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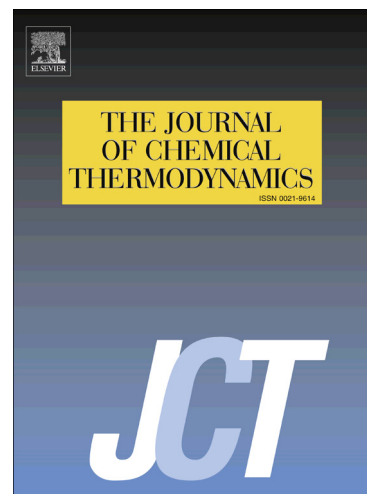
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Liquid-liquid equilibrium measurements and correlation for phase behaviors of alcohols + heptane + ILs ternary systems

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Abstract: Liquid-liquid equilibrium (LLE) for ternary systems of heptane + alcohols (ethanol, 1-propanol and 2-propanol) + ionic liquids (ILs) were carried out at 298.15 K and atmospheric pressure. The values of distribution coefficient (β) and selectivity (S) were calculated for the system to investigate the influence of ionic liquids' anion and length of the n-alkyl chain in alcohols on the LLE. The NRTL and UNIQUAC models were used to correlate the experimental data, and the results indicated that both the models fit the experimental systems. The UNIFAC model was used to predict the LLE behaviors of the studied systems and compare with experimental and correlated tie-lines.

Keywords: Liquid-liquid equilibrium; Ionic liquid; heptane; alcohols; NRTL; UNIQUAC; UNIFAC

1. Introduction

Gasoline is an important fuel which is composed with hydrocarbons, in order to reduce the lead content in gasoline, alcohols and alkanes have coexisted additives as gasoline [1]. This method to reduce the lead content in gasoline has been in industrial application for many years, and different azeotropic mixtures of alcohols and alkanes are present in these industrial processes [2]. The separation of these mixtures is basically impossible by a simple distillation process. Liquid-liquid extraction based on the immiscibility of two phases is one of the most important separation methods to separate these azeotropes [3], and it is pivotal to find suitable solvent.

The conventional organic solvents are negative environmental that lead to a huge interest to research the substitutes of organic solvents. Ionic liquids (ILs) have recently gained recognition as

possible environmentally benign alternative media, interest in ILs stems from this potential application as “green solvents” based on, perhaps, their most important feature: nearly complete nonvolatility at ambient condition compared with volatile organic solvents. ILs have many attractive physicochemical properties, such as chemical and thermal stability, nonflammability, and a good solubilizing capacity of a number of organic compounds [4]. In this work, the two ILs formed by 1-hexyl-3-methylimidazolium [HMIM]⁺ cation were considered to study the phase behavior of alcohols + alkanes + IL systems. The anions of the ILs are tetrafluoroborate ([BF₄]⁻) and bis (trifluoromethylsulfonyl) imide ([NTf₂]⁻), the [BF₄]⁻ anion will hydrolyze when contact with water and producing HF[5], this case was considered in this paper, the experiment of this work was in the absence of water environment.

For industrial application, their physicochemical properties and phase behavior of the corresponding systems should be studied. Lots of investigators studied the liquid-liquid equilibrium (LLE) containing ILs [1, 2, 6-27]. Pereiro *et al.* [2, 6, 18] studied the alcohols + alkanes systems with imidazolium-based ILs and found feasible scaling up some of industrial process. As shown in these literatures, with different IL, the effect for the length alkyl chain of alcohols was different. F Cai *et al.* [15, 16] published LLE data for the systems of methanol +alkanes and imidazolium-based ILs with different anions at T=298.15K and atmospheric pressure. González *et al.* [7-11, 13] investigated the imidazolium-based and pyridinium-based ILs as the extraction agent to separate alcohols and alkanes, the effect of alkyl length was studied. Ramjugernath *et al.* [14] analyzed the ILs with methylsulfate ([MeSO₄]⁻) anion, the effect of alkyl length of cation was studied.

