**Removal of thiophene from model diesel oil with nitrate based ionic liquids at
several temperatures**

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Abstract

In this work the desulfurization ability of two imidazolium based ionic liquids from *n*-decane, which is used as a model of fuel, has been developed. The systems of ternary liquid-liquid equilibria containing ionic liquid+ *n*-decane+ thiophene have been determined at three different temperatures. All systems have been shown the ability of IL's for removal thiophene from *n*-decane. The selectivity and the solute distribution ratio were calculated for all systems. The data obtained have been correlated with non-random two liquid NRTL model. The phase equilibria diagrams for the ternary mixtures including the experimental and calculated tie-lines have been presented.

Keywords: Desulfurization, Thiophene, [Bmim][NO₃], [Omim][NO₃], Diesel Fuel

1. Introduction

Removal of sulfur compounds from fuels is an important process in oil refineries and new environmental regulations are stricter for the reduction of sulfur compounds in fuels. According to the new law enacted in the USA and Europe, allowable level of sulfur compounds in the fuel should be 10 to 15 ppm [1]. Hydro desulfurization (HDS) is one of the most common methods for sulfur compounds removal but this process is hardly able to remove the aromatic sulfur compounds such as thiophenes, benzothiophenes, dibenzothiophenes, and their alkylated derivatives [2]. Moreover, the disadvantages of HDS process include high pressure (>4 MPa), high temperature ($>300^{\circ}\text{C}$) and high energy costs [2]. There are other methods for the aromatic sulfur compounds removal from fuels such as extraction desulfurization, bio-desulfurization, reactive or non-destructive adsorption, N-adsorption, oxidation, alkylation and complexation, and oxidation [3,4]. The extractive desulfurization is considered to be the most effective methods because the operational parameters for this process are in ambient temperature and pressure without any hydrogen consumption [4]. Ionic liquids (ILs) may be applied as an appropriate solvent for extractive desulfurization. These compounds are a new class of solvent that are liquid in room temperature [5]. ILs contain organic cation and inorganic anion and has unique properties like negligible vapor pressure, high chemical and thermal stabilities [2,3,5,6,7]. First, Boessmann et al. reported the desulfurization of diesel fuel by extraction with ILs in 2001 [8]. The ILs containing $[\text{PF}_6]$ and $[\text{BF}_4]$ anions were studied for this process [9]. Up to present time, many researchers have been examined different kinds of ILs to find out the appropriate IL for extractive desulfurization. Selection of an appropriate IL for desulfurization process is an important step. The desulfurization ability of IL is different with the cation and anion type [10].

Rodríguez-Cabo et al. [11,12] studied the desulfurization process with imidazolium and pyridinium based ILs. They found that the alkyl side chains on the IL's cation effect on desulfurization efficiency.

Most of the researches in this area belong to the effect of alkane chain length on desulfurization process and change of anion or cation type of ILs [13-16]. Krolikowski et al. [17] investigated the effect of temperature on desulfurization of benzothiophene and thiophene from *n*-heptane using 1-ethyl-3-methylimidazolium tricyanomethanide ([EMIM][TCM]). They observed the low impact of temperature on phase diagram.

Yu et al. [18] studied deep desulfurization of model fuel oils using a low-viscosity ionic liquid, 1-ethyl-3-methylimidazolium dicyanamide [C₂mim][N(CN)₂]. They found that the extraction is insensitive to temperature. However, the effect of temperature may be sensitive to the viscous ILs. The effect of temperature on extraction of aromatic from alkane using IL was studied by Al-tuwaim et al. [19,20]. They found the distribution coefficient values slightly increases as the temperature increases and the selectivity values decreases.

The present research is the continuation of our previous work on desulfurization of nitrate based ILs [4]. The removal of thiophene from *n*-decane is studied using 1-butyl 3- methyl imidazolium nitrate ([Bmim][NO₃]) and 1-methyl 3-octylimidazolium nitrate ([Omim][NO₃]) ILs at different temperatures. *n*-Decane is selected as a model fuel because it is the most important component in diesel fuel. Liquid-liquid equilibrium (LLE) data for the ternary systems of [Bmim][NO₃] or [Omim][NO₃]+ *n*-decane+ thiophene are reported at different temperatures and the effects of the cation's chain length on the extraction of thiophene is investigated. The experimental data are correlated using the NRTL model.

