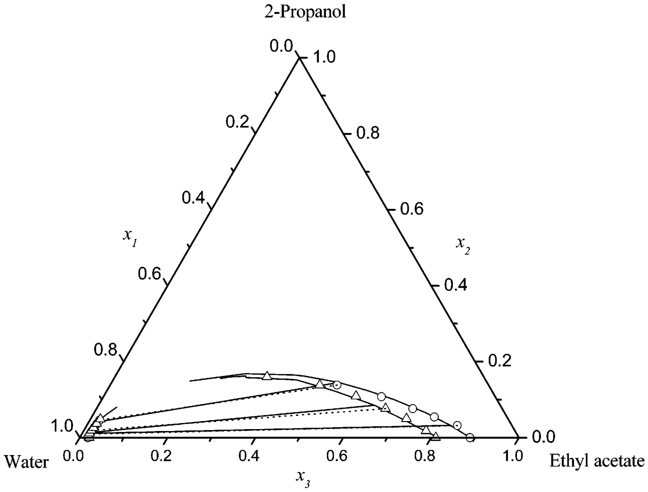

Figure 1. LLE phase diagram for water (1) + 2-propanol (2) + ethyl acetate (3): ○, this work at 283.15 K; △, this work at 323.15 K; —, ref 6 data and tie-line; ····, this work tie-line.

Table 2. LLE Data for Water (1) + 2-Propanol (2) + Methyl Methacrylate (3) at Atmospheric Pressure

	organic phase (I)			aqueous phase (II)		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
288.15	0.0559	0.0	0.9441	0.9969	0.0	0.0031
	0.0769	0.0305	0.8926	0.9801	0.0164	0.0035
	0.1274	0.0981	0.7746	0.9603	0.0359	0.0038
	0.1611	0.1308	0.7081	0.9539	0.0423	0.0038
	0.2181	0.1813	0.6006	0.9414	0.0545	0.0041
	0.3158	0.2265	0.4578	0.9261	0.0688	0.0051
	0.4035	0.2605	0.3360	0.9169	0.0772	0.0059
	0.4508	0.2646	0.2846	0.9128	0.0805	0.0066
	0.5349	0.2608	0.2043	0.9102	0.0823	0.0075
	0.6120	0.2440	0.1440	0.8957	0.0932	0.0111
318.15	0.0778	0.0	0.9222	0.9972	0.0	0.0028
	0.1076	0.0406	0.8518	0.9863	0.0107	0.0030
	0.1673	0.1111	0.7216	0.9718	0.0245	0.0037
	0.2062	0.1386	0.6552	0.9659	0.0301	0.0041
	0.2582	0.1865	0.5553	0.9574	0.0383	0.0043
	0.3448	0.2292	0.4260	0.9494	0.0456	0.0050
	0.4320	0.2549	0.3132	0.9366	0.0575	0.0059
	0.4747	0.2587	0.2666	0.9329	0.0604	0.0067
	0.5930	0.2445	0.1625	0.9091	0.0802	0.0107
	0.6691	0.2183	0.1127	0.9004	0.0865	0.0131

Table 3. LLE Data for Water (1) + 2-Propanol (2) + Butyl Methacrylate (3) at Atmospheric Pressure

	organic phase (I)			aqueous phase (II)		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
288.15	0.0513	0.0	0.9487	1.0000	0.0	0.0000
	0.0714	0.0603	0.8683	0.9735	0.0265	0.0000
	0.0746	0.1016	0.8238	0.9642	0.0358	0.0000
	0.0921	0.1633	0.7447	0.9456	0.0544	0.0000
	0.1160	0.2267	0.6573	0.9359	0.0642	0.0000
	0.1529	0.2891	0.5579	0.9229	0.0772	0.0000
	0.1893	0.3370	0.4737	0.9156	0.0844	0.0000
	0.2325	0.3640	0.4035	0.9083	0.0917	0.0000
	0.2844	0.3877	0.3279	0.9018	0.0982	0.0000
	0.3082	0.3904	0.3014	0.8993	0.1007	0.0000
318.15	0.0642	0.0	0.9358	1.0000	0.0	0.0000
	0.0886	0.0777	0.8338	0.9820	0.0180	0.0000
	0.0918	0.1144	0.7938	0.9741	0.0259	0.0000
	0.1155	0.1824	0.7021	0.9644	0.0356	0.0000
	0.1386	0.2371	0.6243	0.9568	0.0432	0.0000
	0.1784	0.2972	0.5245	0.9466	0.0534	0.0000
	0.2156	0.3378	0.4466	0.9369	0.0631	0.0000
	0.2640	0.3606	0.3755	0.9296	0.0704	0.0000
	0.3129	0.3790	0.3080	0.9244	0.0756	0.0000
	0.3396	0.3812	0.2792	0.9216	0.0784	0.0000