The phase behavior of ILs with alcohols and water has been investigated in our previous work [22, 28], this work continue studying the application of ILs as extractive agent in the separation processes. The two ILs formed by 1-hexyl-3-methylimidazolium [HMIM]⁺ cation were considered to study the phase behavior of alcohols + alkanes + IL systems, the effects for anion and length of the n-alkyl chain in alcohols were researched. The systems of heptane + [HMIM][BF₄]/[HMIM][NTf₂] with ethanol 1-propanol and 2-propanol were studied in this paper, the LLE data for these systems has not been published before. The distribution coefficient and selectivity were used to calculate ability of ILs as extraction agents. The LLE data for all of systems in our study were correlated with the UNIQUAC [29] and NRTL [30] activity coefficient

models, and the UNIFAC [31] model was used to predict the LLE data. The root-mean-square-deviation (*rmsd*) values between the experimental and calculated data were also calculated.

2. Theory

2.1 Solvent extraction parameters

The distribution coefficient (β) and selectivity (S) were used to evaluate the capabilities of studied ILs as solvents for the extraction alcohols from alkanes. The distribution coefficient of alcohols is defined

$$\beta = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (1)$$

x_2^{II} is the mole fraction of alcohol in the IL rich phase and x_2^{I} is the mole fraction of alcohol in the organic rich phase. The selectivity of alcohol is defined as

$$S = \frac{(x_2^{\text{II}}/x_1^{\text{II}})}{(x_2^{\text{I}}/x_1^{\text{I}})} \quad (2)$$

x_1^{I} is the mole fraction of heptane in the organic rich phase and x_1^{II} is the mole fraction of alkane in the IL rich phase.

2.2. Liquid-liquid equilibrium model

The experimental data for tie line were correlated by NRTL and UNIQUAC models. During the regression of the parameters, the activity coefficient and mole fraction can be determined using the following equations:

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

where x_i^{I} is the mole fraction of component i in upper phase, x_i^{II} is the mole fraction of component i in lower phase and $\gamma_i^{\text{I}}, \gamma_i^{\text{II}}$ are the activity coefficients of component i in organic rich phase and IL rich phase. In the NRTL model, the values of α_{ij} which were obtained by optimization are shown in Table 5, and α_{ij} is equal to α_{ji} . In the UNQUAC model, the molecular volume structure parameter r and the molecular surface area parameter q was from the reference [32]. Parameters r , q , and q' of IL in UNIQUAC model are listed in Table 2.

The UNIFAC model was used to predict the experimental data in this paper, the excess Gibbs energy is composed of combinatorial and residual part, the activity coefficient are given by

equations

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4)$$

where γ_i^C is the combinatorial contribution part and the γ_i^R is the residual part to the activity coefficient.

In the UNIFAC model, the combinatorial contribution part that accounts for the size and shape differences between the molecules is given by

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^N x_j l_j \quad (5)$$

$$r_i = \sum_{k=1}^m v_k^i R_k \quad (6)$$

$$q_i = \sum_{k=1}^m v_k^i Q_k \quad (7)$$

$$\theta_i = \frac{r_i x_i}{\sum_{i=1}^m r_i x_i} \quad (8)$$

$$\phi_i = \frac{q_i x_i}{\sum_{i=1}^m q_i x_i} \quad (9)$$

where $Z=10$, R_k is the volume parameter and Q_k is the surface parameter of group k .

