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Liquid–Liquid Equilibria for Ternary Mixtures of Water + Ethanol with 1-Hexanol, Butyl Propionate, or Ethyl Caproate

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Liquid–liquid equilibrium (LLE) data were measured for the ternary mixtures of water + ethanol + 1-hexanol, water + ethanol + butyl propionate, and water + ethanol + ethyl caproate at atmospheric pressure over a temperature range of 283.15 K to 323.15 K. All three ternary systems exhibit type I behavior of LLE. The area of the two-phase region decreases with increasing temperature for each ternary system; its magnitude follows the order of the mixtures containing ethyl caproate > butyl propionate > 1-hexanol. The NRTL and the UNIQUAC models correlated the LLE data very well, except for the region near the plait point. The NRTL model is generally better than the UNIQUAC model for representing the LLE behavior for the three investigated systems.

Introduction

Ethanol (or ethyl alcohol, EtOH) is a well-known solvent with many uses. It can also be used as an automotive fuel or blended with gasoline. Because an ethanol molecule contains an oxygen atom, it facilitates more complete combustion, resulting in cleaner emissions. There are various resources to produce ethanol. One of the common ways is to recover ethanol from a fermentation broth, followed by distillation. Unfortunately, its purity would be limited to the azeotropic composition of the mixture of ethanol + water, that is, 0.95 mole fraction ethanol. Heterogeneous azeotropic distillation¹ has been suggested as a potential solution to the problem to produce high-purity ethanol. The related phase equilibrium data are fundamentally important to simulation and design of such separation processes. In the present study, the liquid–liquid equilibrium (LLE) data are measured for the ternary mixtures of water + ethanol with one of three potential entrainers: 1-hexanol, butyl propionate, and ethyl caproate at temperatures from 283.15 K to 323.15 K. No literature data were found for these ternary mixtures at comparable conditions. The new LLE data are correlated with the NRTL² and the UNIQUAC³ models.

Experimental Section

Materials. Butyl propionate (99+ mass %) and ethyl caproate (99+ mass %) were purchased from Aldrich, USA. 1-Hexanol (99+ mass %) was supplied by Fluka, USA. Ethanol (99.5 mass %) was purchased from Shimadzu, Japan. Deionized distilled water was prepared in our laboratory. No impurity peak was detected in the chromatographic analysis of any of the chemicals. These chemicals were used without further purification.

Apparatus and Procedures. The LLE apparatus used in this work is similar to that of Peschke and Sandler.⁴ The equilibrium cell is made of glass with a jacket in which thermostatic water is circulated to control the temperature of the cell within ± 0.1 K. The internal volume of the equilibrium cell is about 30 cm³. The cell temperature was

Table 1. Uncertainties of Composition Analysis

mixture	phase	average deviation ^a
water + 1-hexanol	organic	0.0018
	aqueous	0.0002
water + butyl propionate	organic	0.0026
	aqueous	0.0002
water + ethyl caproate	organic	0.0025
	aqueous	0.0001
ethanol + 1-hexanol	organic	0.0014
	aqueous	0.0014
ethanol + butyl propionate	organic	0.0021
	aqueous	0.0021
ethanol + ethyl caproate	organic	0.0023
	aqueous	0.0023

^a Average deviation = $(1/n_p) \sum_{j=1}^{n_p} (|x^{\text{calb}} - x^{\text{act}}|)_j$, where n_p is the number of calibration points and x is the mole fraction of the minor constituent compound. The superscript “calb” represents the calibrated values, and “act” refers to the actual values.

measured by a precision thermometer (model-1506, Hart Scientific, USA) with a platinum RTD probe accurate to within ± 0.02 K. A magnetic stirrer vigorously agitated the liquid mixture in the cell. For each run, the contents were agitated longer than 4 h to thoroughly mix the compounds. The mixture was allowed to settle for at least 8 h to completely separate the two liquid phases. A sample of the organic-rich phase was taken with a syringe from the top opening of the cell and the water-rich phase was sampled from the sampling port at the bottom of the cell to avoid cross contamination by the other phase during the sampling procedure.

The composition of samples was analyzed with gas chromatography (model 8700, China Chromatography Co., Taiwan) with a thermal conductivity detector. High-purity helium (99.99%) was used as a carrier gas. A stainless steel column packed with 10% Porapak Qs 80/100 (2 m \times 1/8 in.) can suitably separate the constituent compounds. Calibrations were made with gravimetrically prepared samples in two composition ranges, in accordance with those in the organic-rich and the water-rich phases for each aqueous binary system. The uncertainties of sample analysis for the minor components are tabulated in Table 1.

