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Measurement and Study on the Liquid–Liquid Equilibrium of Ionic Liquids with Aliphatic Alcohols

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ABSTRACT: In this work, liquid—liquid equilibria (LLE) for several binary systems of ionic liquids with aliphatic alcohols have been measured by the cloud point method from 280 K to the boiling point of the solvent. These binary systems include 1-hexyl-3-methylimidazolium tetrafluoroborate + 1-butanol/1-pentanol/1-hexanol/isobutanol and 1-octyl-3-methylimidazolium tetrafluoroborate + 1-butanol/1-pentanol/1-hexanol/isobutanol. The experimental data are analyzed, and some rules for the solubility of ILs are concluded, which can provide some instructions for the extraction and separation process. The equilibrium data are correlated by the nonrandom two-liquid (NRTL) model. The interaction parameters of the model for the systems are obtained. The minimum and maximum of the overall average deviation are 0.37 % and 2.67 %, respectively.

■ INTRODUCTION

Room-temperature ionic liquids, which are liquids at ambient temperature, are normally composed of relatively large organic cations and inorganic or organic anions.¹ Ionic liquids (ILs) have been suggested as a kind of potential "green" solvents to replace volatile organic solvents in electrochemistry, organic synthesis, and separation processes due to their superb physicochemical properties. The knowledge of liquid—liquid equilibria (LLE) is necessary for design and optimization of a new separation process. The measurement of solubility of ILs in organic solvents is increasingly popular.

To study the use of ILs for extracting an aromatic hydrocarbon from the mixture of an aromatic and an aliphatic hydrocarbon, Selvan et al.² reported liquid–liquid phase equilibria data of ILs [emim]I₃ and [bmim]I₃ with toluene and heptane. Rolandra et al.³ reported the LLE data for *n*-hexane + toluene + (N-methyl-2-pyrrolidinone + a solvent). Maduro et al.^{4,5} studied the LLE of ternary systems for different IL + aromatic + aliphatic systems. Letcher et al.^{6,7} determined the LLE data for ILs + benzene + alkane ternary systems. The effectiveness of extracting an alkanol from mixtures containing alkanes by determining the ternary LLE for the mixtures of IL + alkanol + alkane are also studied.^{8,9} Arce et al.^{10,11} presented a systematic study of the impact of different ILs on the phase behavior with tert-amyl ethyl ether or ethanol. Jork et al.¹² studied the influence of ILs on the phase behavior of aqueous azeotropic systems. Alonso et al. $^{13-16}$ have studied the solvent extraction of thiophene from alkanes by using ILs. Recently, more LLE data have been reported. ILs + water, alcohol, polyhydric alcohols, alkanes, alkenes, aromatics, chlori-nated hydrocarbons, ethers, and other binary mixtures^{17–22} and ILs + water + alcohols, ILs + ethyl + *tert*-amyl ethyl ether, ILs + water + nonionic surfactants, ILs + benzene + alkane, and other ternary mixtures²³⁻²⁵ have been reported. Some other types of organic systems²⁶⁻³⁰ also have been mentioned.

However, few articles have reported data about 1-hexyl-3methylimidazolium tetrafluoroborate ([hmim][BF₄]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF₄]), which are commonly used ILs. To develop the applications of the ILs, it is important to understand the factors that impact their phase behavior with other liquids. In this work, the LLE for binary mixtures of the two ILs with aliphatic alcohols (1-butanol, isobutanol, 1-pentanol, 1-hexanol, and 1-octanol) have been studied.

EXPERIMENTATION

Materials. [hmim][BF₄] and [omim][BF₄] were both supplied by Shanghai Cheng Jie Chemical Co. Ltd. with quoted purity of > 0.99 mass fraction. They were used after being vacuumed for at least 48 h to remove trace amounts of water. A Karl Fischer titration showed that the water content for [hmim][BF₄] and [omim][BF₄] after the vacuum treatment was < $7.80 \cdot 10^{-4}$ and < $7.00 \cdot 10^{-4}$ mass fraction, respectively. Organic solvents were dried over 0.4 nm molecular sieves and were particularly degassed by ultrasound prior to their use. The mass fraction purities tested by gas chromatography were as follows: 1-butanol (> 0.998), isobutanol (> 0.998), 1-pentanol (> 0.998), 1-hexanol (> 0.998), and 1-octanol (> 0.998). The water contents (mass fraction) of them were as follows: 1-butanol (0.02 %), isobutanol (0.02 %), 1-pentanol (0.02 %), net 1-octanol (0.1 %).

