

# Extraction of Benzene or Thiophene from *n*-Heptane Using Ionic Liquids. NMR and Thermodynamic Study

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Received: December 18, 2009; Revised Manuscript Received: February 12, 2010

In this work,  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy were used to study the interactions between thiophene or benzene with three imidazolium based ionic liquids (ILs): 1-butyl-3-methylimidazolium tetrafluoroborate, 1,3-dimethylimidazolium methylphosphonate, and 1-butyl-3-methylimidazolium thiocyanate. NMR study indicates that solubility of thiophene or benzene in ionic liquid strongly depends on the structure of the ionic liquid. Structural organizations of such systems have been proposed. From these results, liquid–liquid equilibria (LLE) measurements of ternary mixtures containing benzene or thiophene with *n*-heptane and these ILs were carried out at 298.15 K in order to check the ability of these ILs to act as extractive solvents.

## Introduction

Liquid–liquid extraction is a separation process commonly used in many areas of industry (chemical, pharmaceutical, and nuclear). Nevertheless, nowadays improvements regarding environmental regulations and economic considerations have to be made in order to obtain a safe and environmentally benign process. Chemical industry has to reduce the use of pollutant solvents and the development of a sustainable green chemistry. Many industrial processes need to separate azeotropic systems such as those containing aromatics and saturated hydrocarbons or alcohols and aliphatic hydrocarbons. Indeed, the separation of aromatic or alcohol compounds from aliphatic hydrocarbon is challenging because these compounds have similar boiling points and several combinations form azeotropes. Considerable attention has also been paid to deep desulfurization of gasoline and diesel fuels as the environment regulations on the sulfur limits of fuels are increasingly stringent. It is critically important to develop new desulfurization technologies to minimize the negative health and environmental pollutions from diesel exhaust gas.

The application of ionic liquids (ILs) for separation processes is promising because of their nonvolatile nature. Compared to conventional organic solvents, the use of ILs for many applications has a number of advantages determined by the unique combination of their properties. These liquids have good thermal stability and negligible vapor pressure. ILs are miscible with substances having a very wide range of polarities, and they can simultaneously dissolve organic and inorganic substances. Physical properties of ILs can be modified and adjusted by employing different cation–anion combinations. These features offer opportunities for a large number of applications including catalysis, synthesis, gas separations, and liquid–liquid extractions.<sup>1–3</sup> Thermodynamic measurements such as activity coefficients at infinite dilution have proved that ILs are good candidates as alternative solvents in order to replace volatile organic compounds (VOCs) in separation processes. Indeed, the selectivities at infinite dilution for a specific separation using

ILs are in most cases higher than those with solvents classically used.<sup>4</sup> This is mainly due to the low miscibility of aliphatic compounds and the high solubility of polar compounds in ILs. It was recently shown that imidazolium based ionic liquids could be used in the liquid–liquid extraction of benzene or thiophene from aliphatic hydrocarbons.<sup>5–7</sup> Moreover, numerous studies have been carried out on the interaction between aromatics or sulfur compounds with ionic liquids. Su and co-workers demonstrated using nuclear magnetic resonance (NMR) analysis that thiophene molecules are accommodated into the ionic pair structure of the ionic liquids, enabling the selective and extractive removal of aromatic sulfur compounds from fuels.<sup>8</sup> A unique feature of ionic liquids as salts is their mobility and flexibility, which allow for a facile restructuring of the ionic liquids in the process of thiophene dissolution. The restructuring process is primarily driven by the interaction of thiophene with the imidazolium cations of the ionic liquids, and the maximum absorption capacity of thiophene by ionic liquids is primarily determined by the size and structure of both cations and anions.<sup>8</sup>

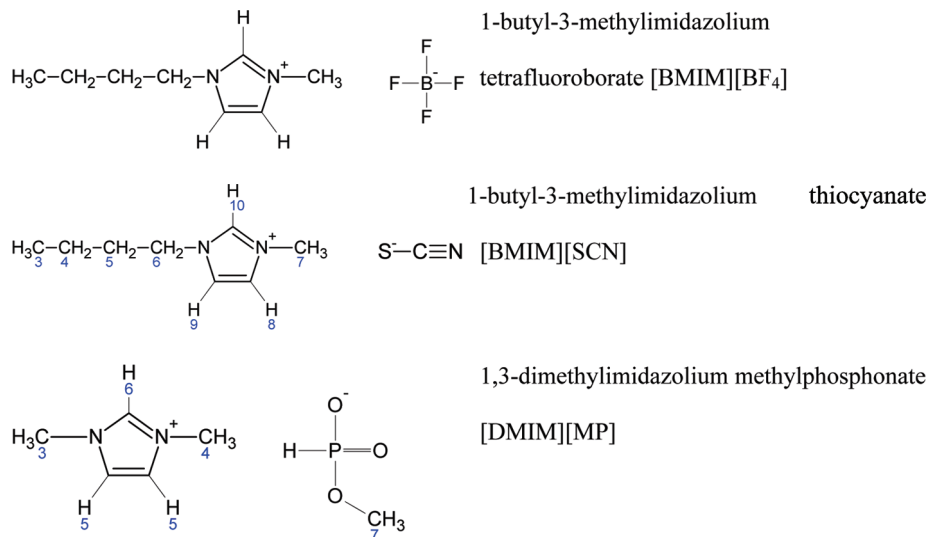
In our previous works,<sup>9–13</sup> we have contributed to develop a large databank on thermodynamic properties of imidazolium based ionic liquids by determining activity coefficients at infinite dilution of organic compounds in ILs using inverse gas chromatography. While researchers have an interest in ionic liquids, physicochemical properties of pure ionic liquid and their mixtures needed to design processes are lacking.

The aim of this study is to investigate the possible use of ILs as solvents for two separation problems frequently encountered in chemical industry: {aromatic + aliphatic} or {sulfur