Table 4. LLE Data for Water (1) + 2-Propanol (2) + Isobutyl Methacrylate (3) at Atmospheric Pressure

	organic phase (I)			aqueous phase (II)		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
288.15	0.0480	0.0	0.9520	1.0000	0.0	0.0000
	0.0708	0.0656	0.8636	0.9728	0.0272	0.0000
	0.0721	0.1008	0.8270	0.9637	0.0363	0.0000
	0.0880	0.1528	0.7592	0.9455	0.0545	0.0000
	0.1149	0.2219	0.6632	0.9366	0.0634	0.0000
	0.1563	0.2890	0.5548	0.9234	0.0767	0.0000
	0.1968	0.3350	0.4682	0.9153	0.0847	0.0000
	0.2393	0.3625	0.3983	0.9077	0.0923	0.0000
	0.2911	0.3858	0.3231	0.9032	0.0968	0.0000
	0.3107	0.3888	0.3005	0.9024	0.0976	0.0000
318.15	0.0741	0.0	0.9259	1.0000	0.0	0.0000
	0.0851	0.0832	0.8317	0.9820	0.0180	0.0000
	0.0909	0.1200	0.7892	0.9739	0.0262	0.0000
	0.1203	0.1813	0.6984	0.9647	0.0353	0.0000
	0.1424	0.2373	0.6202	0.9550	0.0450	0.0000
	0.1857	0.2958	0.5185	0.9469	0.0531	0.0000
	0.2223	0.3373	0.4404	0.9379	0.0621	0.0000
	0.2510	0.3614	0.3876	0.9315	0.0685	0.0000
	0.3212	0.3782	0.3006	0.9238	0.0762	0.0000
	0.3678	0.3839	0.2483	0.9140	0.0860	0.0000

at comparable conditions for those ternary systems above, the LLE measurements of the water + 2-propanol + ethyl acetate system were conducted to test the validity of our experimental procedure. Figure 1 compares the experimental results with the literature values.[6] It shows that our measurements agree with literature values within the experimental uncertainties.

2-Propanol was obtained from Fluka Chemicals (Germany). Methyl methacrylate was supplied by Showa Chemical Co. Ltd. Butyl methacrylate was purchased from Alfa Aesar. Isobutyl methacrylate was obtained from Acros Organics. Deionized distilled water was prepared in our laboratory. The purities of these liquids were greater than 99 %. All the chemicals were used without further purification.

Experimental Results

The LLE measurements were made at temperatures of 288.15 K and 318.15 K under atmospheric pressure. Tables 2 to 4 list the experimental results for water + 2-propanol with methyl methacrylate, butyl methacrylate, and isobutyl methacrylate, respectively. The superscript I represents the organic-rich phase and II represents the aqueous phase. Figures 2 to 4 are the phase diagrams for the ternary systems of water + 2-propanol + methyl methacrylate, water + 2-propanol + butyl methacrylate, and water + 2-propanol + isobutyl methacrylate at 288.15 K, respectively. Because water + methacrylic is the only pair that is partially miscible, all investigated ternary systems behave as type 1 of LLE. Very small amounts of the organic compounds were found in the aqueous phase, whereas water dissolved appreciably in the organic-rich phase, especially near the plait point. The experimental results show that the magnitude of solubility of water in methyl methacrylate is greater than in butyl methacrylate or in isobutyl methacrylate at the same conditions. The areas of the two-phase region, therefore, decrease in the mixture containing methyl methacrylate > butyl methacrylate or isobutyl methacrylate.