Method and Procedure. The cloud point method was applied to determine the bimodal coexisting curves of the LLE and the solubility of aromatic compounds in imidazolium-based ILs. The apparatus used in the work which was illustrated in Figure 1 mostly included a jacketed glass vessel, which was enclosed by a circulating water bath with a thermostat (type 501A, Shanghai Laboratory Instrument Works) controlling the bath temperature with an uncertainty of \pm 0.01 K. The vessel was sealed to prevent the evaporation of solvent or solute, and the procedure was

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Figure 1. Setup of the phase equilibrium measurement: 1, DDC camera; 2, jacketed glass vessel; 3, platinum resistance thermometer; 4, addition device; 5, magnetic stirrer rod; 6, magnetic stirrer; 7, circulating thermostat; 8, slit; 9, light source.

monitored by a digital camera to determine the cloud point during the measurement. As shown in Figure 1, the light emitted through the pore plate made the soluble phenomenon clear. In the experiment, the camera can take pictures which indicated the degree of solubility at any time.²⁹

Solubility of Aliphatic Alcohol.²⁹ The measurement started with a known mass of IL added into the vessel and stirred during the whole experiment. After a known mass of organic solvent was added into the IL, the temperature was increased at a rate of 0.1 $\text{K} \cdot \text{min}^{-1}$; while the organic compounds dissolved, the rate turned to 0.05 K \cdot min⁻¹ and finally became 0.01 K \cdot min⁻¹ until the turbid liquid became transparent. The temperature T_1 when the turbid liquid became transparent was recorded. The temperature continued increasing by about 2 K. Then the thermostat was adjusted to decrease the temperature at a rate of 0.01 K \cdot min⁻¹. The temperature T_2 was recorded when the transparent liquid became turbid. By comparing T_1 and T_2 , we confirmed that the difference between the two temperatures was less than 0.03 K. This procedure was repeated three times and took the average as the cloud-point temperature. Then another known mass organic solute was added, and the cloud-point temperature was measured again. The addition of organic solute was continued until the temperature reached the boiling point of the organic solvent or 95 °C which is the upper limit of the water bath.

Solubility of the ILs. Compared to the solubility of organic compounds in ILs, the solubility of the ILs in organic solvents was relatively smaller. The procedures were the same as above.

The overall uncertainty in the measurement depended on the purity of the solvent, solute, and precision of the calibrated thermometer and electronic digital balance. The liquids added to the vessel were prepared by mass using a BP210s balance which accuracy was within \pm 0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than \pm 0.0001.²⁹

Table 1. Experimental Liquid—Liquid Equilibrium Data forthe Binary Systems: [hmim][BF4] + 1-Butanol/1-Pentanol/1-Hexanol/Isobutanol

1-bi	1-butanol 1-pentanol		1-hexanol		isobutanol		
$x_{\rm IL}$	T/K	$x_{\rm IL}$	T/K	$x_{\rm IL}$	T/K	$x_{\rm IL}$	T/K
0.0085	288.45	0.0068	293.73	0.0080	307.10	0.0055	286.98
0.0113	291.22	0.0095	298.05	0.0127	313.06	0.0083	292.11
0.0147	293.80	0.0120	300.96	0.0181	316.65	0.0117	295.60
0.0190	296.25	0.0155	304.00	0.0253	319.44	0.0161	298.57
0.0256	298.41	0.0193	306.03	0.0352	321.74	0.0225	300.80
0.0339	299.90	0.0247	308.20	0.0486	323.45	0.0319	302.70
0.0454	301.05	0.0310	309.80	0.0656	324.61	0.0442	303.83
0.0582	301.41	0.0395	311.06	0.0930	325.06	0.0623	304.30
0.1326	301.70	0.0514	312.11	0.1479	325.45	0.0864	304.40
0.1524	301.31	0.0682	312.85	0.1715	325.25	0.1382	303.85
0.1791	300.80	0.0914	313.15	0.1951	324.95	0.1877	302.65
0.2127	299.90	0.1354	313.00	0.2236	324.46	0.2189	301.55
0.2556	297.72	0.1538	312.84	0.2652	323.40	0.2388	300.61
0.2977	295.15	0.1834	312.52	0.2997	322.11	0.2686	299.00
0.3277	293.09	0.2041	312.15	0.3465	319.76	0.2907	297.53
0.3525	291.25	0.2223	311.55	0.3771	317.95	0.3102	296.15
0.3768	289.47	0.2532	310.56	0.4030	316.45	0.3450	293.65
0.4112	286.15	0.2974	308.63	0.4253	314.86	0.4452	284.50
0.4462	282.77	0.3261	307.15	0.4568	312.00		
		0.3724	304.05	0.4913	309.33		
		0.4090	301.16	0.5204	306.10		
		0.4381	298.55	0.5509	302.86		
		0.4728	295.10	0.5778	299.26		
		0.5073	291.43	0.5988	296.65		
		0.5357	288.30	0.6135	294.65		
		0.5611	285.35				
		0.5834	282.66				