The residual activity coefficient of component i is given by

$$\ln \gamma_i^R = \sum_{k=1}^m v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (10)$$

where

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_{j=1}^m \bar{\theta}_j \varphi_{jk} \right) - \sum_{j=1}^m \frac{\bar{\theta}_j \varphi_{jk}}{\sum_{n=1}^m \bar{\theta}_j \varphi_{nk}} \right] \quad (11)$$

$$\varphi_{jk} = \exp \left(- \frac{U_{jk} - U_{kk}}{RT} \right) = \exp \left(- \frac{a_{jk}}{T} \right) \quad (12)$$

$$\bar{\theta}_j = \frac{Q_j X_j}{\sum_{n=1}^m Q_n X_n} \quad (13)$$

$$X_j = \frac{\sum_{i=1}^N x_i^i v_j^i}{\sum_{i=1}^N \sum_{k=1}^m x_i v_k^i} \quad (14)$$

All the parameters used in this paper for UNIFAC model are from Z Lei et al [33] and are shown in Table 3.

2.3 Model evaluation and parameter estimation

The binary parameters of NRTL and UNIQUAC models were determined through minimizing the following objective function:

$$OF = \sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 \left(x_{ijk}^{exp} - x_{ijk}^{calc} \right)^2 \quad (15)$$

where M is the number of tie-lines, x^{exp} and x^{calc} indicate the experimental and calculated mole fraction, respectively, the i, j , and k indicate component, phase, and tie-line, respectively.

The root-mean-square-deviation (rmsd) was used to evaluate the models by comparing the experimental and calculated data, which is defined as

$$rmsd = \left(\frac{\sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 \frac{(x_{ijk}^{exp} - x_{ijk}^{calc})^2}{6M}} \right)^{1/2} \quad (16)$$

where x is the mole fraction and the subscripts i, j , and M denote the component, phase, and tie-line, respectively.

3. Experiment

3.1 Chemicals

The chemical purities of ethanol, n-propanol, 2-propanol, heptane (purchased from Tianjin Kermel Chemical Reagent Co., Ltd. with a stated purity of >0.990 mass fraction) were checked by gas chromatography, the ILs [Hmim][BF₄] and [Hmim][NTf₂] were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, with a stated purity >0.990 mass fraction. The list of chemicals used in this work with information about source and purity is presented in Table 1. The water content reported in this work was measured by the supplier of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences using moisture teller. All materials were used without further purification.

3.2 Apparatus and procedure

LLE data were obtained by preparing mixtures with a different composition in the two-phase region. These mixtures were put into the equilibrium kettle designed by ourselves, and stirred vigorously by the mechanical stirrer. The temperature was controlled by a low temperature thermostat of HX-105, which was purchased from Changliu Instrument Factory of Beijing in China. The fluctuation range of temperature that the thermostat controls was ± 0.05 K. The sample mixtures were stirred rigorously in the equilibrium cell for 3 h and then settled for about 15 h to ensure a complete split of the equilibria phases. In pre-experiment, the experimental time was determined. In order to make the LLE data cover the entire two-phase region as large as possible, during the mix of the pure components, the content of ILs was fixed and the proportion

span of alcohol/heptane was determined by the pre-experiment using the cloud point method [34]. For example, heptane and IL were mixed with the ratio of 1:1 and added ethanol dropwise, such as the mass of heptane and IL was 0.5 g, when the mixture became clarification homogeneous phase, the mass of intrans ethanol was 1.2 g. We calculated the range of heptane/alcohol ratio for the system of heptane + ethanol + [HMIM][BF₄] by these results. The samples were respectively taken out from the upper and lower layers to analyze specific phase composition. In previous work[28], the procedure and equipment used for the determination of LLE data had been described. The relative compositions of volatile compounds were determined by a gas chromatograph equipped (GC-2014C) with a thermal conductivity detector (TCD) using an internal standard method, and ethanol is the internal standard substance for 1-propanol and 2-propanol systems, 1-propanol is the internal standard substance for ethanol systems. A GDX-104 (2 m×3 mm) packed column is connected to a pre-column to avoid the nonvolatile IL reaching the column. The detection conditions for the systems of alcohol + heptane + IL were shown as follows: helium was used (>99.999% purity) as carrier gas. The temperature of the injector was 503.15 K, the column oven was maintained at 438.15 K for 3 min and subsequently submitted to the following heating program: from 438.15 K to 503.15 K at a rate of 15 K/min, maintained at 503.15 K for 3 min, and the detector was 523.15 K. In order to determine the IL composition in the samples, the subtraction method which calculating the mass difference before and after the vaporization of solvents was used. All the measurements were repeated at least three times.