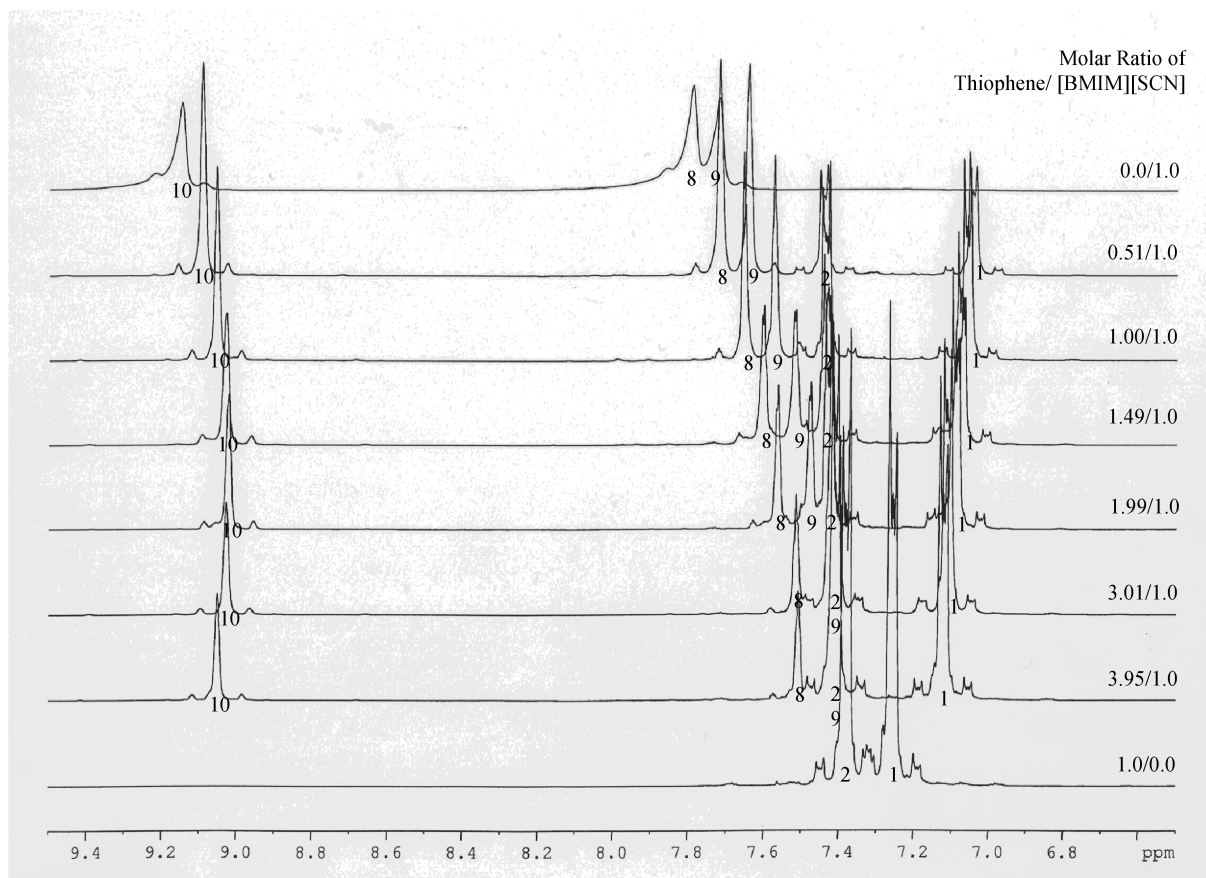
TABLE 1: GC Operating Conditions for Composition Analysis

injector temperature	250 °C
carrier gas	helium
capillary column	WCOT Ulti-Metal coated with HT-SIMDIST-CB (10 m × 0.53 mm × 0.53 μm) with an empty precolumn
flow rate	2 mL·min <sup>-1</sup>
column oven	70 °C → 125 °C (5 °C/min), 5 min
detector type	FID
detector temperature	250 °C

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**Figure 1.** Structures and proton NMR signal assignments of thiophene and ionic liquids.



**Figure 2.** <sup>1</sup>H NMR signal assignments of the ring protons in thiophene and [BMIM][SCN] at various molar ratios of thiophene/[BMIM][SCN]. (The top spectrum is the neat [BMIM][SCN], and the bottom spectrum is the neat thiophene.)

compound + aliphatic}. This work is focused on three ILs: 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>], 1,3-dimethylimidazolium methylphosphonate, and 1-butyl-3-methylimidazolium thiocyanate.

In the first part of this article, a study based on NMR spectroscopy has been carried out to investigate the structural change of neat ionic liquids when a sulfur compound such as thiophene or an aromatic such as benzene is added. <sup>1</sup>H and <sup>31</sup>P NMR spectroscopies were used to have a better understanding of the structural organization of such systems. It is clear that the structures of the ionic liquid cation and anion play an

important role in the solubility of benzene or thiophene. The second section of our article proposes an application of these ILs to act as solvents for extraction of such organic compounds from aliphatic hydrocarbons. Therefore, liquid–liquid equilibria (LLE) measurement of ternary mixtures for six systems were then measured at 298.15 K and atmospheric pressure: {benzene + *n*-heptane + 1-butyl-3-methylimidazolium tetrafluoroborate}, {benzene + *n*-heptane + 1,3-dimethylimidazolium methylphosphonate}, {benzene + *n*-heptane + 1-butyl-3-methylimidazolium thiocyanate}, {thiophene + *n*-heptane + 1-butyl-3-methylimidazolium tetrafluoroborate}, {thiophene + *n*-heptane

+ 1,3-dimethylimidazolium methylphosphonate}, and {thiophene + *n*-heptane + 1-butyl-3-methylimidazolium thiocyanate}. Experimental data were correlated using the NRTL and UNIQUAC activity coefficient models. Finally, values of solute distribution ratio  $\beta$  and selectivity  $S$  obtained from thermodynamic study are compared with the NMR analysis.

### Experimental Procedures and Results

**Materials or Chemicals.** Benzene and *n*-heptane were supplied by Aldrich with a quoted purity of 99 and 99.5%, respectively. Thiophene was purchased from Acros, with a purity of 99.5% (benzene free). The ionic liquids investigated in this work were from Solvionic for 1-butyl-3-methylimidazolium tetrafluoroborate (99.5%) and 1,3-dimethylimidazolium methylphosphonate (98%). 1-Butyl-3-methylimidazolium thiocyanate was obtained from Fluka and was reported to have a purity >95%. Before measurements, the ionic liquids were purified by subjecting the liquid under a vacuum for approximately 12 h to remove possible traces of solvents and moisture. Analysis for the water content for the ionic liquids using the Karl Fischer technique showed that the water contents ranged from 300 (1-butyl-3-methylimidazolium tetrafluoroborate) to 700 ppm.

**Apparatus and Experimental Procedure. NMR Studies for Investigations on Solute–IL Interactions.** Binary mixtures of thiophene or benzene with ionic liquids were weighted using an analytical balance and were stirred for 2 h to get a good contact between both phases and kept overnight in order to settle down. In order to determine the solubility of solutes in ionic liquids, the ionic liquid phase was analyzed using gas chromatography (GC). The operator conditions are given in Table 1. For NMR analysis, approximately 0.3 mL of the ionic liquid phase with a predetermined solute/ionic liquid ratio was added into a 5 mm NMR tube. A stem coaxial capillary tube loaded with acetone-*d*<sub>6</sub> (CD<sub>3</sub>COCD<sub>3</sub>) was inserted into the 5 mm NMR tube. The deuterium in acetone was used for the external lock of the NMR magnetic field, and the residual CHD<sub>2</sub>COCD<sub>3</sub> in acetone-*d*<sub>6</sub> was used as the <sup>1</sup>H NMR external reference at 2.050 ppm. When <sup>1</sup>H NMR data are obtained in this way, the reference signal of CHD<sub>2</sub>COCD<sub>3</sub> will remain as a constant and not be affected by change in sample concentration.

NMR spectra were collected using Bruker Avance 300 MHz (300 MHz for <sup>1</sup>H) and Mercury Varian-400 (400 MHz for <sup>1</sup>H and 162 MHz for <sup>31</sup>P) NMR spectrometers.