2. Material and method

Thiophene, *n*-decane and acetone were provided by Merck; the suppliers and the purities of all chemicals are given in Table1.

Table 1. The purities and suppliers of the chemicals

[Bmim][NO₃] and [Omim][NO₃] were synthesized by Chemistry and Chemical Engineering Research Center of Iran (CCERCI) laboratory according to the method described in the literature [21,22]. The detailed description of the procedure is available in our previous works [23,24].

The structure of the synthesized ILs was checked with nuclear magnetic resonance (NMR) spectroscopy. The purified ILs were dried and degassed for 24 h at 343.15 K under vacuum, and were kept in bottle under argon gas. The mass fractions of water in the dried products, measured by a Metrohm model 852 Karl Fischer coulometer, were less than 1×10^{-3} .

The experimental LLE were determined by preparation of immiscible mixtures of three components of IL+ alkane+ thiophene with total mass of 3g. The concentration of the ternary mixtures were selected in a region that the two liquid phases were formed. These mixtures were placed into 10 mL glass vials. Each component was weighted by a laboratory balance (Ohaus, Adventurer AV264C model) with the precision of $\pm 10^{-4}$ g. The mixture in the glass vial was closed firmly with a cap and septum and stirred by a shaker (IKA HS-260) for 120 min at 300 strokes per minute. The glass vials were placed for at least 12 hr into a water bath with a precision of ± 0.1 K (Huber, K20-NR). The two phases in the glass vials were separated and analyzed after the equilibrium condition was attained. The composition of each phase was

determined using gas chromatography (GC) Varian model, cp 3800 with FID detector, capillary column CP-SIL 5CB (Chrompack, 25 m × 0.3 mm × 1.2 μm) and injector and detector temperature of 250 and 280°C, respectively. As it was discussed in previous work [4] no IL exists in the top phase and all the IL is in the bottom phase. The GC cannot detect the IL composition and a liner was placed between column and injector for collecting the IL and protection of the column. The bottom phase compositions was determined by diluting the sample with acetone. All analysis was repeated three times and the experimental uncertainties for the top and bottom phase compositions are less than $\pm 1.10^{-3}$ and $\pm 2.10^{-3}$ in mole fraction, respectively.

3. Results & Discussion

3.1 Experimental data

The experimental data for the ternary systems of [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) and [Bmim][NO₃](1) + *n*-decane(2) + thiophene(3) at temperatures 288.15, 298.15 and 313.15 K and ambient pressure are reported in tables 2 and 3. The corresponding triangular diagrams with the experimental tie-lines for each system are shown in figures 1-2. The selectivity (S) and solute distribution ratio coefficient (β) defined by following equations:

$$S = \frac{x_3^{II} x_2^I}{x_3^I x_2^{II}} \quad (1)$$

$$\beta = \frac{x_3^{II}}{x_3^I} \quad (2)$$

where x is mole fraction, subscripts 2 and 3 refer to *n*-decane and thiophene and superscripts *I* and *II* refer to *n*-decane rich phase and IL rich phase respectively.

From Table 2, it is found that for [Bmim][NO₃] the highest selectivity occurs at 288.15 K. The selectivity and distribution coefficient decreases with increasing the temperature and increases when the mole fraction of thiophene in the hydrocarbon-rich phase decreases. Similar behavior is observed in table 3 for [Omim][NO₃]. It means these ILs can be utilized for deep desulfurization process.