4. Result and discussion

4.1 Experimental data

Liquid-liquid equilibrium experiments were carried out at 298.15 K and atmospheric pressure. The experimental data for the ternary systems of ethanol + heptane + [HMIM][BF₄], 1-propanol + heptane + [HMIM][BF₄], 2-propanol + heptane + [HMIM][BF₄], and 2-propanol + heptane + [HMIM][NTf₂] are shown in Table 3. The solubility for the heptane with ILs are shown in Figs. 1-4, which are from reference [21, 35]. The tendency is accordant for our experimental data and these solubility. The distribution coefficient and selectivity values are listed in Table 2 and the values of β and S for the four ternary systems are shown in Figs. 5-6 graphically. For the same content of alcohol in IL rich phase, the extractive result of [NTf₂]⁻ anion is better than [BF₄]⁻ anion

based IL, and for the same IL of [HMIM][BF₄], the extractive result of ethanol is greater than 1-propanol and 2-propanol is better than 1-propanol. Revelli A-L *et al* [1] studied [BF₄]⁻ with different alcohols, the result is consented with our work. The β values decrease with the arise of alcohol mole fraction, and all of the values for selectivity S are greater than 1, which means that extraction of alcohol from heptane by ILs in this study is feasible.

4.2 correlation and prediction for experimental data

The experimental data are shown in Table 4 and correlated with NRTL and UNIQUAC models. The binary interaction parameters of NRTL, UNIQUAC models were determined via data regression using the nonlinear least squares method in MATLAB in this work. The binary interaction parameters and *rmsd* values indicating the accuracy of the data regression are presented in Table 5. As shown in Figs. 1-4, both models correlate the data for the system studied properly. And the binodal curve predicted by UNIFAC model can be observed in Figs. 1-4, the prediction of data is not properly agreed with experimental data, indicating that the experiment of the LLE for these systems is necessary, and the good binary parameters for the NRTL and UNIQUAC models can be obtained by experimental data.

5. Conclusion

In this work, we focused on a study of the ternary systems containing alcohols (ethanol, 1-propanol and 2-propanol), heptane and ILs ([Hmim] [BF₄], [Hmim] [NTf₂]) at 298.15 K and atmospheric pressure. The new LLE data for alcohol + alkane + IL systems were received. Then, the capability of IL as liquid-liquid extraction solvent was assessed through the distribution coefficient (β) and selectivity (S). For the same content of alcohol in IL rich phase, the extractive result of [NTf₂]⁻ anion is better than [BF₄]⁻ anion based IL, and for the same IL of [HMIM][BF₄], the extractive result of ethanol is greater than 1-propanol and 2-propanol is better than 1-propanol too. The values of S are greater than 1 indicates that the extraction of alcohol from mixtures using ILs in this study is feasible. The LLE data for the systems studied were correlated by NRTL and UNIQUAC models, and the calculated data were obtained by computing with the binary interaction parameters which determined with experimental data regression. The comparative results of *rmsd* between the experimental and calculated data show that both models correlate the data for the systems studied in this work properly. The binodal lines were predicted by UNIFAC

model, and UNIFAC based LLE behavior predicted by the interaction and structural parameters from literatures, which were not obtained from this experiment, is not properly agreed with experimental and correlated tie lines, indicating that the experiment of the LLE for these systems is necessary.