RESULTS AND DISCUSSION

Experimental Data. In this work, the LLE for a number of binary [hmim][BF₄] + aliphatic alcohol systems and [omim]-[BF₄] + aliphatic alcohol systems were measured.

The experimental data of LLE for $[hmim][BF_4] + 1$ -butanol, 1-pentanol, 1-hexanol, and isobutanol are shown in Table 1, and the experimental data of LLE for $[omim][BF_4] + 1$ -butanol, 1-pentanol, 1-hexanol, 1-octanol, and isobutanol are shown in Table 2.

Phase Diagrams of ILs + Aliphatic Alcohol Systems. Phase diagrams of ILs with aliphatic alcohols are shown in Figures 2 to 5: Figure 2 for [hmim][BF₄] + 1-butanol/1-pentanol/1-hexanol binary systems, Figure 3 for [omim][BF₄] + 1-butanol/1-pentanol/1-octanol systems, Figure 4 for [hmim][BF₄] + 1-butanol/isobutanol systems, and Figure 5 for [omim][BF₄] + 1-butanol/isobutanol systems.

From Figure 2, it is clear that the upper critical solution temperature (UCST) increases as the chain length of the alcohol increases. The same trend can be observed in Figure 3.

In Figures 4 and 5 it is found that in the UCST of these systems significant differences can be observed. For a given composition on the ionic liquid rich side of the diagram, the phase transition temperature is increased for the alcohols that have more branches.

Table 2. Experimental Liquid–Liquid Equilibrium Data for the Binary Systems: [omim][BF₄] + 1-Butanol/1-Pentanol/ 1-Hexanol/1-Octanol/Isobutanol

1	-butanol	1-pe	entanol	1-h	exanol	1-0	ctanol	isob	utanol
x_{IL}	T/K	x _{IL}	T/K	$x_{ m IL}$	T/K	x _{IL}	T/K	$x_{ m IL}$	T/K
0.0158	276.98	0.0113	280.55	0.0029	279.97	0.0099	301.75	0.0155	281.85
0.0178	277.45	0.0183	283.40	0.0037	280.15	0.0128	303.85	0.0183	282.54
0.0201	277.97	0.0249	284.76	0.0055	283.85	0.0173	305.85	0.0223	283.30
0.0230	278.37	0.0282	285.25	0.0070	286.55	0.0223	307.46	0.0279	283.95
0.0276	278.90	0.0314	285.40	0.0088	288.10	0.0320	309.30	0.0353	284.35
0.0348	279.34	0.0346	285.50	0.0103	289.50	0.0464	310.55	0.0437	284.47
0.0453	279.49	0.0418	285.85	0.0118	290.55	0.0941	312.67	0.0882	284.25
0.0694	279.47	0.0482	285.96	0.0135	290.90	0.1140	312.35	0.1026	283.77
0.0841	279.15	0.0566	286.08	0.0150	291.26	0.1393	311.91	0.1177	283.35
0.0961	278.81	0.0806	286.25	0.0174	292.27	0.1759	311.25	0.1330	282.87
0.1084	278.45	0.0859	286.15	0.0270	295.59	0.2233	310.46	0.1485	282.41
0.1220	278.05	0.0928	286.05	0.0361	296.20	0.2588	309.36	0.1642	281.77
0.1347	277.73	0.0983	285.95	0.0444	296.45	0.2804	308.25	0.1789	281.21
0.1466	277.33	0.1026	285.85	0.0547	296.65	0.3011	307.20	0.1920	280.70
0.1567	276.97	0.1082	285.75	0.0996	297.75	0.3255	305.76	0.2045	279.87
		0.1145	285.75	0.1062	297.65	0.3466	304.36	0.2158	279.29
		0.1271	285.36	0.1179	297.36	0.3710	302.21	0.2250	278.86
		0.1423	285.15	0.1322	297.07			0.2334	278.27
		0.1684	284.45	0.1576	296.51			0.2409	277.77
		0.1977	283.65	0.1835	295.85			0.2475	277.37
		0.2306	282.18	0.2013	295.35				
		0.2508	281.15	0.2172	294.76				
		0.2600	280.66	0.2339	294.05				
		0.2675	280.40	0.2496	293.25				
		0.2750	279.86	0.2633	292.60				
		0.2804	279.65	0.2814	291.55				
				0.2990	290.38				
				0.3163	289.20				
				0.3317	288.05				
				0.3457	286.95				
				0.3612	285.65				
				0.3784	284.15				
				0.3920	282.81				