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Table 2. LLE Data for Water (1) + Ethanol (2) + 1-Hexanol (3) at Atmospheric Pressure

<i>T</i> /K	organic phase			aqueous phase		
	x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
283.15	0.2795	0.0000	0.7205	0.9987	0.0000	0.0013
	0.2882	0.0512	0.6606	0.9799	0.0187	0.0014
	0.3126	0.0826	0.6048	0.9644	0.0341	0.0015
	0.3234	0.1316	0.5450	0.9444	0.0539	0.0017
	0.3690	0.2074	0.4236	0.9281	0.0699	0.0020
	0.4140	0.2491	0.3369	0.8897	0.1078	0.0025
	0.4794	0.2815	0.2391	0.8687	0.1286	0.0027
	0.5206	0.2912	0.1882	0.8514	0.1445	0.0041
	0.3052	0.0000	0.6948	0.9989	0.0000	0.0011
	0.3199	0.0586	0.6215	0.9746	0.0241	0.0013
308.15	0.3355	0.0992	0.5653	0.9690	0.0296	0.0014
	0.3599	0.1527	0.4874	0.9498	0.0483	0.0019
	0.4189	0.2092	0.3719	0.9247	0.0732	0.0021
	0.4791	0.2413	0.2796	0.9050	0.0925	0.0025
	0.5475	0.2593	0.1932	0.8796	0.1157	0.0047
	0.6082	0.2570	0.1348	0.8502	0.1392	0.0106
	0.3175	0.0000	0.6825	0.9991	0.0000	0.0009
	0.3298	0.0534	0.6168	0.9830	0.0159	0.0011
	0.3277	0.1104	0.5619	0.9711	0.0277	0.0012
	0.3776	0.1511	0.4713	0.9533	0.0452	0.0015
323.15	0.4556	0.2060	0.3384	0.9297	0.0682	0.0021
	0.5365	0.2225	0.2410	0.8896	0.1078	0.0026
	0.5760	0.2455	0.1785	0.8850	0.1109	0.0041
	0.7041	0.2080	0.0879	0.8497	0.1445	0.0058

Table 3. LLE Data for Water (1) + Ethanol (2) + Butyl Propionate (3) at Atmospheric Pressure

<i>T</i> /K	organic phase			aqueous phase		
	x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
283.15	0.0323	0.0000	0.9677	0.9997	0.0000	0.0003
	0.0470	0.0643	0.8887	0.9296	0.0697	0.0007
	0.0733	0.1371	0.7896	0.8628	0.1365	0.0007
	0.1120	0.2257	0.6623	0.8348	0.1639	0.0013
	0.1694	0.2978	0.5328	0.8258	0.1722	0.0020
	0.2236	0.3409	0.4355	0.7986	0.1966	0.0048
	0.3180	0.3807	0.3013	0.7648	0.2241	0.0111
	0.3786	0.3824	0.2390	0.7430	0.2404	0.0166
	0.4302	0.3772	0.1926	0.7236	0.2544	0.0220
	0.0527	0.0000	0.9473	0.9999	0.0000	0.0001
308.15	0.0733	0.0545	0.8722	0.9697	0.0296	0.0007
	0.0829	0.1310	0.7861	0.9267	0.0700	0.0033
	0.1348	0.2182	0.6470	0.8717	0.1229	0.0054
	0.1994	0.2978	0.5028	0.8355	0.1583	0.0062
	0.2970	0.3605	0.3425	0.8165	0.1757	0.0078
	0.3863	0.3731	0.2406	0.7792	0.2065	0.0143
	0.4329	0.3705	0.1966	0.7572	0.2236	0.0192
	0.4893	0.3698	0.1409	0.7097	0.2566	0.0337
	0.0611	0.0000	0.9389	0.9997	0.0000	0.0003
	0.0927	0.0665	0.8408	0.9659	0.0338	0.0003
323.15	0.1101	0.1486	0.7413	0.9223	0.0770	0.0007
	0.1826	0.2423	0.5751	0.8905	0.1080	0.0015
	0.2246	0.2965	0.4789	0.8607	0.1362	0.0031
	0.2707	0.3264	0.4029	0.8440	0.1524	0.0036
	0.3849	0.3459	0.2692	0.8107	0.1816	0.0077
	0.4574	0.3514	0.1912	0.7748	0.2109	0.0143
	0.4810	0.3537	0.1653	0.7560	0.2239	0.0201