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Figure captions

Fig. 1. Experimental, calculated and predicted LLE data in mole fraction for the systems of ethanol (1) + heptane (2) + [Hmim] [BF₄] (3). (■), solubility of heptane and IL, from reference[35]; (●), experimental value; (▲), calculated value by NRTL model; (▼), calculated value by UNIQUAC model, (—); binodal curve predicted using UNIFAC model.

Fig. 2. Experimental, calculated and predicted LLE data in mole fraction of 1-propanol (1) + heptane (2) + [Hmim] [BF₄] (3). (■), solubility of heptane and IL, from reference[35] (●), experimental value; (▲), calculated value by NRTL model; (▼), calculated value by UNIQUAC model, (—), binodal curve predicted using UNIFAC model.

Fig. 3. Experimental, calculated and predicted LLE data in mole fraction of 2-propanol (1) + heptane (2) + [Hmim] [BF₄] (3). (■), solubility of heptane and IL, from reference[35] (●), experimental value; (▲), calculated value by NRTL model; (▼), calculated value by UNIQUAC model, (—), binodal curve predicted using UNIFAC model.

Fig. 4. Experimental, calculated and predicted LLE data in mole fraction of 2-propanol (1) + heptane (2) + [Hmim] [NTf₂] (3). (■), solubility of heptane and IL, from reference[21] (●), experimental value; (▲), calculated value by NRTL model; (▼), calculated value by UNIQUAC model, (—), binodal curve predicted using UNIFAC model.

Fig. 5. Distribution coefficient (β) for ternary systems of for the systems of alcohol + heptane + IL, x_2' is the mole fraction of heptane in heptane-rich phase. (■), ethanol + heptane + [Hmim] [BF₄]; (●), 1-propanol + heptane + [Hmim] [BF₄]; (▲), 2-propanol + heptane + [Hmim] [BF₄]; (▼), 2-propanol + heptane + [Hmim] [NTf₂].

Fig. 6. Selectivity (S) for ternary systems of for the systems of alcohol + heptane + IL x_2' is the mole fraction of heptane in heptane-rich phase. (■), ethanol + heptane + [Hmim] [BF₄]; (●), 1-propanol + heptane + [Hmim] [BF₄]; (▲), 2-propanol + heptane + [Hmim] [BF₄]; (▼), 2-propanol + heptane + [Hmim] [NTf₂].

Table 1.

Sources, CAS number, molar mass, purification, water contents by mass, w_w , and analysis method of the chemicals used in this work.

Chemical	Source	CAS number	Molar mass/(g · mol ⁻¹)	Mass purity stated by supplier	w_w /10 ⁻⁶	Analysis method
ethanol	Tianjin Kermel Chemical Reagent Co., Ltd.	64-17-5	46.07	0.995 ^a		GC
1-propanol	Tianjin Kermel Chemical Reagent Co., Ltd.	71-23-8	60.10	0.995 ^a		GC
2-propanol	Tianjin Kermel Chemical Reagent Co., Ltd.	67-63-0	60.10	0.995 ^a		GC
heptane	Tianjin Kermel Chemical Reagent Co., Ltd.	142-82-5	100.2	0.995 ^a		GC
[HMIM][BF ₄]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	244193-50-8	254.08	0.990 ^a	<500 ^a	
[HMIM][NTf ₂]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	382150-50-7	447.42	0.990 ^a	<500 ^a	

^aAnalysis by supplier

Table 2.

Volume (r_i) and surface area (q_i, q_i') of UNIQUAC equation

Component	r_i	q_i	q_i'
ethanol ^a	2.576	2.588	0.920
1-propanol ^a	2.821	2.448	2.448
2-propanol ^a	2.779	2.508	2.508
heptane ^a	5.174	4.396	4.396
[Hmim] [BF ₄] ^a	9.209	7.254	7.254
[Hmim] [NTf ₂] ^b	13.048	10.097	10.097

^aFrom reference[32]^bFrom reference[28]

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Table 3.