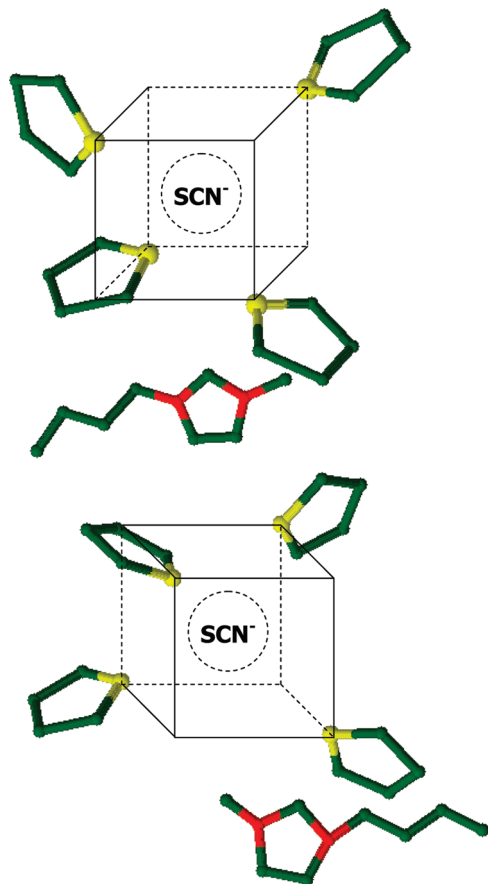
**Determination of Tie Lines of Ternary Mixtures.** The LLE measurements of ternary mixtures have been performed in jacketed glass cells. The experimental set up consists of a cell with an internal volume of about 30 cm<sup>3</sup> kept at a constant temperature of 298.15 K using a thermostatted bath. The temperature inside the cell is measured by a platinum resistance thermometer PT-100 with an accuracy of ±0.1 K. The ternary mixtures, with compositions inside the immiscible region of the system, are weighted using a METTLER analytical balance with a precision of ±0.0001 g. All of the mixtures were vigorously stirred using a Teflon coated magnet for 2 h to get a good contact between both phases and kept overnight in order to settle down.

Then, samples of both layers were taken from the cell using a syringe. The compositions of organic compounds such as *n*-heptane, benzene, or thiophene were determined by gas chromatography. The GC operating conditions are given in Table 1. All GC analysis were repeated three times to check reproducibility. The sample concentration was given according to the area of each chromatograph peak and the calibration curve made prior for all of the solutes. For determination of the ionic liquid composition, density measurements of both phases were

TABLE 2: <sup>1</sup>H Chemical Shift of the Thiophene in [BMIM][SCN]<sup>a</sup>

R	H 1	H 2	H 3	H 4	H 5	H 6	H 7	H 8	H 9	H 10
thiophene	7.38	7.258								
3.95	7.406 (+0.026)	7.121 (−0.137)	0.908 (0.161)	1.273 (0.087)	1.745 (−0.040)	4.104 (−0.157)	9.052 (−0.097)	7.406 (−0.312)	7.508 (−0.280)	3.785 (−0.207)
3.01	7.412 (+0.032)	7.113 (−0.145)	0.891 (0.144)	1.258 (0.072)	1.736 (−0.049)	4.102 (−0.159)	9.029 (−0.120)	7.412 (−0.306)	7.515 (−0.273)	3.780 (−0.212)
1.99	7.428 (+0.048)	7.090 (−0.168)	0.824 (0.077)	1.253 (+0.067)	1.727 (−0.058)	4.115 (−0.146)	9.023 (−0.126)	7.478 (−0.240)	7.566 (−0.222)	3.821 (−0.171)
1.49	7.433 (+0.053)	7.073 (−0.185)	0.814 (0.067)	1.213 (0.027)	1.735 (−0.050)	4.131 (−0.130)	9.030 (−0.119)	7.518 (−0.200)	7.603 (−0.185)	3.857 (−0.135)
1.00	7.436 (+0.056)	7.059 (−0.199)	0.795 (0.048)	1.200 (0.014)	1.737 (−0.048)	4.160 (−0.101)	9.056 (−0.093)	7.652 (−0.066)	7.674 (−0.114)	3.879 (−0.113)
0.51	7.442 (+0.062)	7.043 (−0.215)	0.770 (0.023)	1.178 (−0.008)	1.751 (−0.034)	4.199 (−0.062)	9.093 (−0.056)	7.681 (−0.037)	7.717 (−0.071)	3.922 (−0.070)
[BMIM][SCN]			0.747	1.186	1.785	4.261	9.149	7.718	7.788	3.992

<sup>a</sup> ( ):  $\delta_0 - \delta_R$ , where  $\delta_0$  is the proton chemical shift of neat thiophene or of neat ionic liquid and  $\delta_R$  is the proton chemical shift of thiophene and of the ionic liquid for a molar ratio *R*.



**Figure 3.** Proposed structure of thiophene in the ionic liquid [BMIM][SCN].

performed at 298.15 K with a vibrating tube densimeter (Anton Paar, model DMA601). The uncertainty in the measurements is  $\pm 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . The estimated uncertainty in the determination of mole fraction compositions is  $\pm 10^{-4}$ . NMR analysis of the hydrocarbon-rich phase was also performed to check its possible contamination with ionic liquid. An example of spectra is presented in Figure 1S of the Supporting Information.

## Results and Discussion

**Study on the Interaction between Thiophene and [BMIM][SCN] Ionic Liquid Using  $^1\text{H}$  NMR Spectroscopy.** To investigate the interaction and the specific local structure of thiophene with [BMIM][SCN], the binary systems were analyzed using  $^1\text{H}$  NMR spectroscopy in order to follow the local structure changes of the ionic liquid at various levels of solute absorption. The proton NMR signals corresponding to the protons on thiophene and to those on the imidazolium cation

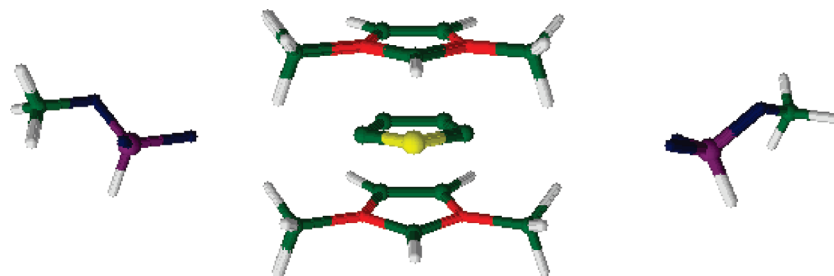
of ionic liquids for these systems are assigned in Figure 1. The  $^1\text{H}$  NMR chemical shifts  $\delta$  of neat thiophene and neat [BMIM][SCN] at different molar ratios of thiophene/[BMIM][SCN] are reported in Table 2. In Figure 2,  $^1\text{H}$  NMR spectra and signal assignment for protons in aromatic rings of thiophene and imidazolium cation of the system thiophene/[BMIM][SCN] are shown. The variation of chemical shifts could be explained by several contributions such as the aromatic ring current effect (i.e.,  $\pi$ - $\pi$  interaction), C-H- $\pi$  interaction between the cation and the thiophene, the anion effect, the dilution effect, and the electrostatic field effect.<sup>8</sup> The dilution of [BMIM][SCN] by thiophene does not break apart the strong Coulombic interactions between the cation and the anion. Indeed, phase equilibria of the binary system containing {[BMIM][SCN] + thiophene} indicates that thiophene has a low solubility in this ionic liquid. Therefore, the dilution effect does not lead to a noticeable variation of the chemical shift.