The comparison of the selectivities in Tables 2 and 3 show that the [Bmim][NO₃] selectivities values are more than [Omim][NO₃]. In other words, increasing the alkane chain length on IL cation decreases selectivities and [Bmim][NO₃] is more suitable solvent than [Omim][NO₃]. The thiophene selectivity as a function of thiophene mole fraction in the hydrocarbon-rich phase for systems [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) and [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at several temperatures are represented in Figures 3 and 4. As the figures are indicating, the selectivity decreased as the solute mole fractions in the hydrocarbon-rich phase increased. In addition, the selectivity of thiophene was reduced with increasing the temperature. Increasing the temperature reduced the viscosity of IL rich phase and thiophene can be easily transferred to the alkane rich phase. Physical properties such as viscosity and density especially can effect on selectivity parameter. The great effect is related to density property. Densities of [Omim][NO₃] and [Bmim][NO₃] are 1.0642 and 1.1565 (g.cm⁻³) respectively [23]. [Omim][NO₃] with longer alkyl chains has more rooms to attract other components. The experimental data show that this IL has more distribution coefficient in comparison with [Bmim][NO₃] but solubility of model fuel in [Omim][NO₃] is much more than [Bmim][NO₃]. For this reason, "the selectivity values for [Bmim][NO₃] are more higher than [Omim][NO₃]. It shows that ILs with higher density have more selectivity and lower distribution coefficients [7].

Regarding to viscosity, when this parameter decreases, contact between two phases and mass transfer increases. Also, growth of temperature reduces the viscosity of IL rich phase sharply but the variation of density is slightly [23]. With increasing the temperature, the molecular space in IL rich phase is nearly constant, but enhancing the mass transfer is happened with increasing surface contact between the two phases.

The selectivity values for both ILs are compared and the selectivity values for [Bmim][NO₃] are more higher than [Omim][NO₃]. This means [Bmim][NO₃] is a more suitable solvent.

The thiophene distribution ratio values of both types of studied ILs with thiophene mole fraction in the alkane rich phase are compared in Figures 5 and 6. As the Figures show, the thiophene distribution ratio values for [Omim][NO₃] are more than ones for [Bmim][NO₃] that means, in equal conditions less amount of [Omim][NO₃] is needed as a solvent. Moreover, increasing temperature reduces the thiophene distribution ratio.

The Othmer-Tobias [25] equation is used to check the reliability of the experimental data.

$$\ln\left(\frac{1-w_2^I}{w_2^I}\right) = a + b \ln\left(\frac{1-w_1^{II}}{w_1^{II}}\right) \quad (3)$$

where w_1^{II} is the mass fractions of IL in the IL rich phase, w_2^I is the mass fractions of *n*-decane in the alkane rich phase and *a*, *b* are adjustable parameters. The adjustable parameters and the standard deviation (R^2) for the Othmer-Tobias equation are reported in Tables 4. As Table 4 indicates, since the standard deviations are near to unity the experimental data are in good agreement with Othmer-Tobias equation.

Table 2. Experimental LLE data in mole fraction and calculated thiophene selectivity (S) and solute distribution ratios (β) for ternary systems [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures and 88KPa.

Table 3. Experimental LLE data in mole fraction and calculated thiophene selectivity(S) and solute distribution ratios (β) for ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures and 88KPa.

Table 4. The Othmer – Tobias parameters and the standard deviation (R^2) for ternary systems of IL(1)+ *n*-decane(2) + thiophene(3).

In Figures 7 - 8 , the comparison of selectivities and solute distribution ratio for our ILs against mole fraction of thiophene in the *n*-decane rich phase with previous work are demonstrated [26].

The figures show that for all systems when thiophene concentration decreases, the solute distribution coefficient and selectivity increases. The selectivity remarkably increases as chain length of IL's cation decreases for all systems while the solute distribution coefficient decreases slightly. As can be seen, the selectivities of the system containing [Bmim][NO₃] is so higher than others ILs such as [Omim][SCN], [Omim][NO₃] and [Hmim][SCN]. This behavior may be related to the densities of ILs. Densities of [Bmim][NO₃], [Omim][NO₃], [Hmim][SCN] and [Omim][SCN] at 25°C are 1.1565, 1.0642, 1.057 and 1.0083 (g.cm³) respectively [23]. The experimental data indicated that ILs with higher density value has more distribution coefficient, more solubility of fuel model and lower selectivity parameter. Moreover, high alkane solubility was obtained which causes loss of fuel and consequently higher recycling costs.