Consistency of Experimental Tie-Line Data

In this study, the Othmer−Tobias correlation (eq 1) and the Bachman correlation (eq 2) were used to ensure the quality of the obtained experimental tie-line data, where w_{11} is the mass fraction of water in the aqueous phase; w_{32} is the mass fraction of methacrylic in the organic-rich phase; and *A*, *B*, *A*′, and *B*′ are the parameters of the Othmer−Tobias correlation and the

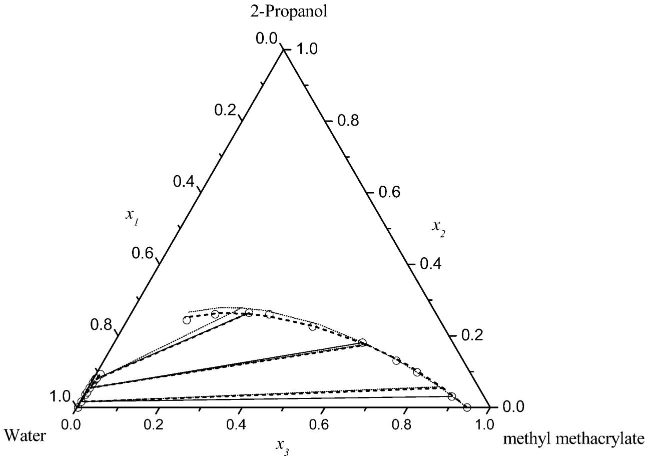

Figure 2. LLE phase diagram for water (1) + 2-propanol (2) + methyl methacrylate (3) at 288.15 K: ○, exptl data; —, exptl tie-line; ----, NRTL correlation; ····, UNIQUAC correlation.

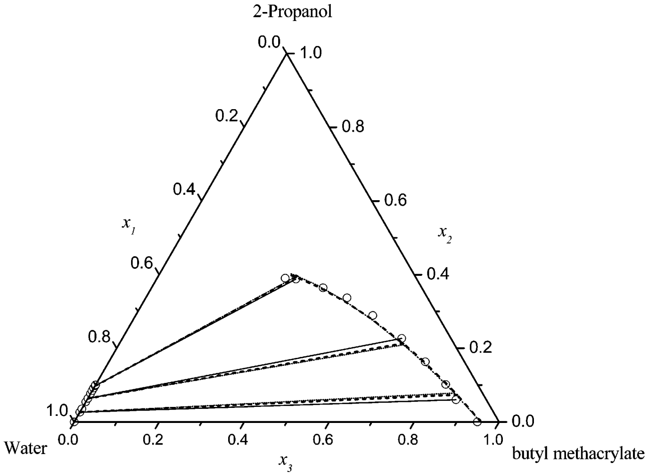

Figure 3. LLE phase diagram for water (1) + 2-propanol (2) + butyl methacrylate (3) at 288.15 K: ○, exptl data; —, exptl tie-line; ----, NRTL correlation; ····, UNIQUAC correlation.

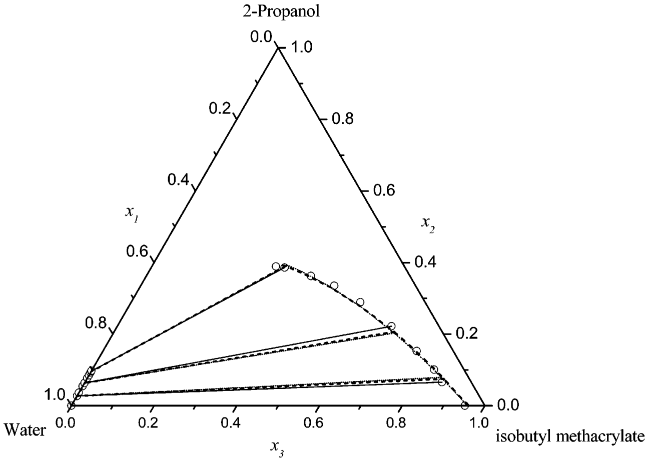

Figure 4. LLE phase diagram for water (1) + 2-propanol (2) + isobutyl methacrylate (3) at 288.15 K: ○, exptl data; —, exptl tie line; ----, NRTL correlation; ····, UNIQUAC correlation.