C-H- $\pi$  interaction between the cation and the thiophene could also induce a quasi-equal variation in the chemical shift for the protons. Moreover, the acidic hydrogen atoms of the imidazolium cation form weak hydrogen bonds to the sulfur of the thiocyanate anions.<sup>14</sup>

The electric field effect is not a dominant factor in measuring the absorption capacity of thiophene in binary mixtures. Indeed, a similar chemical shift effect may be observed in other solvents such as *n*-alkanes. However, apolar solvents are known to have a very low solubility in ionic liquids and no chemical shift can be observed.

$^1\text{H}$  NMR chemical shifts of the ring protons in neat thiophene (bottom spectrum) are more upfield than those in neat [BMIM][SCN] liquid (top spectrum), indicating that the aromatic ring current effect is stronger in neat thiophene than in neat [BMIM][SCN] because thiophene molecules are tightly packed. In our case, the bulky  $\text{SCN}^-$  anion prevents the  $\text{BMIM}^+$  cation from coming close, thus greatly reducing the aromatic current effect.<sup>8</sup>

The aromatic ring current effect is shown by a decrease of the chemical shifts of protons situated above or below the shielding cone of the aromatic ring (i.e., they move upfield), whereas the protons situated outside the shielding cone are shifted downfield. In our case, the chemical shift  $\delta(1[\text{CH}])$  of neat thiophene is less upfield than that in mixtures whereas  $\delta(2[\text{CH}])$  of neat thiophene is less downfield than that in mixtures. According to chemical shifts, protons 5, 6, and 7 are in the shielding cone of thiophene while protons 3 and 4 are outside of this zone. The molar ratio of thiophene dissolved in [BMIM][SCN] was found to be 3.95/1. From NMR study, we can propose a structural organization of the system {thiophene + [BMIM][SCN]} in Figure 3. According to the solubility of thiophene in [BMIM][SCN], i.e., 3.95 mol of thiophene for 1 mol of ionic liquid, four thiophene molecules form a pseudo-tetrahedron geometry surrounding the  $\text{BMIM}^+$  cation with the



**Figure 4.** Proposed structure of thiophene in the ionic liquid [DMIM][MP].



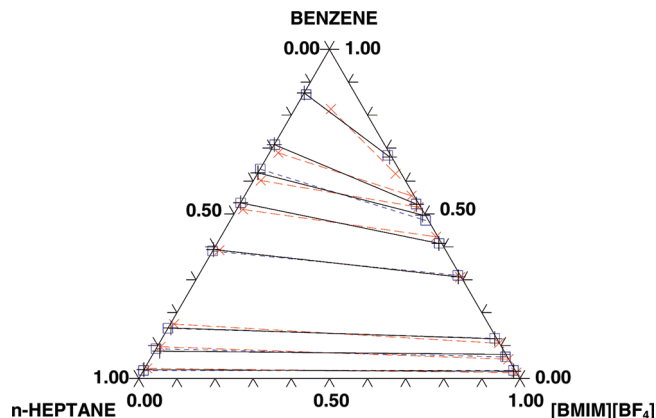
**TABLE 3: Compositions of Experimental Tie Lines, Solute Distribution Ratios  $\beta$ , and Selectivity  $S$  for All Ternary Systems at  $T = 298.15$  K**

hydrocarbon-rich phase			IL-rich phase			$\beta$	$S$
$x_1^{\text{HC}}$	$x_2^{\text{HC}}$	$x_3^{\text{HC}}$	$x_1^{\text{IL}}$	$x_2^{\text{IL}}$	$x_3^{\text{IL}}$		
Benzene (1) + Heptane (2) + [BMIM][BF <sub>4</sub> ] (3)							
0.0229	0.9771	0.	0.0223	0.0053	0.9724	0.97	179.5
0.0830	0.9036	0.0134	0.0735	0.0085	0.9181	0.89	94.1
0.1536	0.8391	0.0073	0.1208	0.0060	0.8732	0.79	110.0
0.3916	0.6084	0	0.3090	0.0071	0.6839	0.79	67.6
0.5337	0.4663	0	0.4106	0.0075	0.5819	0.77	47.8
0.6248	0.3752	0	0.4967	0.0070	0.4963	0.79	42.6
0.7109	0.2891	0	0.5292	0.0067	0.4641	0.74	32.1
0.8676	0.1324	0	0.6731	0.0056	0.3213	0.78	18.3
Benzene (1) + Heptane (2) + [DMIM][MP] (3)							
0.03350	0.96650	0	0.02694	0.00054	0.97252	0.80	1434.5
0.10480	0.89520	0	0.03751	0.00038	0.96211	0.36	837.1
0.20600	0.79400	0	0.05503	0.00053	0.94444	0.27	399.9
0.42460	0.57540	0	0.07867	0.00039	0.92094	0.19	274.2
0.58800	0.41200	0	0.09823	0.00038	0.90139	0.17	180.2
0.69210	0.30790	0	0.10174	0.00048	0.89778	0.15	94.4
0.86650	0.13350	0	0.11856	0.00024	0.88121	0.14	77.4
0.93320	0.06680	0	0.12332	0.00017	0.87652	0.13	52.7
Benzene (1) + Heptane (2) + [BMIM][SCN] (3)							
0.0223	0.9777	0	0.0446	0.0081	0.9474	2.00	238.4
0.0539	0.9461	0	0.0774	0.0078	0.9148	1.44	175.2
0.1497	0.8503	0	0.1549	0.0092	0.8358	1.03	95.2
0.3665	0.6335	0	0.3730	0.0096	0.6175	1.02	67.3
0.5094	0.4906	0	0.4876	0.0103	0.5021	0.96	45.8
0.6493	0.3507	0	0.5707	0.0090	0.4203	0.88	34.2
0.7055	0.2945	0	0.6152	0.0091	0.3757	0.87	28.2
0.8240	0.1760	0	0.6961	0.0086	0.2953	0.84	17.2
Thiophene (1) + Heptane (2) + [BMIM][BF <sub>4</sub> ] (3)							
0.0308	0.9692	0	0.0528	0.0044	0.9428	1.71	375.3
0.0939	0.9061	0	0.1520	0.0067	0.8412	1.62	217.6
0.1684	0.8316	0	0.2749	0.0081	0.7169	1.63	166.8
0.2640	0.7360	0	0.3905	0.0088	0.6006	1.48	123.1
0.3007	0.6993	0	0.4184	0.0089	0.5726	1.39	109.0
0.3858	0.6142	0	0.5007	0.0095	0.4898	1.30	84.4
0.5187	0.4813	0	0.5849	0.0101	0.4050	1.13	53.5
0.6034	0.3966	0	0.6319	0.0108	0.3573	1.05	38.3
0.7104	0.2896	0	0.6592	0.0097	0.3311	0.93	27.8
Thiophene (1) + Heptane (2) + [DMIM][MP] (3)							
0.0284	0.9716	0	0.0314	0.0008	0.9678	1.11	1370.1
0.0554	0.9446	0	0.0443	0.0007	0.9550	0.80	1074.3
0.0986	0.9014	0	0.0704	0.0006	0.9291	0.71	1152.3
0.1861	0.8139	0	0.0951	0.0007	0.9042	0.51	590.9
0.3424	0.6576	0	0.1335	0.0007	0.8658	0.39	349.1
0.5310	0.4690	0	0.1687	0.0004	0.8309	0.32	388.6
0.6828	0.3172	0	0.1810	0.0004	0.8186	0.27	237.6
0.7787	0.2213	0	0.1938	0.0003	0.8059	0.25	178.5
0.8983	0.1017	0	0.2137	0.0002	0.7861	0.24	109.6
Thiophene (1) + Heptane (2) + [BMIM][SCN] (3)							
0.0432	0.9568	0	0.0899	0.0070	0.9031	2.08	284.4
0.1085	0.8915	0	0.2069	0.0080	0.7851	1.91	212.5
0.1732	0.8268	0	0.3191	0.0085	0.6724	1.84	179.3
0.3234	0.6766	0	0.4428	0.0093	0.5478	1.37	99.2
0.3536	0.6464	0	0.5405	0.0104	0.4491	1.53	94.9
0.3753	0.6247	0	0.5409	0.0100	0.4491	1.44	90.0
0.6080	0.3920	0	0.6461	0.0105	0.3434	1.06	39.8
0.7517	0.2483	0	0.6813	0.0109	0.3077	0.91	20.6
0.8304	0.1696	0	0.7032	0.0107	0.2861	0.85	13.4