In other words, decreasing the alkane chain length on IL cation increases selectivities and [Bmim][NO₃] is more suitable solvent than others.

3.2 Thermodynamic modeling

Modeling the experimental data has a great importance for any separation process. In this work, the experimental data was correlated with the NRTL (nonrandom liquid equation) model [27].

The activity coefficients in the NRTL model are expressed as:

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \left(\frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \right) \left(\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mi} x_m G_{mi}}{\sum_{k=1}^n x_k G_{kj}} \right) \quad (4)$$

$$\Delta g_{ij} = g_{ij} - g_{ji}, \quad (5)$$

$$G_{ij} = \exp(-\alpha \cdot \tau_{ij}) \quad (6)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (7)$$

where x is the mole fraction, R is the gas constant, T is absolute temperature, and Δg_{ij} is the binary energy parameter. The NRTL nonrandom parameter (α) was set to 0.3, which has given the best results of the correlation. The objective function is defined as the differences between the experimental and calculated mole fractions of each component and the energy parameters are calculated by minimization of this function.

$$F = \sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}}}{x_{ijk}^{\text{exp}}} \right)^2 \quad (8)$$

where m is the number of tie lines, n is the number of component, k is the number of phases, and superscripts of “exp” and “cal” refer to experimental and calculated mole fraction values,

respectively. The minimization was performed with the Solver in Excel software and the calculated energy parameters are given in Table 5. In this Table, RMSD is the root mean square deviation that represents the standard deviation of the differences between the experimental and correlated values.

$$rmsd = \left[\frac{\sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{exp} - x_{ijk}^{cal}}{x_{ijk}^{exp}} \right)^2}{6m} \right]^{1/2} \times 100, \quad (9)$$

where m is the number of the tie lines, n is the number of the components in the mixtures and k is the number of phases.

The comparisons of experimental data with those obtained from the NRTL model are plotted in Figures 1 and 2. As the Figures show, there are good agreements between the experimental and correlated results.

Table 5. Binary interaction parameters and root mean square deviation for NRTL equation for the ternary systems ILs(1)+ *n*-decane(2) + thiophene(3).

4. Conclusions

Experimental LLE data for ternary system of [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) and [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) are reported at different temperatures. The values of selectivity and distribution ratio are calculated from experimental data. The results indicated the selectivity values are reduced with increasing temperature. The effect of temperature in desulfurization is very low and their comparison show that the selectivity and distribution ratio decrease with increasing temperature. Also [Bmim][NO₃] exhibits a better extractive

performance for thiophene removal. It was shown that the length of ionic liquid's cationic chain is effective on selectivity and distribution ratio.

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1 **Figure captions**

2 **Figure 1.** Experimental LLE data (●, solid lines) and calculated with the NRTL correlation (Δ, dotted
3 lines) for the ternary systems of [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures.

4 **Figure 2.** Experimental LLE data (●, solid lines) and calculated with the NRTL correlation (Δ, dotted
5 lines) for the ternary systems of [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures.

6 **Figure 3.** Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich
7 phase for the ternary system [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K; ▲,
8 313.15 K.

9 **Figure 4.** Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich
10 phase for the ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K;
11 ▲, 313.15 K.

12 **Figure 5.** Plot of the thiophene distribution ratio, (β) against thiophene mole fraction in the hydrocarbon-
13 rich phase for the ternary systems [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15
14 K; ▲, 313.15 K.

15 **Figure 6.** Plot of the thiophene distribution ratio, (β) against thiophene mole fraction in the hydrocarbon-
16 rich phase for the ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15
17 K; ▲, 313.15 K.