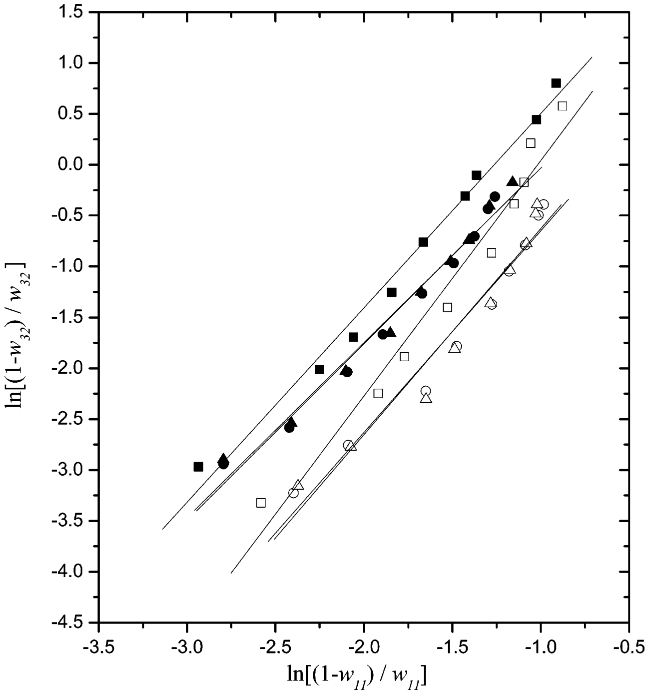

Figure 5. Othmer−Tobias correlations for three investigated systems at different temperatures: □, methyl methacrylate at 288.15 K; ■, methyl methacrylate at 318.15 K; ○, butyl methacrylate at 288.15 K; ●, butyl methacrylate at 318.15 K; △, isobutyl methacrylate at 288.15 K; ▲, isobutyl methacrylate at 318.15 K; —, Othmer−Tobias correlation.

Table 5. Constants of Othmer−Tobias and Bachman Equations System

	Othmer−Tobias			Bachman		
T/K	*A*	*B*	*σ*	*A*′	*B*′	*σ*
Water (1) + 2-Propanol (2) + Methyl Methacrylate (3)						
288.15	2.3577	2.3157	0.2429	−0.2093	1.0641	0.0375
318.15	2.4136	1.9100	0.1433	−0.1896	1.0955	0.0226
Water (1) + 2-Propanol (2) + Butyl Methacrylate (3)						
288.15	1.3314	1.9808	0.1990	−0.5280	1.3463	0.0446
318.15	1.7066	1.7335	0.1314	−0.4312	1.3310	0.0238
Water (1) + 2-Propanol (2) + Isobutyl Methacrylate (3)						
288.15	1.4014	2.0269	0.2335	−0.4836	1.3024	0.0443
318.15	1.6867	1.7171	0.1364	−0.4120	1.3110	0.0239

Bachman correlation, respectively. The correlation parameters and the standard deviations σ were determined by the least-squares method by a Marquardt algorithm. The correlated results are represented in Table 5. The Othmer−Tobias and Bachman plots are also shown in Figures 5 and 6, respectively, for those three investigated systems. Because very small amounts of the organic compounds were found in the aqueous phase, the Othmer−Tobias equation is very sensitive to those LLE data. In Table 5, we can find that the standard deviations from the Othmer−Tobias correlation are larger than those from the Bachman correlation. As seen from Figures 5 and 6, the linearity of the plot reveals the degree of consistency of measured LLE data in this study.

$$\ln\left(\frac{1-w_{32}}{w_{32}}\right) = A + B\ln\left(\frac{1-w_{11}}{w_{11}}\right) \quad \text{Othmer−Tobias correlation} \quad (1)$$

$$w_{32} = A' + B'(w_{32}/w_{11}) \quad \text{Bachman correlation} \quad (2)$$

LLE Calculation

At liquid−liquid equilibrium, the mole fractions x_i^{I} and x_i^{II} of two coexistent liquid phases can be calculated using the following criteria (eq 3) together with the material balance equation.