In other words, at a given temperature the solubility of the linear alcohol in the ionic liquid rich phase is lower than alcohols have branches. This may be explained by specific hydrogen-bonding interactions between acidic hydrogen atoms on the imidazolium cation ring and the hydroxyl of the alcohols. With the growth of alkyl chain on the imidazolium cation, the UCST had more significant differences between *n*-alcohols and iso-alcohols in the IL systems.

To illuminate the effect of the length of the imidazolium cation alkyl chain on the solubility, the data for $[hmim][BF_4]$ and $[omim]-[BF_4]$ in the same aliphatic alcohols are shown in Figures 6 to 9.

Figure 6 is the LLE phase diagram for the IL [hmim]- $[BF_4]/[omim][BF_4] + 1$ -butanol systems. The UCST is significantly higher for the IL with shorter alkyl chains. The same trend can be observed in the LLE phase diagram of [hmim][BF_4] systems from Figures 7 to 9. By extending the alkyl chain, the UCST decreases, and the IL alcohol mutual solubilities increase at any particular temperature below the UCST. The enhancement in solubility with increased alkyl chain length is most likely to due to the increased via van der Waals interactions between the

longer alkyl chain on the cation and the alkyl portion of the alcohol.

Thermodynamic Model. The NRTL model was used to correlate the experimental data. All formulas used are as follows:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 \cdot G_{21}} \right)^2 + \frac{\tau_{12} \cdot G_{12}}{\left(x_1 \cdot G_{12} + x_2 \right)^2} \right]$$
(1)

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 \cdot G_{12}} \right)^2 + \frac{\tau_{21} \cdot G_{21}}{\left(x_2 G_{21} + x_1 \right)^2} \right]$$
(2)

$$G_{12} = \exp(-\alpha_{12} \cdot \tau_{12}) \tag{3}$$

$$G_{21} = \exp(-\alpha_{12} \cdot \tau_{21}) \tag{4}$$



Figure 2. Experimental LLE for the binary systems $[hmim][BF_4](1) + aliphatic alcohol (2): <math>\blacksquare$, 1-butanol; \blacklozenge , 1-pentanol; \bigstar , 1-hexanol; solid line, the NRTL model calculation.



Figure 3. Experimental LLE for the binary systems $[\text{omim}][\text{BF}_4](1) +$ aliphatic alcohol (2): \blacksquare , 1-butanol; \bigstar , 1-pentanol; \spadesuit , 1-hexanol; \bigstar , 1-octanol; aolid line, the NRTL model calculation.

$$\tau_{12} = a_{12} + b_{12}/T + e_{12} \ln T + f_{12}T$$
(5)

$$\tau_{21} = a_{21} + b_{21}/T + e_{21} \ln T + f_{21}T \tag{6}$$

$$a_{12} = c_{12} + d_{12}(T - 273.15 \text{ K}) \tag{7}$$

When the data were regressed, $c_{12} = c_{21}$, $d_{12} = d_{21}$. The objective function was as eq 8:

$$Q = \sum_{N=1}^{NDG} \omega_{x} \sum_{i=1}^{NP} \left[\left(\frac{T_{ej} - T_{m,i}}{\sigma_{Tj}} \right)^{2} + \left(\frac{P_{ej} - P_{m,i}}{\sigma_{P,i}} \right)^{2} + \sum_{j=1}^{NC - 1} \left(\frac{x_{ej,j} - x_{mj,j}}{\sigma_{x,ij}} \right)^{2} + \sum_{j=1}^{NC - 1} \left(\frac{y_{ei,j} - y_{m,i,j}}{\sigma_{y,i,j}} \right)^{2} \right]$$
(8)





310

305

300

Figure 4. Experimental LLE for the binary systems: \blacksquare , [hmim][BF₄] (1) + 1-butanol (2); \bigoplus , [hmim][BF₄] (1) + isobutanol (2).