Experimental Results

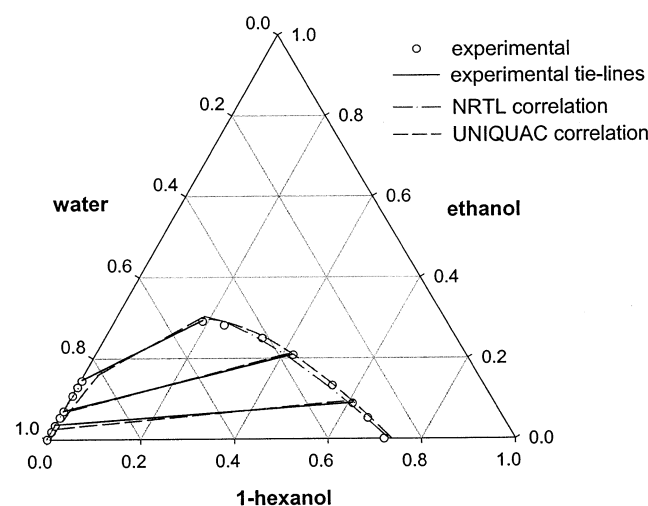
The LLE measurements were made at temperatures from 283.15 K to 323.15 K at atmospheric pressure. Tables 2–4 list the experimental results for the two-phase ternary systems of water + ethanol with 1-hexanol, butyl propionate, and ethyl caproate, respectively. The superscript I represents the organic-rich phase, and II is the aqueous phase. Five samples were taken for each phase at each experimental condition. The reported data are the average of replicate measurements. The repeatability is generally within 0.2%. Figures 1–4 show the phase diagrams for the ternary systems of water + ethanol + 1-hexanol, water + ethanol + butyl propionate, and water + ethanol + ethyl

Table 4. LLE Data for Water (1) + Ethanol (2) + Ethyl Caproate (3) at Atmospheric Pressure

<i>T</i> /K	organic phase			aqueous phase		
	x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
283.15	0.0227	0.0000	0.9773	0.9999	0.0000	0.0001
	0.0405	0.0845	0.8750	0.9326	0.0668	0.0006
	0.0745	0.1914	0.7341	0.8854	0.1135	0.0011
	0.1192	0.2654	0.6154	0.8560	0.1423	0.0017
	0.1708	0.3395	0.4897	0.8210	0.1759	0.0031
	0.2155	0.3770	0.4075	0.7964	0.1988	0.0048
	0.2787	0.4035	0.3178	0.7768	0.2153	0.0079
	0.3497	0.4167	0.2336	0.7388	0.2457	0.0155
	0.4355	0.4131	0.1514	0.7012	0.2798	0.0190
	0.0548	0.0000	0.9452	0.9999	0.0000	0.0001
308.15	0.0619	0.0713	0.8668	0.9666	0.0325	0.0009
	0.1035	0.1778	0.7187	0.9235	0.0753	0.0012
	0.1504	0.2818	0.5678	0.8887	0.1100	0.0013
	0.2133	0.3490	0.4377	0.8492	0.1464	0.0044
	0.2621	0.3806	0.3573	0.8244	0.1679	0.0077
	0.3104	0.3994	0.2902	0.7911	0.1976	0.0113
	0.3824	0.4057	0.2119	0.7446	0.2313	0.0241
	0.4709	0.3935	0.1356	0.6784	0.2870	0.0346
	0.0630	0.0000	0.9370	1.0000	0.0000	0.0000
	0.0752	0.0834	0.8414	0.9592	0.0406	0.0002
323.15	0.1061	0.1711	0.7228	0.9080	0.0914	0.0006
	0.1354	0.2294	0.6352	0.8822	0.1167	0.0011
	0.1664	0.3000	0.5336	0.8563	0.1419	0.0018
	0.2121	0.3515	0.4364	0.8297	0.1670	0.0033
	0.2699	0.3790	0.3511	0.8124	0.1817	0.0059
	0.3383	0.3932	0.2685	0.7863	0.2052	0.0085
	0.3929	0.3935	0.2136	0.7488	0.2323	0.0189
	0.4839	0.3727	0.1434	0.7140	0.2586	0.0274

caproate. Because water + entrainer is the only pair that is partially miscible, all the investigated ternary LLE systems behave as type I systems. While the amount of organic material is very minute in the aqueous phase, water dissolves appreciably in the organic-rich phase. The experimental results also show that the solubility of water in the entrainers increases with an increase of temperature, and the magnitude of solubility of water in the entrainers follows the order of 1-hexanol > butyl propionate > ethyl caproate at the same conditions. The area of the two-phase region, therefore, is narrower at higher temperatures for each ternary system, and its magnitude is in the sequence of the mixtures containing ethyl caproate > butyl propionate > 1-hexanol.