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \quad (3)$$

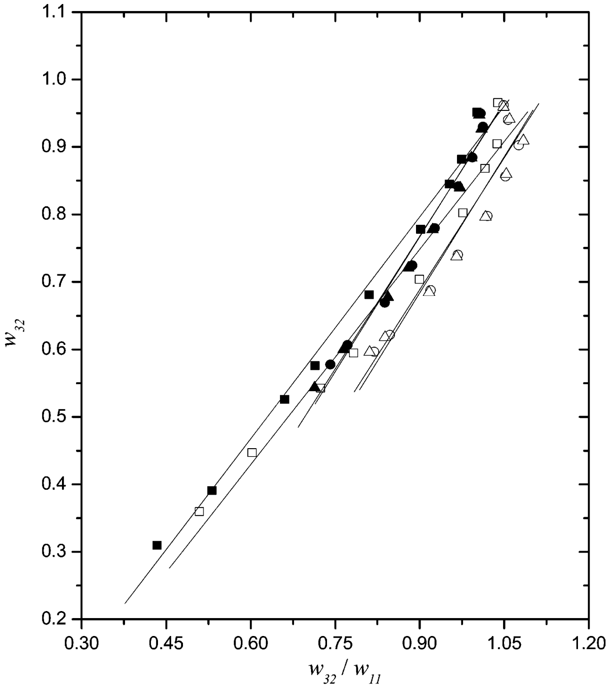

Figure 6. Bachman correlations for three investigated systems at different temperatures: □, methyl methacrylate at 288.15 K; ■, methyl methacrylate at 318.15 K; ○, butyl methacrylate at 288.15 K; ●, butyl methacrylate at 318.15 K; △, isobutyl methacrylate at 288.15 K; ▲, isobutyl methacrylate at 318.15 K; —, Bachman correlation.

where γ_i^{I} and γ_i^{II} are the activity coefficients of component i in phases I and II, respectively. The calculation procedure was detailed in Walas.[7] On the basis of 1 mol of feed with total composition z_i, the compositions of the coexistent liquid phases are solved simultaneously from the following equations

$$1 - \sum_{i=1}^{n_c} \frac{z_i}{\beta + K_i(1 - \beta)} = 0 \qquad (4)$$

with

$$K_i = x_i^{\mathrm{II}}/x_i^{\mathrm{I}} = \gamma_i^{\mathrm{I}}/\gamma_i^{\mathrm{II}} \qquad (5)$$

where n_c is the number of components; K_i is the distribution ratio for component i; β is the fraction of the total material that is present in the first liquid phase (the organic-rich phase); and the activity coefficient γ_i can be calculated from a solution model. In this paper, the isothermal ternary LLE data were correlated with the NRTL and the UNIQUAC models by adjusting six model parameters simultaneously. The objective function Δ of the parameter determination is defined as

$$\Delta = \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \left| (x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}}) \right| \right) / 6n \qquad (6)$$

where n is the number of tie-lines and x_{ijk}^{calcd} and x_{ijk}^{obsd} are the calculated and the observed mole fractions of component i in phase j on tie-line k, respectively. Tables 6 and 7 present the correlated results from the NRTL and the UNIQUAC models, respectively. In general, the average deviations from the NRTL model are slightly smaller than those from the UNIQUAC model. The value of overall average deviations from NRTL correlations for the three investigated systems is 0.0040, and that from UNIQUAC correlations is 0.0063, respectively. Figures 2 to 4 also compare the calculated binodal locus and tie-lines from the NRTL and UNIQUAC models with the experimental results. As seen from Figures 2 to 4, good agreements between the calculated results from the solution models and experimental values have been obtained for the three investigated systems.