Figure 5. Experimental LLE for the binary systems: \blacksquare , [omim][BF₄] (1) + 1-butanol (2); \bullet , [omim][BF₄] (1) + isobutanol (2).



Figure 6. Experimental LLE for the binary systems: \blacksquare , [hmim][BF₄] (1) + 1-butanol (2); \bullet , [omim][BF₄] (1) + 1-butanol (2).

where NDG is the number of the groups of regression data; ω_x is the quality of the *n*th group of the data; NP is the number of



Figure 7. Experimental LLE for the binary systems: \blacksquare , [hmim][BF₄] (1) + isobutanol (2); ●, [omim][BF₄] (1) + isobutanol (2).



Figure 8. Experimental LLE for the binary systems: \blacksquare , [hmim][BF₄] (1) + 1-pentanol (2); ●, [omim][BF₄] (1) + 1-pentanol (2).

experimental points; NC is the number of substance species; T, p, x, and y are the temperature, pressure, liquid, and vapor phase mole fraction; e is estimate values; m is experimental values; i is the *i*-th data; j is the mole fraction of component j; σ is the standard deviation.

The average relative error AAD expression was:

$$AAD = \frac{1}{NP} \sum \frac{|x_{exp} - x_{cal}|}{x_{exp}} \cdot 100 \%$$
(9)

where NP is the number of experimental points; x_{exp} is experimental data; x_{cal} is the calculated value.

The regression parameters from experimental data by the NRTL model and average relative error of each system are shown in Tables 3 and 4.



Figure 9. Experimental LLE for the binary systems: \blacksquare , [hmim][BF₄] (1) + 1-hexanol (2); ●, [omim][BF₄] (1) + 1-hexanol (2).

Table 3. Interaction Parameters of the NRTL Model and the Overall Average Deviation for x_{IL} in Each of the Binary Systems: [hmim][BF₄] + Aliphatic Alcohols

IL	$[hmim][BF_4]$				
solvents	1-butanol	isobutanol	1-pentanol	1-hexanol	
<i>a</i> ₁₂	-25.7426	-35.0661	232.3846	160.4096	
<i>a</i> ₂₁	43.9184	87.1935	41.5519	195.3647	
b_{12}	4219.1556	9636.2011	-23782.2730	-20637.1800	
b_{21}	2735.3712	-1070.5883	13819.5050	-21665.0500	
c_{12}	0.0605	0.3660	0.2583	0.0346	
<i>d</i> ₁₂	0.0002	0.0057	0.0007	0.0007	
e ₁₂	0.2799	0.0489	-13.6052	-9.2402	
e ₂₁	-6.9192	-11.7593	-24.3219	-1.2296	
f_{12}	0.0099	0.0098	-0.2540	-0.1513	
f_{21}	-0.0008	-0.0433	0.1870	-0.3410	
AAD/%	2.5704	1.3969	0.9683	0.3670	

Table 4. Interaction Parameters of the NRTL Model and the Overall Average Deviation for x_{IL} in Each of the Binary Systems: [omim][BF₄] + Aliphatic Alcohols

IL		[omim][BF ₄]				
solvents	1-butanol	isobutanol	1-pentanol	1-hexanol	1-octanol	
<i>a</i> ₁₂	-21.7718	97.7760	45.3817	12.6399	80.1877	
<i>a</i> ₂₁	-8.8432	37.6278	50.8316	113.7768	70.0454	
b_{12}	14147.5415	41304.6873	7244.4285	13227.3013	29520.9086	
b_{21}	5566.5650	7127.6666	3484.0764	-2313.4417	6893.4625	
c_{12}	0.5779	0.4683	0.4596	0.3483	0.0084	
d_{12}	0.0205	0.0161	0.0136	0.0096	0.0145	
e ₁₂	-5.0834	-47.7406	-12.4784	-12.1556	-31.2572	
e_{21}	-1.3690	-10.3756	-10.5636	-13.7383	-15.5996	
f_{12}	0.0021	0.0916	0.0007	0.0412	0.0156	
f_{21}	-0.0004	-0.0025	-0.0001	-0.0829	0.0012	
AAD/%	1.3260	0.5258	1.4815	2.6718	1.4819	