Group Parameters of volume (R_i) and surface area (Q_i) of UNIFAC equation.

Component	R_i	Q_i
CH ₃	0.9011	0.8480
CH ₂	0.6744	0.5400
[MIM][BF ₄]	6.5669	4.0050
[MIM][NTf ₂]	8.3145	7.392
OH	1.0000	1.2000

From reference [33]

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Table 4.

Experimental LLE data on mole fraction x , solute distribution, β and selectivity, S for ternary systems of heptane (1) + alcohol (2) + IL (3) at $T = 298.15 \text{ K}^a$ and $p = 0.1 \text{ MPa}$.

Upper phase		Lower phase		β	S
x_1	x_2	x_1	x_2		
heptane (1) + ethanol (2) + [Hmim][BF ₄] (3)					
0.986	0.014	0.031	0.233	16.643	529.350
0.966	0.034	0.031	0.450	13.235	412.429
0.948	0.052	0.032	0.516	9.923	293.971
0.877	0.123	0.044	0.539	4.382	87.344
0.742	0.258	0.053	0.624	2.419	33.861
0.526	0.473	0.060	0.683	1.444	12.659
0.438	0.558	0.070	0.698	1.251	7.827
0.392	0.603	0.077	0.730	1.211	6.163
0.330	0.661	0.087	0.741	1.121	4.252
heptane (1) + 1-propanol (2) + [Hmim][BF ₄] (3)					
0.988	0.012	0.046	0.123	10.250	220.152
0.896	0.103	0.048	0.206	2.124	37.298
0.832	0.168	0.051	0.283	1.617	27.428
0.755	0.245	0.055	0.333	1.243	18.683
0.622	0.378	0.066	0.473	1.251	11.793
0.548	0.452	0.074	0.532	1.177	8.716
0.495	0.502	0.089	0.586	1.167	6.492
0.426	0.566	0.107	0.611	1.080	4.298
0.374	0.610	0.125	0.641	1.051	3.144
heptane (1) +2-propanol (2) + [Hmim][BF ₄] (3)					
0.990	0.010	0.075	0.147	14.700	194.040
0.909	0.091	0.080	0.267	2.934	33.338
0.819	0.181	0.089	0.346	1.912	17.591
0.759	0.241	0.095	0.389	1.614	12.896
0.706	0.293	0.094	0.430	1.468	11.022
0.655	0.344	0.098	0.480	1.395	9.326
heptane (1) +2-propanol (2) + [Hmim][NTf ₂] (3)					
0.939	0.061	0.079	0.193	3.164	37.607
0.900	0.100	0.089	0.305	3.050	30.843
0.827	0.172	0.094	0.400	2.326	20.460
0.771	0.226	0.094	0.513	2.036	17.065
0.704	0.296	0.097	0.616	2.081	15.104

^a Standard uncertainties u are $u(x_i) = 0.003$, $u(T) = 0.05 \text{ K}$, $u(p) = 0.0015 \text{ MPa}$

Table 5.

Binary interaction parameters Δg_{ij} , Δg_{ji} and nonrandomness factor α for NRTL model, binary interaction parameters Δu_{ij} and Δu_{ji} for UNIQUAC model and root mean square deviations, obtained from the experimental LLE data of studied ternary systems by NRTL and UNIQUAC models at $T = 298.15 \text{ K}$ $p = 0.1 \text{ MPa}$.