To estimate the capability of the auxiliary agents for separation of ethanol from aqueous solutions at LLE, the separation factors (*S*) were calculated for each system. The

**Figure 1.** LLE phase diagram for water + ethanol + 1-hexanol at 283.15 K.

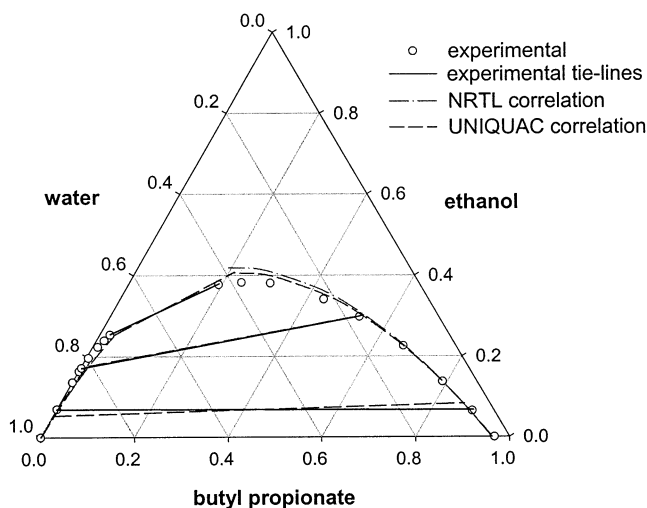


Figure 2. LLE phase diagram for water + ethanol + butyl propionate at 283.15 K.

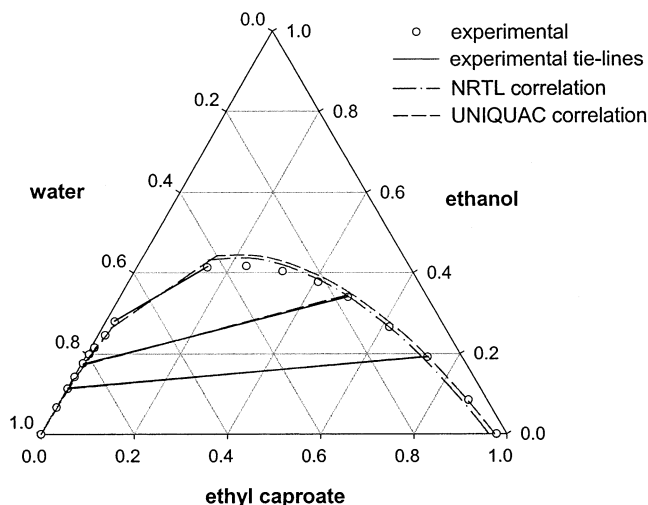


Figure 3. LLE phase diagram for water + ethanol + ethyl caproate at 283.15 K.

separation factor is defined as

$$S = \frac{X_{\text{EtOH}}^{\text{I}}(1 - X_{\text{EtOH}}^{\text{II}})}{X_{\text{EtOH}}^{\text{II}}(1 - X_{\text{EtOH}}^{\text{I}})} \quad (1)$$

with

$$X_{\text{EtOH}}^{\text{I}} = \frac{x_{\text{EtOH}}^{\text{I}}}{x_{\text{EtOH}}^{\text{I}} + x_{\text{W}}^{\text{I}}} \quad (\text{in the organic phase}) \quad (2)$$

$$X_{\text{EtOH}}^{\text{II}} = \frac{x_{\text{EtOH}}^{\text{II}}}{x_{\text{EtOH}}^{\text{II}} + x_{\text{W}}^{\text{II}}} \quad (\text{in the aqueous phase}) \quad (3)$$

where X_{EtOH} represents the mole fraction of ethanol on an entrainer-free basis. Figure 5 presents the variations of both $X_{\text{EtOH}}^{\text{I}}$ and the separation factor S with $X_{\text{EtOH}}^{\text{II}}$ for water + ethanol + 1-hexanol, water + ethanol + butyl propionate, and water + ethanol + ethyl caproate at 308.15 K. It shows that ethyl caproate gives the highest separation factor.