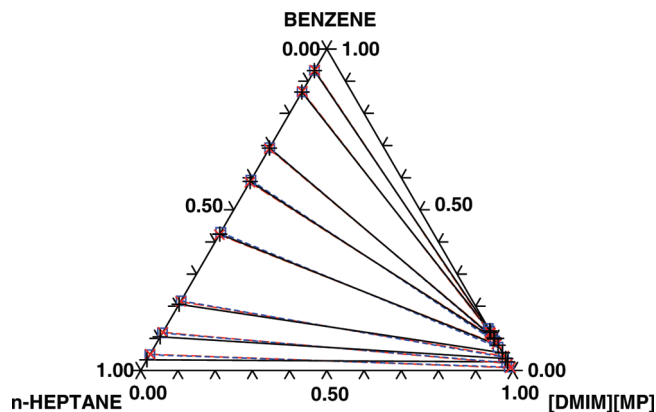
sulfur atom pointing toward the anion  $\text{SCN}^-$ . The  $\text{BMIM}^+$  cation is located in the shielding cone of thiophene due to the upfield chemical shift effect observed with protons of  $\text{BMIM}^+$ .

**Study on the Interaction between Thiophene and [DMIM]-[MP] Ionic Liquid Using  $^1\text{H}$  and  $^{31}\text{P}$  NMR Spectroscopies.** Similar investigations were made to understand the interactions between thiophene and 1,3-dimethylimidazolium methylphos-

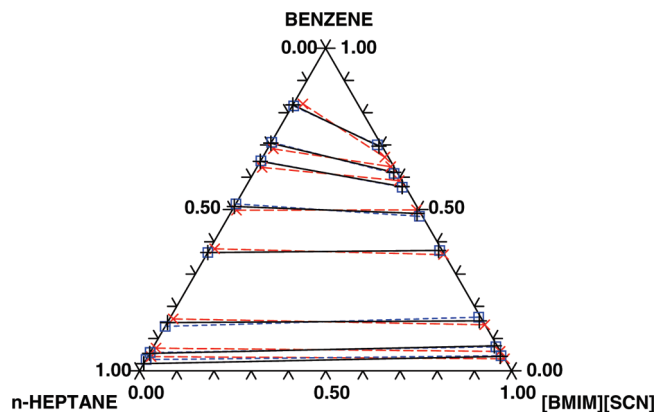
phonate. The solubility of thiophene in [DMIM][MP] was equal to 0.91 mol for 1 mol of ionic liquid. The  $^1\text{H}$  NMR spectra obtained with different molar ratios of thiophene in [DMIM]-[MP] are given in Figure 2S of the Supporting Information. The chemical shift variations of thiophene and [DMIM][MP] followed the same trend as those of thiophene and [BMIM]-[SCN]: the chemical shifts of thiophene protons are more



**Figure 5.** Tie lines for ternary mixture {benzene + heptane + [BMIM][BF<sub>4</sub>]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.



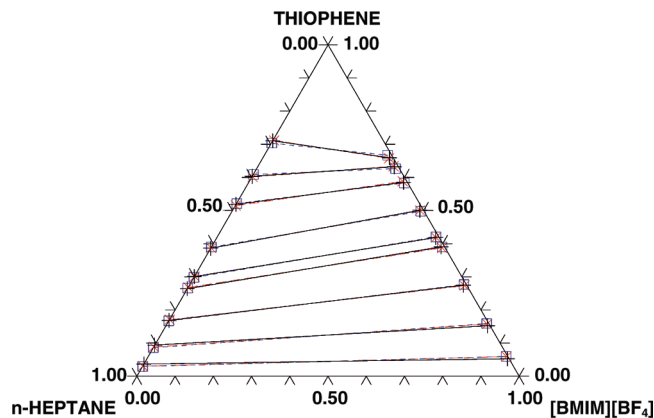
**Figure 6.** Tie lines for ternary mixture {benzene + heptane + [DMIM][MP]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.



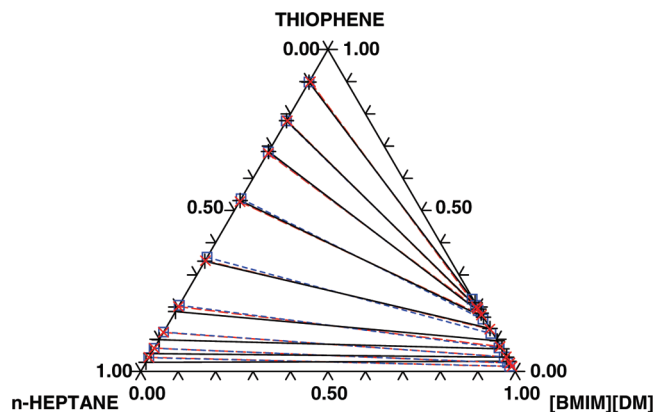
**Figure 7.** Tie lines for ternary mixture {benzene + heptane + [BMIM][SCN]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.

downfield when the thiophene is in a mixture with ionic liquid, although the ionic liquid proton chemical shifts are upfield.