18 **Figure 7.** Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich
19 phase for the ternary systems of ILs (■ Bmim[NO₃], ● Omim[NO₃], ▲ Hmim[SCN]²⁶ and ♦
20 Omim[SCN]²⁶) + *n*-decane+ thiophene at 298.15 K.

21 **Figure 8.** Plot of thiophene distribution ratio, (β) versus the thiophene mole fraction in the hydrocarbon-
22 rich phase for the ternary systems of ILs (■ Bmim[NO₃], ● Omim[NO₃], ▲ Hmim[SCN]²⁶ and ♦
23 Omim[SCN]²⁶) + *n*-decane+ thiophene at 298.15 K.

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Table 1. The purities and suppliers of the chemicals

Chemical name	Supplier	purity	M.W.	Water content
<i>n</i> -Decane	Merck	≥%99	142.29	<%0.01
Thiophene	Merck	≥%99	84.14	<%0.05
Acetone	Merck	≥%99	58.07	<%0.3
[Bmim][NO3]	(CCERCI) laboratory	≥%99	201.33	<%0.1
[Omim][NO3]	(CCERCI) laboratory	≥%99	257.33	<%0.1

Table 2. Experimental LLE data in mole fraction and calculated thiophene selectivity (S) and solute distribution ratios (β) for ternary systems [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures and 88KPa.

Feed			Alkane rich phase ¹			IL rich phase ²				
x ₁	x ₂	x ₃	x ₁ ^I	x ₂ ^I	x ₃ ^I	x ₁ ^{II}	x ₂ ^{II}	x ₃ ^{II}	β	S
T=288.15 K										
0.419	0.059	0.523	0.000	0.434	0.566	0.481	0.003	0.516	0.91	157.90
0.405	0.121	0.473	0.000	0.484	0.516	0.537	0.002	0.460	0.89	177.22
0.389	0.182	0.428	0.000	0.547	0.453	0.582	0.002	0.416	0.92	250.84
0.394	0.234	0.372	0.000	0.630	0.370	0.625	0.002	0.373	1.01	317.95
0.408	0.247	0.345	0.000	0.652	0.348	0.655	0.002	0.343	0.99	318.54
0.390	0.296	0.314	0.000	0.680	0.320	0.689	0.002	0.309	0.97	352.90
0.418	0.372	0.210	0.000	0.801	0.199	0.778	0.002	0.220	1.11	482.08
0.403	0.417	0.180	0.000	0.839	0.161	0.800	0.002	0.198	1.23	500.60
0.399	0.483	0.118	0.000	0.895	0.105	0.866	0.002	0.132	1.26	613.51
0.402	0.543	0.054	0.000	0.951	0.049	0.936	0.002	0.062	1.27	634.05
T=298.15 K										
0.402	0.067	0.531	0.000	0.381	0.619	0.484	0.002	0.513	0.83	140.80
0.383	0.126	0.490	0.000	0.461	0.539	0.525	0.002	0.472	0.88	162.10
0.393	0.176	0.431	0.000	0.534	0.466	0.584	0.002	0.414	0.89	232.57
0.395	0.231	0.374	0.000	0.621	0.379	0.626	0.002	0.371	0.98	253.11
0.391	0.265	0.344	0.000	0.657	0.343	0.652	0.002	0.345	1.01	237.66
0.386	0.302	0.313	0.000	0.693	0.307	0.681	0.002	0.316	1.03	426.51
0.405	0.356	0.239	0.000	0.758	0.242	0.761	0.002	0.236	0.98	258.79
0.396	0.417	0.187	0.000	0.829	0.171	0.795	0.002	0.202	1.18	357.01
0.408	0.480	0.113	0.000	0.902	0.098	0.869	0.002	0.129	1.31	691.99
0.400	0.523	0.077	0.000	0.929	0.071	0.914	0.002	0.084	1.17	769.79
0.385	0.554	0.061	0.000	0.943	0.057	0.932	0.002	0.066	1.11	768.05
T=313.15 K										
0.370	0.092	0.538	0.000	0.373	0.627	0.487	0.003	0.510	0.81	111.83
0.384	0.173	0.444	0.000	0.507	0.493	0.578	0.003	0.419	0.85	144.08
0.403	0.209	0.388	0.000	0.579	0.421	0.628	0.002	0.369	0.88	205.64
0.381	0.306	0.312	0.000	0.657	0.343	0.713	0.002	0.284	0.83	234.55
0.412	0.361	0.227	0.000	0.769	0.231	0.774	0.003	0.223	0.97	296.96
0.402	0.387	0.211	0.000	0.788	0.212	0.788	0.002	0.210	0.99	312.43
0.412	0.440	0.148	0.000	0.858	0.142	0.842	0.002	0.155	1.09	386.06
0.424	0.483	0.093	0.000	0.909	0.091	0.902	0.002	0.095	1.05	415.30
0.401	0.517	0.082	0.000	0.920	0.080	0.913	0.002	0.085	1.06	449.11
0.386	0.561	0.053	0.000	0.950	0.050	0.940	0.002	0.057	1.14	483.92