LLE Calculations

At liquid–liquid equilibrium, the compositions of two coexisting liquid phases can be calculated from the criteria

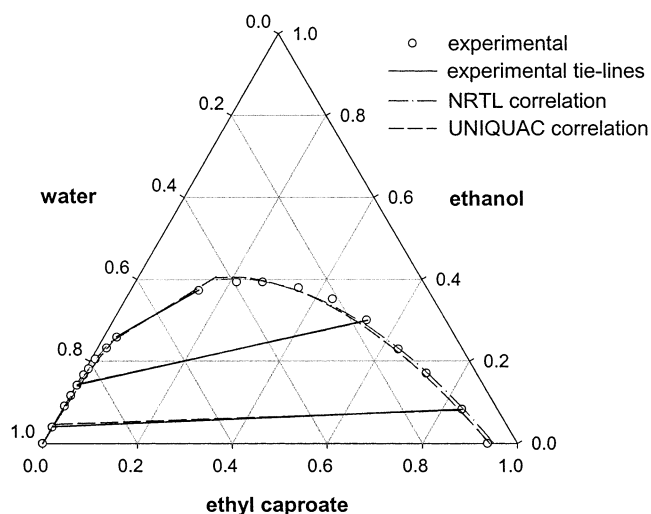


Figure 4. LLE phase diagram for water + ethanol + ethyl caproate at 323.15 K.

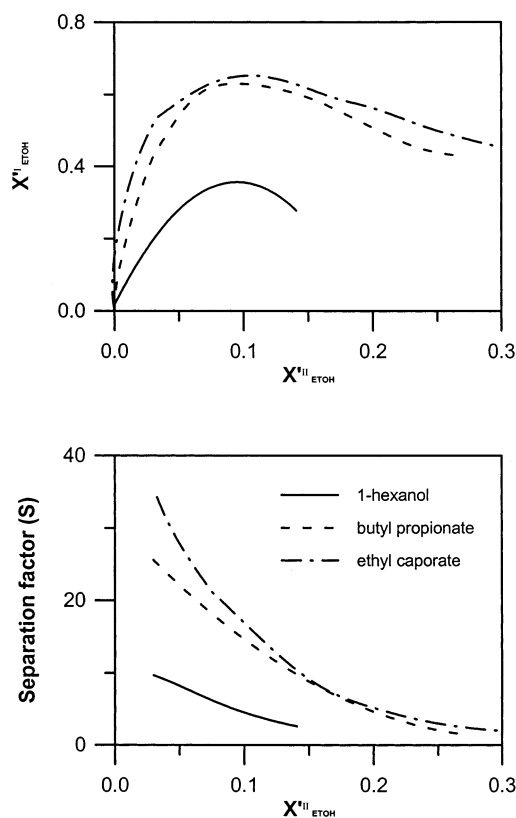


Figure 5. Separation factors and distributions of ethanol in two liquid phases at 308.15 K.

of LLE (equality of the constituent fugacities between the coexistent phases) together with the material balance equation. The calculation procedure was detailed in Walas.⁵ 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:

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

with

$$K_i = x_i^{\text{II}}/x_i^{\text{I}} = \gamma_i^{\text{I}}/\gamma_i^{\text{II}} \quad (5)$$

Table 5. Correlated Results from the NRTL Model

mixture ^a	<i>T</i> /K	α_{ij}	<i>i</i> – <i>j</i>	a_{ij}^b /K	a_{ji}^b /K	Δ^c
M1	283.15	0.2946	1–2	505.45	–6.85	0.0063
		0.2	1–3	2969.61	72.44	
		0.2	2–3	0.12	481.22	
	308.15	0.2946	1–2	505.45	–6.85	0.0062
		0.2	1–3	4196.38	269.10	
		0.2	2–3	13.81	367.34	
	323.15	0.2946	1–2	505.45	–6.85	0.0080
		0.2	1–3	4648.81	331.84	
		0.2	2–3	13.70	355.46	
M2	283.15	0.2946	1–2	505.45	–6.85	0.0176
		0.2	1–3	1926.97	487.64	
		0.2	2–3	–127.35	679.25	
	308.15	0.2946	1–2	505.45	–6.85	0.0083
		0.2	1–3	2243.32	369.66	
		0.2	2–3	–85.48	612.23	
	323.15	0.2946	1–2	505.45	–6.85	0.0094
		0.2	1–3	2283.12	362.02	
		0.2	2–3	–171.36	614.17	
M3	283.15	0.2946	1–2	505.45	–6.85	0.0094
		0.2	1–3	2361.13	538.33	
		0.2	2–3	1.40	458.96	
	308.15	0.2946	1–2	505.45	–6.85	0.0106
		0.2	1–3	2870.27	519.54	
		0.2	2–3	4.74	280.52	
	323.15	0.2946	1–2	505.45	–6.85	0.0076
		0.2	1–3	3316.05	637.88	
		0.2	2–3	–3.40	424.28	