Table 6. Correlated Results from the NRTL Model

mixture[a]	T/K	α_{ij}[b]	$i-j$	a_{ij}[c]/K	a_{ji}[c]/K	Δ[d]
M1	288.15	0.2	1−2	1505.32	−650.88	0.0044
			1−3	1596.68	373.00	
			2−3	−200.65	448.00	
	318.15	0.2	1−2	1560.60	−657.35	0.0028
			1−3	1507.07	309.32	
			2−3	−283.77	512.92	
M2	288.15	0.2	1−2	868.18	−216.83	0.0036
			1−3	2496.72	537.02	
			2−3	−3.59	397.13	
	318.15	0.2	1−2	1168.09	−348.31	0.0045
			1−3	2379.46	485.20	
			2−3	68.19	237.09	
M3	288.15	0.2	1−2	902.00	−238.13	0.0044
			1−3	2547.89	555.58	
			2−3	8.56	391.04	
	318.15	0.2	1−2	1093.92	−312.90	0.0043
			1−3	2318.33	460.75	
			2−3	−48.10	351.90	

[a] M1: water (1) + 2-propanol (2) + methyl methacrylate (3). M2: water (1) + 2-propanol (2) + butyl methacrylate (3). M3: water (1) + 2-propanol (2) + isobutyl methacrylate (3). [b] α is the nonrandomness parameter in the NRTL model. [c] $a_{ij} = (g_{ij} - g_{jj})/R$ is a parameter of the NRTL model. [d] $\Delta = (\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} |(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|)/6n$, where n is the number of tie-lines.

Table 7. Correlated Results from the UNIQUAC Model

mixture[a]	T/K	i−j	b_{ij}[b]/K	b_{ji}[b]/K	Δ[c]
M1	288.15	1−2	−486.67	212.32	0.0075
		1−3	−206.24	−479.85	
		2−3	107.68	−337.41	
	318.15	1−2	−639.49	268.53	0.0069
		1−3	−218.87	−499.30	
		2−3	127.31	−368.47	
M2	288.15	1−2	−313.09	124.70	0.0045
		1−3	−297.39	−516.76	
		2−3	153.27	−418.78	
	318.15	1−2	−18.38	−258.76	0.0068
		1−3	48.13	−839.23	
		2−3	80.11	−264.09	
M3	288.15	1−2	−323.84	130.78	0.0057
		1−3	−285.39	−527.65	
		2−3	154.83	−424.91	
	318.15	1−2	−8.72	−254.97	0.0063
		1−3	37.63	−813.37	
		2−3	108.78	−299.83	

	structural parameters[8]	
component	r	q
water	0.9200	1.400
2-propanol	3.2491	3.124
methyl methacrylate	4.2995	3.884
butyl methacrylate	6.3227	5.504
isobutyl methacrylate	6.3219	5.500

[a] M1: water (1) + 2-propanol (2) + methyl methacrylate (3). M2: water (1) + 2-propanol (2) + butyl methacrylate (3). M3: water (1) + 2-propanol (2) + isobutyl methacrylate (3). [b] $b_{ij} = (u_{ij} - u_{jj})/R$ is a parameter of the UNIQUAC model. [c] $\Delta = (\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} |(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|)/6n$, where n is the number of tie-lines.

Conclusions

Liquid−liquid equilibrium (LLE) data for the systems water + 2-propanol + methyl methacrylate, butyl methacrylate, and isobutyl methacrylate were determined at atmospheric pressure over temperatures of 288.15 K and 318.15 K. All the investigated systems formed type 1 phase diagrams of LLE. The two-phase region decreased in the mixture containing methyl methacrylate > butyl methacrylate or isobutyl methacrylate. In general, the binodal locus and tie-lines of LLE could be correlated well with the NRTL and the UNIQUAC models in this research.

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