¹ Exp standard uncertainty= ± 0.001 , ² Exp standard uncertainty= ± 0.002
Standard uncertainty for temperature= ± 0.1 K

1 Table 3. Experimental LLE data in mole fraction and calculated thiophene selectivity(S) and solute
2 distribution ratios (β) for ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different
3 temperatures and 88KPa.

Feed			Alkane rich phase ¹			IL rich phase ²				
x ₁	x ₂	x ₃	x ₁ ^I	x ₂ ^I	x ₃ ^I	x ₁ ^{II}	x ₂ ^{II}	x ₃ ^{II}	β	S
T=288.15 K										
0.394	0.219	0.387	0.000	0.702	0.298	0.544	0.036	0.420	1.41	27.53
0.363	0.332	0.305	0.000	0.763	0.237	0.616	0.032	0.353	1.49	35.78
0.411	0.342	0.247	0.000	0.816	0.184	0.679	0.033	0.289	1.57	39.19
0.413	0.373	0.214	0.000	0.846	0.154	0.709	0.034	0.257	1.67	41.57
0.410	0.409	0.181	0.000	0.862	0.138	0.751	0.032	0.217	1.57	42.29
0.401	0.471	0.128	0.000	0.900	0.100	0.811	0.031	0.158	1.58	45.31
0.405	0.489	0.105	0.000	0.928	0.072	0.824	0.037	0.140	1.94	49.16
0.412	0.504	0.084	0.000	0.943	0.057	0.851	0.037	0.112	1.97	50.08
0.388	0.580	0.032	0.000	0.977	0.023	0.920	0.035	0.045	1.93	53.55
T=298.15 K										
0.376	0.155	0.469	0.000	0.627	0.373	0.471	0.036	0.493	1.32	22.97
0.405	0.231	0.364	0.000	0.713	0.287	0.566	0.040	0.394	1.37	24.58
0.394	0.311	0.294	0.000	0.788	0.212	0.624	0.034	0.342	1.61	37.38
0.414	0.340	0.247	0.000	0.815	0.185	0.681	0.033	0.286	1.55	38.20
0.414	0.411	0.174	0.000	0.868	0.132	0.758	0.033	0.209	1.59	42.31
0.411	0.481	0.108	0.000	0.920	0.080	0.829	0.033	0.138	1.72	48.01
0.401	0.516	0.083	0.000	0.939	0.061	0.861	0.032	0.107	1.74	51.84
0.398	0.539	0.064	0.000	0.955	0.045	0.880	0.034	0.086	1.89	52.73
0.367	0.602	0.031	0.000	0.977	0.023	0.921	0.036	0.044	1.94	53.28
T=313.15 K										
0.393	0.228	0.379	0.000	0.676	0.324	0.563	0.034	0.402	1.24	24.60
0.397	0.288	0.315	0.000	0.751	0.249	0.616	0.032	0.352	1.41	32.68
0.408	0.343	0.249	0.000	0.815	0.185	0.675	0.034	0.290	1.57	37.25
0.416	0.375	0.209	0.000	0.835	0.165	0.725	0.034	0.241	1.46	35.49
0.413	0.412	0.174	0.000	0.859	0.141	0.763	0.034	0.203	1.44	36.22
0.394	0.446	0.160	0.000	0.875	0.125	0.770	0.036	0.194	1.55	37.74
0.409	0.466	0.125	0.000	0.900	0.100	0.817	0.033	0.150	1.50	41.54
0.410	0.484	0.105	0.000	0.917	0.083	0.839	0.033	0.128	1.54	43.31
0.413	0.502	0.085	0.000	0.932	0.068	0.864	0.032	0.104	1.54	44.36
0.383	0.574	0.043	0.000	0.967	0.033	0.910	0.034	0.056	1.66	46.44