^a M1, water (1) + ethanol (2) + 1-hexanol (3); M2, water (1) + ethanol (2) + butyl propionate (3); M3, water (1) + ethanol (2) + ethyl caproate (3). ^b $a_{ij} = (g_{ij} - g_{ji})/R$, where g_{ij} is the interaction energy between the *i*–*j* pair and *R* is the gas constant; the parameters of the 1–2 pair were taken from the literature (ref 6). ^c $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$, where *n* is the number of tie-lines.

where β is the fraction of the total material that is present in the first liquid phase (the organic-rich phase), n_c is the number of components, and K_i is the distribution ratio for component *i*. The activity coefficient γ_i is calculated from a solution model. Among several others, the NRTL and the UNIQUAC models have commonly been chosen to implement LLE calculations.

To represent the binodal locus for a type I LLE system, the isothermal ternary LLE data were correlated with the NRTL and the UNIQUAC models. While the parameters of the water (1) + ethanol (2) pair were taken from the literature,⁶ the parameters of the (1) + (3) and (2) + (3) pairs were determined from LLE calculation by minimization of the following objective function (Δ):

$$\Delta = \left(\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})| \right) / 6n \quad (6)$$

where x_{ijk} and \hat{x}_{ijk} are the observed and the calculated mole fractions of component *i* in phase *j* on tie-line *k*, respectively, and *n* is the number of tie-lines. Tables 5 and 6 present the correlated results from the NRTL and the UNIQUAC models, respectively. The average deviations from the NRTL model are slightly smaller than those from the UNIQUAC model. Figures 1–4 compare the calculated binodal locus and tie-lines from both models with the experimental results.

Table 6. Correlated Results from the UNIQUAC Model

mixture ^a	<i>T</i> /K	<i>i</i> – <i>j</i>	b_{ij}^b /K	b_{ji}^b /K	Δ^c
M1	283.15	1–2	33.57	90.58	0.0089
		1–3	49.89	293.33	
		2–3	–113.39	236.47	
	308.15	1–2	33.57	90.58	0.0133
		1–3	60.87	275.51	
		2–3	–164.44	247.57	
	323.15	1–2	33.57	90.58	0.0112
		1–3	76.67	284.91	
		2–3	–210.39	420.48	
M2	283.15	1–2	33.57	90.58	0.0133
		1–3	30.86	700.77	
		2–3	–113.67	385.12	
	308.15	1–2	33.57	90.58	0.0061
		1–3	22.13	726.13	
		2–3	–143.64	424.41	
	323.15	1–2	33.57	90.58	0.0079
		1–3	43.70	648.03	
		2–3	–165.11	476.52	
M3	283.15	1–2	33.57	90.58	0.0089
		1–3	39.95	764.66	
		2–3	–133.45	420.61	
	308.15	1–2	33.57	90.58	0.0054
		1–3	40.16	679.16	
		2–3	–148.01	420.96	
	323.15	1–2	33.57	90.58	0.0079
		1–3	39.19	707.72	
		2–3	–155.64	472.63	

^a M1, water (1) + ethanol (2) + 1-hexanol (3); M2, water (1) + ethanol (2) + butyl propionate (3); M3, water (1) + ethanol (2) + ethyl caproate (3). ^b $b_{ij} = (u_{ij} - u_{ji})/R$, where u_{ij} is the interaction energy between the *i*–*j* pair and *R* is the gas constant; the parameters of the 1–2 pair were taken from the literature (ref 6). ^c $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$, where *n* is the number of tie-lines.

Conclusions

Liquid–liquid equilibrium data were measured for the ternary mixtures of water + ethanol + 1-hexanol, water + ethanol + butyl propionate, and water + ethanol + ethyl caproate at temperatures from 283.15 K to 323.15 K. All three systems behave as a type I LLE. The experimental results indicated that ethyl caproate is a potent entrainer for separating ethanol from the aqueous solutions. The LLE data are well correlated with the NRTL and the UNIQUAC models.

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