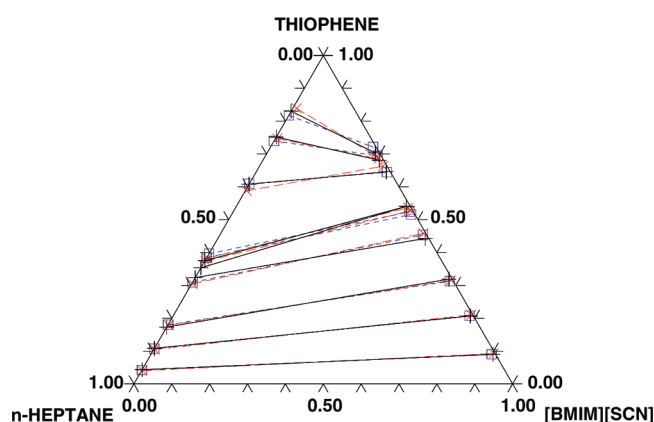
In order to have information on thiophene–methylphosphonate interactions, we also used the <sup>31</sup>P NMR spectroscopy. The chemical shifts of the phosphorus atom were measured at various molar ratios of thiophene in [DMIM][MP]. No variation of chemical shift was observed, indicating that interactions between thiophene and the anion are very weak. The most prominent features in the immediate vicinity of the thiophene are an excess of cations in the polar regions above and below the ring and an



**Figure 8.** Tie lines for ternary mixture {thiophene + heptane + [BMIM][BF<sub>4</sub>]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.



**Figure 9.** Tie lines for ternary mixture {thiophene + heptane + [DMIM][MP]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.



**Figure 10.** Tie lines for ternary mixture {thiophene + heptane + [BMIM][SCN]} at 298.15 K. Experimental data, + and −; NRTL correlation, × and ---; UNIQUAC correlation, □ and —.

excess of anions around the equator of the thiophene. This observation is in good agreement with Hanke and co-workers.<sup>15</sup>

In Figure 4, we proposed a hypothetical structural organization of the binary system {thiophene + [DMIM][MP]}. In this case, thiophene is situated between two imidazolium ring planes with which it strongly interacted, whereas the anions are located around the thiophene equator.

**Study on the Interaction between Benzene and Ionic Liquids Using <sup>1</sup>H NMR Spectroscopy.** For  $0 \leq R \leq 1.91$ , no variation of chemical shift was observed for the benzene. This

observation indicates that the interactions between benzene and BMIM<sup>+</sup> are very weak. Measurements of liquid–liquid equilibria of these binary systems agree well with these results. Variations of chemical shifts were observed with the cation BMIM<sup>+</sup>. The aromatic molecule has a significant quadrupole moment which gives an electrostatic field and attracts positive charges above and below the ring and negative charges around it.<sup>15</sup> The variation of  $\delta$  is probably due to a change of IL structure.<sup>15,16</sup> This observation agrees well with the study of Gutel et al. on toluene + [BMIM] [Tf<sub>2</sub>N]. The molar ratio of benzene dissolved in [BMIM][SCN] was found to be 1.91/1.

A similar behavior with benzene + [DMIM] [MP] should be observed due to its low solubility. Therefore, this system was not studied in this work.

**Thermodynamic Study of the Ternary Systems {Thiophene or Benzene/*n*-Heptane/IL}.** NMR study indicates clearly that the solubility of thiophene or benzene in ionic liquid strongly depends on the structure of the ionic liquid. To complete the study, we propose to investigate the possible use of these ionic liquids to extract such organic compounds and thus to determine LLE of six ternary systems: {benzene + *n*-heptane + 1-butyl-3-methylimidazolium tetrafluoroborate}, {benzene + *n*-heptane + 1,3-dimethylimidazolium methylphosphonate}, {benzene + *n*-heptane + 1-butyl-3-methylimidazolium thiocyanate}, {thiophene + *n*-heptane + 1-butyl-3-methylimidazolium tetrafluoroborate}, {thiophene + *n*-heptane + 1,3-dimethylimidazolium methylphosphonate}, and {thiophene + *n*-heptane + 1-butyl-3-methylimidazolium thiocyanate}.

Table 3 lists the compositions of the experimental tie lines for the six investigated ternary systems at 298.15 K. The phase diagrams of these systems are shown in Figures 5–10. Values of solute distribution ratio  $\beta$  and selectivity  $S$  are also reported in Table 3. These parameters were calculated from experimental data in order to evaluate solvent extraction capacity according to the equations

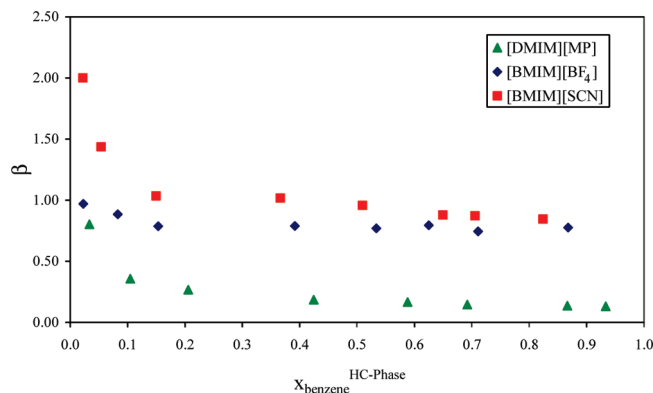
$$\beta = \frac{x_1^{\text{IL}}}{x_1^{\text{HC}}} \quad (1)$$

$$S = \frac{x_1^{\text{IL}} \cdot x_2^{\text{HC}}}{x_1^{\text{HC}} \cdot x_2^{\text{IL}}} \quad (2)$$

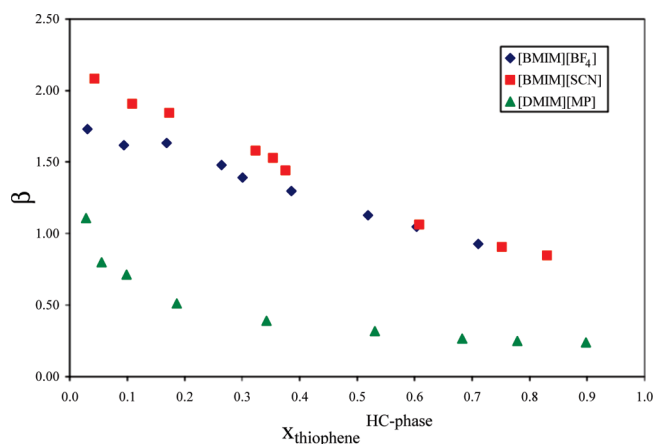
where  $x$  is the mole fraction, subscripts 1 and 2 refer to solute (benzene, thiophene) and to hydrocarbon (*n*-heptane), respectively, and superscripts HC and IL indicate the hydrocarbon-rich phase and the IL-rich phase, respectively. In order to have an adequate separation, values of solute distribution ratios have to be higher than the unit.