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2 Exp standard uncertainty= ± 0.001 , Exp standard uncertainty= ± 0.002
3 Standard uncertainty for temperature= ± 0.1 K

1 Table 4. The Othmer – Tobias parameters and the standard deviation (R^2) for ternary systems of IL(1)+ *n*-
2 decane(2) + thiophene(3).

T	a	b	R^2
[Bmim] [NO ₃] (1)+ thiophene (2) + decane (3)			
288.15	0.6175	1.1658	0.994
298.15	0.7618	1.2219	0.991
313.15	0.9064	1.223	0.995
[Omim] [NO ₃] (1)+ thiophene (2) + decane (3)			
288.15	0.4627	1.3843	0.980
298.15	0.3317	1.3344	0.984
313.15	0.4694	1.3226	0.987

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Table 5. Binary interaction parameters and root mean square deviation for NRTL equation for the ternary systems ILs(1)+ *n*-decane(2) + thiophene(3).

Component	NRTL parameters		RMSD
i-j	$\Delta g_{ij}/(\text{kJ. mol}^{-1})$	$\Delta g_{ji}/(\text{kJ. mol}^{-1})$	
[Bmim] [NO ₃] (1)+ <i>n</i> -decane(2) + thiophene(3)			
1-2	28.298	-5.210	0.597
1-3	5.476	26.101	
2-3	6.037	27.263	
[Omim] [NO ₃] (1)+ <i>n</i> -decane(2) + thiophene(3)			
1-2	15.387	-1.653	1.195
1-3	4.565	10.429	
2-3	6.335	15.847

Figure 1. Experimental LLE data (●, solid lines) and calculated with the NRTL correlation (Δ, dotted lines) for the ternary systems of [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures.

Figure 2. Experimental LLE data (●, solid lines) and calculated with the NRTL correlation (Δ, dotted lines) for the ternary systems of [Oimim][NO₃](1)+ *n*-decane(2)+ thiophene(3) at different temperatures.

Figure 3. Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich phase for the ternary system [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

Figure 4. Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich phase for the ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

Figure 5. Plot of the thiophene distribution ratio, (β) against thiophene mole fraction in the hydrocarbon-rich phase for the ternary systems [Bmim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

Figure 6. Plot of the thiophene distribution ratio, (β) against thiophene mole fraction in the hydrocarbon-rich phase for the ternary systems [Omim][NO₃](1)+ *n*-decane(2)+ thiophene(3) ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

Figure 7. Plot of thiophene selectivity, (S) versus the thiophene mole fraction in the hydrocarbon-rich phase for the ternary systems of ILs (■ Bmim[NO₃], ● Omim[NO₃], ▲ Hmim[SCN]²⁶ and ♦ Omim[SCN]²⁶) + *n*-decane+ thiophene at 298.15 K.

Figure 8. Plot of thiophene distribution ratio, (β) versus the thiophene mole fraction in the hydrocarbon-rich phase for the ternary systems of ILs ($\blacksquare$ Bmim[NO₃], $\bullet$ Omim[NO₃], $\blacktriangle$ Hmim[SCN]²⁶ and $\blacklozenge$ Omim[SCN]²⁶) + *n*-decane+ thiophene at 298.15 K.