<i>i-j</i>	$\Delta g_{ij} (\text{kJ}\cdot\text{mol}^{-1})$	$\Delta g_{ji} (\text{kJ}\cdot\text{mol}^{-1})$	<i>rmsd</i>	α
	NRTL parameters			
heptane (1) + ethanol (2) + [Hmim][BF ₄] (3)				
1-2	7.1457	8.5719	0.0139	0.42
1-3	17.5148	8.8670		
2-3	11.6263	0.2284		
heptane (1) + 1-propanol (2) + [Hmim][BF ₄] (3)				
1-2	4.8675	4.3056	0.0118	0.14
1-3	15.5889	6.1185		
2-3	11.2821	-0.3710		
heptane (1) + 2-propanol (2) + [Hmim][BF ₄] (3)				
1-2	3.4961	2.1911	0.0165	0.24
1-3	23.0480	4.5639		
2-3	13.3477	-2.4699		
heptane (1) + 2-propanol (2) + [Hmim][NTf ₂] (3)				
1-2	3.3489	4.1096	0.0171	0.30
1-3	21.6751	7.0978		
2-3	12.8217	-0.8683		
<i>i-j</i>	$\Delta u_{ij} (\text{kJ}\cdot\text{mol}^{-1})$	$\Delta u_{ji} (\text{kJ}\cdot\text{mol}^{-1})$	<i>rmsd</i>	
	UNIQUAC parameters			
heptane (1) + ethanol (2) + [Hmim][BF ₄] (3)				
1-2	15.3445	-0.2471	0.0139	
1-3	2.7465	0.2390		
2-3	-0.5549	6.6405		
heptane (1) + 1-propanol (2) + [Hmim][BF ₄] (3)				
1-2	0.8552	1.4615	0.0191	
1-3	2.1651	0.0817		
2-3	2.3155	-0.0347		
heptane (1) + 2-propanol (2) + [Hmim][BF ₄] (3)				
1-2	2.3798	-0.1811	0.0115	
1-3	4.1229	-0.5772		

2-3	2.1625	-0.2547	
	heptane (1) + 2-propanol (2) + [Hmim][NTf ₂] (3)		
1-2	1.7070	1.1709	0.0094
1-3	2.3989	-0.1132	
2-3	1.2134	0.8853	

^aStandard uncertainties u are $u(T) = 0.05$ K

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Fig. 1

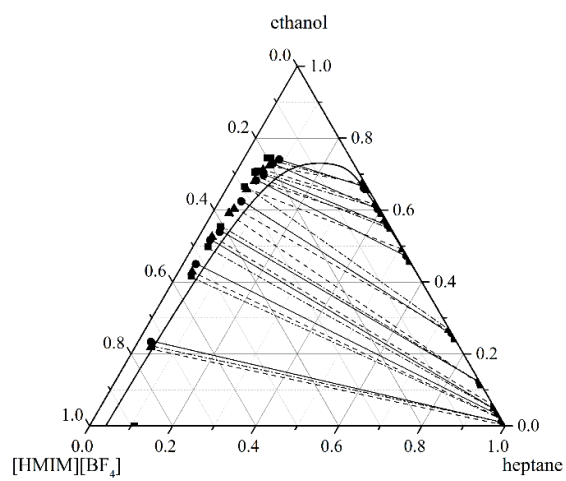
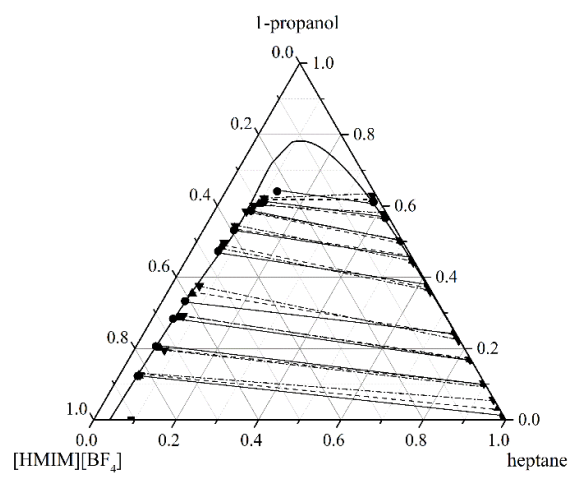
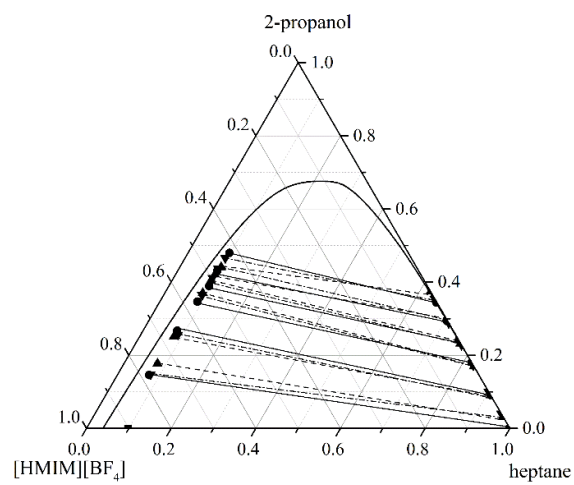