The evolution of the solute distribution ratio for each system as a function of the mole fraction of the solute is plotted in Figures 11 and 12. For ternary systems containing benzene, the benzene distribution coefficients are relatively low and below the unit with the ionic liquid [DMIM][MP]. For a high molar fraction, distribution coefficients are of the same magnitude with [BMIM][BF<sub>4</sub>] and [BMIM][SCN]; nevertheless, at a low concentration of benzene in the hydrocarbon phase,  $\beta$  values are higher than 1 with [BMIM][SCN].

In the case of ternary systems containing thiophene, the same trend was observed but the  $\beta$  values are higher than the unit with [BMIM][BF<sub>4</sub>] and [BMIM][SCN]. The highest values are obtained with [BMIM][SCN]. This fact indicates that this ionic



**Figure 11.** Solute distribution ratio  $\beta$  as a function of the mole fraction of benzene in the hydrocarbon-rich phase for the three systems.



**Figure 12.** Solute distribution ratio  $\beta$  as a function of the mole fraction of thiophene in the hydrocarbon-rich phase for the three systems.

liquid would be a more advantageous choice as a solvent for desulfurization of hydrocarbon fuels.

These results are in good agreement with the NMR study. The highest  $\beta$  values obtained with [BMIM][SCN] indicate a higher solubility of solutes in this ionic liquid than in other ionic liquids which could be explained by the stronger interactions between solutes with [BMIM][SCN] than with [DMIM][MP].

The LLE data of the investigated ternary systems were correlated using the nonrandom two-liquid equation (NRTL) proposed by Renon and Prausnitz<sup>17</sup> and the universal quasi-chemical (UNIQUAC) theory developed by Abrams and Prausnitz.<sup>18</sup>

**NRTL Model.** For the NRTL model, the activity coefficient  $\gamma_i$ , for any component  $i$  of the ternary system, is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left( \tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (3)$$

with

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \quad \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}, \quad \text{and } \alpha_{ji} = \alpha_{ij} = \alpha$$

**TABLE 4: Values of Binary Parameters for the NRTL Equation for the Ternary Mixtures**

system	<i>ij</i>	$\Delta g_{ij}$ (J·mol <sup>-1</sup> )	$\Delta g_{ji}$ (J·mol <sup>-1</sup> )	$\alpha$	rmsd
benzene (1) + heptane (2) + [BMIM][BF <sub>4</sub> ] (3)	12	2043	-134	0.3	0.0236
	13	1381	232		
	23	2554	3755		
benzene (1) + heptane (2) + [DMIM][MP] (3)	12	2043	-134	0.3	0.0067
	13	3687	1074		
	23	5001	3451		
benzene (1) + heptane (2) + [BMIM][SCN] (3)	12	2043	-134	0.3	0.0160
	13	1756	-28		
	23	2455	4208		
thiophene (1) + heptane (2) + [BMIM][BF <sub>4</sub> ] (3)	12	1860	-75	0.3	0.0027
	13	2718	-462		
	23	4430	3032		
thiophene (1) + heptane (2) + [DMIM][MP] (3)	12	1860	-75	0.3	0.0108
	13	2801	599		
	23	6797	4001		
thiophene (1) + heptane (2) + [BMIM][SCN] (3)	12	1860	-75	0.3	0.0110
	13	2770	-580		
	23	2955	3125		

where  $g$  is an energy parameter characterizing the interaction of species  $i$  and  $j$ ,  $x_i$  is the mole fraction of component  $i$ , and  $\alpha$  is the nonrandomness parameter. Although  $\alpha$  can be treated as an adjustable parameter, in this study,  $\alpha$  was set equal to 0.3 according to the literature.<sup>19</sup>

**UNIQUAC Model.** For the UNIQUAC model, the activity coefficient  $\gamma_i$ , for any component  $i$  of the ternary system, is given by

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^m x_j l_j - q_i \ln(\theta_j \tau_{ji}) + q_i - q_i \sum_{j=1}^m \frac{\theta_j \tau_{ji}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad (4)$$

where

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^m r_j x_j}, \theta_i = \frac{q_i x_i}{\sum_{j=1}^m q_j x_j}, l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1),$$

$$\text{and } \tau_{ji} = \exp\left(\frac{-\Delta u_{ji}}{RT}\right)$$

Here, the lattice coordination number  $z$  is assumed to be equal to 10,  $r_i$  and  $q_i$  are, respectively, the relative volume and surface area of the pure component  $i$ . The parameters  $r_i$  and  $q_i$  are, respectively, relative to molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group area parameters  $R_k$  and  $Q_k$ :

$$r_i = \sum_k v_k^i R_k \text{ and } q_i = \sum_k v_k^i Q_k \quad (5)$$

where  $v_k^i$  is the number of groups of type  $k$  in molecule  $i$ . The group parameters  $R_k$  and  $Q_k$  are obtained from van der Waals group volumes and surface areas, and  $V_k$  and  $A_k$  taken from the UNIFAC group contributions:<sup>20</sup>

$$R_k = \frac{V_k}{15.17} \text{ and } Q_k = \frac{A_k}{2.5 \times 10^9} \quad (6)$$

The values of 15.17 and  $2.5 \times 10^9$  are, respectively, the standard segment volume and standard segment area of a methylene group.<sup>20</sup>

This means that a total of two adjustable parameters per binary  $\Delta g_{ji}$  or  $\Delta u_{ji}$  have to be fitted for both models. The binary interaction parameters of {benzene + *n*-heptane} are taken from the literature.<sup>21</sup> In the case of {thiophene + *n*-heptane}, interaction parameters for both models are not available in the literature at 298 K. These parameters are then fitted using the data for the three ternary mixtures.

Binary interaction parameters for both NRTL and UNIQUAC equations are those which minimize the difference between the experimental and calculated mole fractions:

**TABLE 5: Values of the Binary Parameters for the UNIQUAC Equation**

system	<i>ij</i>	$\Delta u_{ij}$ (J·mol <sup>-1</sup> )	$\Delta u_{ji}$ (J·mol <sup>-1</sup> )	rmsd
benzene (1) + heptane (2) + [BMIM][BF <sub>4</sub> ] (3)	12	-534	1215	0.0058
	13	1119	68	
	23	7053	487	
benzene (1) + heptane (2) + [DMIM][MP] (3)	12	-534	1215	0.0071
	13	6870	0	
	23	7926	640	
benzene (1) + heptane (2) + [BMIM][SCN] (3)	12	-534	1215	0.0054
	13	2288	-1009	
	23	5481	367	
thiophene (1) + heptane (2) + [BMIM][BF <sub>4</sub> ] (3)	12	426	340	0.0042
	13	5883	-1906	
	23	2107	1436	
thiophene (1) + heptane (2) + [DMIM][MP] (3)	12	426	340	0.0106
	13	7181	-326	
	23	5049	619	
thiophene (1) + heptane (2) + [BMIM][SCN] (3)	12	426	340	0.0120
	13	9230	-2358	
	23	7530	-274	



$$F_{\text{obj}} = \sum_{k=1}^N \sum_{i=1}^3 \{ (x_{i,k}^{\text{I,exp}} - x_{i,k}^{\text{I,calc}})^2 + (x_{i,k}^{\text{II,exp}} - x_{i,k}^{\text{II,calc}})^2 \} \quad (7)$$

where  $N$  is the number of tie lines in the data set,  $x_{i,k}^{\text{I,exp}}$  and  $x_{i,k}^{\text{I,calc}}$  are the experimental and calculated mole fractions of one phase, and  $x_{i,k}^{\text{II,exp}}$  and  $x_{i,k}^{\text{II,calc}}$  are the experimental and calculated mole fractions of the second phase.