Figure 10. Diagram for [hmim][BF₄] (1) + aliphatic alcohols (2): \blacksquare , 1-butanol; ●, 1-pentanol; ▲, 1-hexanol. A comparison is made with the data of Wagner et al.¹⁸ for [hmim][BF₄] with: \Box , 1-butanol; \bigcirc , 1-pentanol; △, 1-hexanol.



Figure 11. Diagram for [hmim][BF₄] (1) + 1-hexanol (\blacktriangle). A comparison is made with the data of Crosthwaite et al.³¹ for [hmim][BF₄] + 1-hexanol (\triangle).

Discussion of the Literature Data. Some systems of this study have been reported by other researchers. The comparisons of the T-x data between this work and the literature are shown in Figures 10 to 13. From Figures 10 to 12, the phenomenon which the values of the phase transition temperatures from literature are always higher than the values observed in this study cannot be ignored. This phenomenon may be due to the different water content in different works. The water contents of this study for [hmim][BF₄] and [omim][BF₄] are < 780 ppm and < 700 ppm mass fraction. Meanwhile, the water content is 410 ppm of [hmim][BF₄] for Crosthwaite et al.³¹ and 100 ppm of [omim][BF₄] for Crosthwaite et al.¹⁹ Crosthwaite et al.³¹ have proposed a supposition for this phenomenon that the presence of high water impurity levels would cause a decrease in the phase transition temperature to illustrate the difference of the phase transition temperature between their work and Wagner's. However, it was found in Figure 13 that the system with less water



Figure 12. Diagram for $[\text{omim}][BF_4](1)$ + aliphatic alcohols (2): \blacktriangle , 1-hexanol; \blacksquare , 1-octanol. A comparison is made with the data of Crosthwaite et al.¹⁹ for $[\text{omim}][BF_4]$ with: \triangle , 1-hexanol; \Box , 1-octanol.



Figure 13. Diagram for $[\text{omim}][BF_4] + 1$ -pentanol (\blacktriangle). A comparison is made with the data of Heintz et al.²² for $[\text{omim}][BF_4]$ with 1-pentanol (\triangle, \Box).

Table 5. Comparison of the Average Relative Error

	literature ADD/%	this study ADD/%
$[hmim][BF_4] + 1$ -hexanol ³¹	3.2592	0.3670
$[\text{omim}][\text{BF}_4] + 1\text{-pentanol}^{22}$	3.4006	1.4815
$[\text{omim}][\text{BF}_4] + 1\text{-hexanol}^{19}$	3.4289	2.6718
$[\text{omim}][BF_4] + 1 \text{-octanol}^{19}$	4.2967	1.4819

contamination (700 ppm) in this work had considerably lower phase transition temperatures than the system with high water content (0.17 wt %) reported by Heintz et al.,²² which is conflicted with the anticipation of Crosthwaite et al.³¹ It may be due to the unusual water content of their ILs. However, considering the different equipment and different method used in experiments, the slight difference of phase transition temperature could be acceptable. From these figures, it can be seen that the data in this study have a wider range of concentration than those in the literature, which could prove that this study is more universal. Besides, the solubility data were not correlated in the literature. In this study some reported data were correlated by the NRTL model as mentioned above. The results are shown in Table 5. It can be found that the data in this work had a lower average relative error than the same system reported in the literature.

CONCLUSION

In this work, LLE data for aliphatic alcohols with ILs [hmim]- $[BF_4]$ and $[omim][BF_4]$ were measured. It is found that most systems have an UCST and their mutual solubility increases with the increasing length of the alkyl chain on the aliphatic alcohols. The branched level of the alkyl chain can influence the UCST, and the growth of the alkyl chain on the imidazolium cation makes the UCST of the binary mixtures decrease. Based on the experimental data, the NRTL model parameters for these systems are obtained.

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