Fig. 2



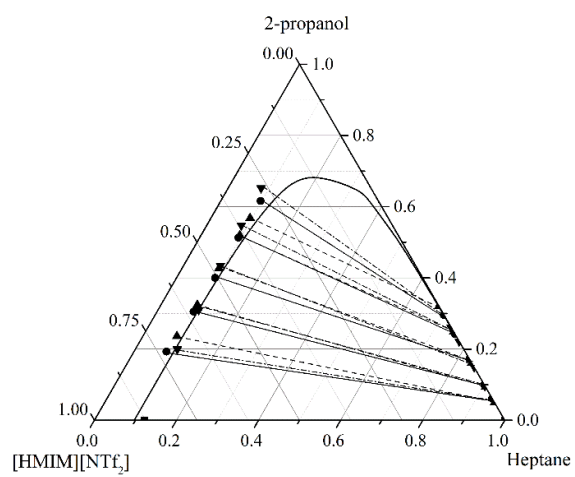
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Fig. 3



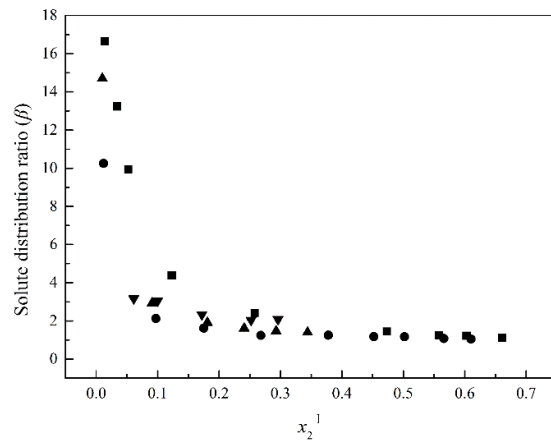
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Fig. 4



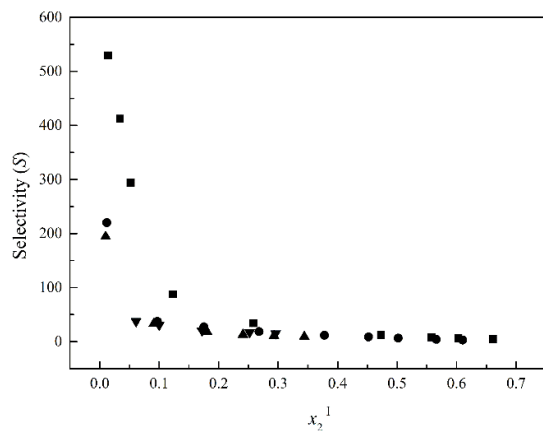
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Fig. 5



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Fig. 6



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Highlights

1. Liquid-liquid equilibria data of heptane + alcohol + IL were measured.
2. Influence of alkyl chain length of alcohols and ionic liquids' anion on the liquid-liquid equilibria was discussed.
3. The NRTL and UNIQUAC models were applied to correlate the studied system and the UNIFAC model was used to predict these systems with reasonable accuracy.

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