The binary parameters and root-mean-square deviation (rmsd), calculated using the procedure above, of the NRTL and UNIQUAC equations are given in Tables 4 and 5, respectively. The rmsd values, which provide a measure of the accuracy of the correlations, were calculated according to the following equation:

$$\text{rmsd} = \left( \frac{\sum_{k=1}^N \sum_{i=1}^3 \{ (x_{i,k}^{\text{I,exp}} - x_{i,k}^{\text{I,calc}})^2 + (x_{i,k}^{\text{II,exp}} - x_{i,k}^{\text{II,calc}})^2 \}}{6N} \right)^{1/2} \quad (8)$$

As can be inferred from the rmsd values, fairly good correlation of the experimental values with NRTL and UNIQUAC was obtained.

## Conclusions

In this work, NMR study allowed us to understand the interactions between benzene or thiophene and [BMIM][SCN] or [DMIM][MP]. In the case of strong interaction between solute and ionic liquid, hypothetical structural organizations have been proposed. The ability of three ionic liquids—1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium thiocyanate, and 1,3-dimethylimidazolium methylphosphonate—to act as solvent for the liquid–liquid extraction of benzene or thiophene from *n*-heptane was analyzed. Phase equilibria of six ternary systems involving [BMIM][BF<sub>4</sub>], [BMIM][SCN], [DMIM][MP], thiophene, benzene, and *n*-heptane were measured at 298.15 K. The experimental results have been successfully correlated using the NRTL and UNIQUAC models. [BMIM][SCN] seems to be a good choice to act as solvent for benzene extraction or desulfurization.

## List of Symbols

$A$	surface area
$F_{\text{obj}}$	objective function
$G$	NRTL parameter
$\Delta g$	binary interaction parameter of NRTL model
$l$	bulk factor
$N$	number of tie lines
$q$	surface parameter in UNIQUAC model
$Q$	group area parameter
$r$	volume parameter in UNIQUAC model
$R$	group volume parameter
rmsd	root-mean-square deviation
$S$	selectivity
$T$	temperature
$\Delta u$	binary interaction parameter of UNIQUAC model

$V$	volume
$x$	molar fraction
$z$	coordination number

## Greek Letters

$\alpha$	NRTL parameter
$\beta$	solute distribution ratio
$\delta$	chemical shift
$\gamma$	activity coefficient
$\Phi$	volume fraction
$\theta$	area fraction
$\tau$	energy parameter
$\nu$	number of groups

## Super/Subscripts

calc	calculated
exp	experimental
HC	hydrocarbon-rich phase
$i, j$	components
IL	ionic-liquid-rich phase

**Supporting Information Available:** Figures showing <sup>1</sup>H NMR spectra of the hydrocarbon-rich phase free of ionic liquid for the ternary mixture {benzene + *n*-heptane + [BMIM][SCN]} and <sup>1</sup>H NMR signal assignments of the ring protons in thiophene and [DMIM][MP]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, *47*, 2384–2389.
- Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2084.
- Alonso, L.; Arce, A.; Francisco, M.; Soto, A. *Fluid Phase Equilib.* **2008**, *270*, 97–102.
- Mutelet, F.; Revelli, A.-L.; Jaubert, J.-N.; Sprunger, L. M.; Acree, W. E.; Baker, G. A. *J. Chem. Eng. Data* **2010**, *55*, 234–242.
- Gao, H.; Luo, M.; Xing, J.; Wu, Y.; Li, Y.; Li, W. *Ind. Eng. Chem. Res.* **2008**, *47*, 8384–8388.
- Alonso, L.; Arce, A.; Francisco, M.; Soto, A. *J. Solution Chem.* **2008**, *37*, 1355–1363.
- Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. *Green Chem.* **2008**, *10*, 1294–1300.
- Su, B.-M.; Zhang, S.; Zhang, Z. C. *J. Phys. Chem. B* **2004**, *108*, 19510–19517.
- Mutelet, F.; Jaubert, J.-N. *J. Chromatogr., A* **2006**, *1102*, 256–267.
- Mutelet, F.; Jaubert, J.-N.; Rogalski, M.; Harmand, J.; Sindt, M.; Mieloszynski, J.-L. *J. Phys. Chem. B* **2008**, *112*, 3773–3785.
- Revelli, A.-L.; Mutelet, F.; Turmine, M.; Solimando, R.; Jaubert, J.-N. *J. Chem. Eng. Data* **2009**, *54*, 90–101.
- Revelli, A.-L.; Mutelet, F.; Jaubert, J.-N. *J. Chromatogr., A* **2009**, *1216*, 4775–4786.
- Revelli, A.-L.; Sprunger, L. M.; Gibbs, J.; Acree, W. E., Jr.; Baker, G. A.; Mutelet, F. *J. Chem. Eng. Data* **2009**, *54* (3), 977–985.
- Nockemann, P.; Thijs, B.; Postelmans, N.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K. *J. Am. Chem. Soc.* **2006**, *128*, 13658–13659.
- Hanke, C. G.; Johansson, A.; Harper, J. B.; Lynden-Bell, R. M. *Chem. Phys. Lett.* **2003**, *374*, 85–90.
- Gutel, T.; Santini, C. C.; Pádua, A. A. H.; Fenet, B.; Chauvin, Y.; Lopes, J. N. C.; Bayard, F.; Gomes, M. F. C.; Pensado, A. S. *J. Phys. Chem. B* **2009**, *113*, 170–177.
- Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135–144.
- Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116–128.
- Simoni, L. D.; Chapeaux, A.; Brennecke, J. F.; Stadtherr, M. A. *Ind. Eng. Chem. Res.* **2009**, *48*, 7257–7265.
- Kato, R.; Gmehling, J. *J. Chem. Thermodyn.* **2005**, *37*, 603–619.
- Gmehling, J.; Onken, U.; Arlt, W. *Vapor-liquid Equilibrium Collection, Chemistry Data Series, Vol. I, Part 6b*; DECHEMA: Frankfurt/Main, Germany, 1980.

JP911978A