J. Chem. Eng. Data **2010,** *55,* 773–777 **773**

Phase Equilibria of (1-Hexyl-3-methylimidazolium Thiocyanate + Water, Alcohol, or Hydrocarbon) Binary Systems

Urszula Domańska,* Marta Królikowska, and Monika Arasimowicz

Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Imidazolium ionic liquid has been prepared from 1-methylimidazolium as a substrate. The work includes specific basic characterization of a synthesized compound by NMR spectra, water content, and a glass transition temperature determined by the differential scanning calorimetry (DSC). The mutual solubilities of 1-hexyl-3-methylimidazolium thiocyanate, [HMIM][SCN], with water, alcohols, *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, or *n*-decane), aromatic hydrocarbons (benzene, toluene, or ethylbenzene), and cyclic hydrocarbons (cyclohexane or cycloheptane) have been measured at ambient pressure by a dynamic method in a range of temperatures from (200 to 420) K. The simple eutectic system was observed for water with complete miscibility in the liquid phase. Complete miscibility has been observed in the systems of [HMIM][SCN] with alcohols ranging from methanol to 1-decanol at a temperature of $T = 298.15$ K. The upper critical solution temperatures (UCSTs) were observed for the systems with *n*-alkanes and the lower critical solution temperatures (LCSTs) for the systems with aromatic hydrocarbons. The solubility decreases with an increase of the molecular weight of the solvent. The liquid−liquid phase equilibria (LLE) have been correlated using the nonrandom two-liquid (NRTL) equation. The average root-mean square deviation of the equilibrium mole fraction for all of the LLE data was 0.0021.

Introduction

Ionic liquids (ILs) have received considerable attention in recent years because of their unique physical and chemical properties and solution thermodynamic behavior.[1–5] The immiscibility of ILs with *n*-alkanes and several acyclic organic solvents makes ILs ready to replace traditional organic solvents in many chemical and manufacturing processes. Knowledge about physicochemical properties such as viscosity, density, or heat capacity and thermodynamic properties including phase equilibria is necessary to design any process involving ILs on an industrial scale.[2–10] The solid−liquid phase equilibria (SLE) and liquid−liquid phase equilibria (LLE) measurements of IL systems based on imidazolium cations[3,5,6] are attracting increasing attention for applications in liquid−liquid extraction.

It was proved by Domańska and Laskowska[8] by the measurements of the activity coefficient at infinite dilution, γ_{13}^{∞}, and by Domańska and Marciniak[9] that thiocyanate anion $[\mathrm{SCN}]^-$ has high extraction efficiency. The selectivities $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$ for the hexane/thiophene or hexane/benzene separation problems were calculated for [BMIM][SCN][8] and [EMIM][SCN][9] from the γ_{13}^{∞}. The selectivities for hexane/thiophene at $T = 298.15$ K are 186.2 and 231.5, respectively. The capacity $k_j^{\infty} = 1/\gamma_{j3}^{\infty}$ for the sulfur (thiophene) separation problem is 0.82, which is quite high. The selectivities for hexane/benzene at $T = 298.15$ K are 106.1 and 95.4, respectively. The capacities $k_j^{\infty} = 1/\gamma_{j3}^{\infty}$ for the (benzene) separation problem are 0.47 and 0.29. These are very promising results for the separation of sulfur from mixtures of an industrial importance and for the separation of alkanes from aromatics.

The LLE diagrams with a miscibility gap with the upper critical solution temperature (UCST) were observed in mixtures of {[BMIM][SCN] + *n*-alkane}[10] and with the lower critical solution temperature (LCST) in mixtures of {[BMIM][SCN] + aromatic hydrocarbon}.[10] The liquidus curves exhibited a similar shape for different solvents. The evident differences were observed in the liquid phase for aromatic hydrocarbons: the mutual solubility of [BMIM][SCN] in benzene and its alkyl derivatives decreases with an increase of the alkyl substituent at the benzene ring.[10] Thiocyanate-based ILs are soluble in water. A simple eutectic system was observed for [BMIM][SCN].[10]

The phase diagrams of ILs with benzene and benzene derivatives differ from those for the aliphatic hydrocarbons. ILs present a usually much lower immiscibility gap in benzene than in alkanes. The solubility of ILs is much higher in aromatic hydrocarbons than in aliphatic hydrocarbons, which is the result of interaction with the benzene ring.

The present study continues our characterization of the thiocyanate-based ILs. This work is concerned with the investigation of phase equilibria of mixtures containing the [HMIM][SCN] with water, alcohols (from C_1 to C_{10}), *n*-alkanes (from C_6 to C_{10}), aromatic hydrocarbons (benzene, toluene, or ethylbenzene), and cyclic hydrocarbons (cyclohexane or cycloheptane).

Experimental Section

Materials. Water for the solubility measurements was twice distilled, degassed, deionized, and filtered with Milipore Elix 3. The other solvents used, that is, 1-alcohols, were obtained from Sigma Aldrich with a purity of over 99.8 %. The other chemicals were as follows: *n*-hexane (CAS No. 110-54-3, Merck, 99 %); *n*-heptane (CAS No. 142-82-5, Sigma-Aldrich, 99 %); *n*-octane (CAS No. 111-65-9, Sigma-Aldrich, 99 %); *n*-nonane (CAS No. 111-84-2, Sigma-Aldrich, > 99 %); *n*-decane (CAS No. 124-18-5, Sigma-Aldrich, > 99 %); benzene

---

* Corresponding author. Telephone: + 48-22-6213115. Fax: + 48-22-6282741. E-mail: ula@ch.pw.edu.pl.

10.1021/je900460m

Table 1. Thermophysical Constants of the Pure IL[a]

	M	$\rho^{298.15}$	$\eta^{298.15}$	$T_{tr,1(g)}$	$\Delta C_{p(g)}$	T_{dec}
IL	$g \cdot mol^{-1}$	$kg \cdot m^{-3}$	$mPa \cdot s$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K
[HMIM][SCN]	211.33	1.05692	93.6206	189.9	118	535[b]

[a] Molecular mass, M; density, $\rho^{298.15}$; viscosity, $\eta^{298.15}$; temperature of glass transition, $T_{tr,1(g)}$; $\Delta C_{p(g)}$ at the glass transition and temperature of the decomposition, T_{dec}. [b] The step of the decomposition, 20 % mass loss.

(CAS No. 71-43-2, Sigma-Aldrich, > 99.97 %); toluene (CAS No. 108-88-3, Fluka, > 99.7 %); ethylbenzene (CAS No. 100-41-4, Sigma-Aldrich, 99 %), cyclohexane (CAS No. 110-82-7, Sigma-Aldrich, 99.5 %); cycloheptane (CAS No. 291-64-5, Sigma-Aldrich, 98 %). The solvent's purities are in mass fraction.

For the synthesis a 250 mL flask, equipped on a magnetic stirrer and condenser, was used. The substances 1-methylimidazolium (0.4 mol) (Merck 99 %, distilled over KOH) and 1-bromohexane (0.5 mol) (Aldrich 98 %, used as received) were charged. The reaction mixture was stirred at a temperature of 333 K for 3 h. 1-Bromohexane has been removed by extraction with hexane, ethyl acetate, and diethyl ether. Product was dried in vacuum (0.37 mol, yield 93 %).

1-Hexyl-3-methylimidazolium bromide (0.37 mol), sodium thiocyanate (0.37 mol, Aldrich 98 % in mass fraction), and 100 mL of distilled water were charged into a flask and stirred for 24 h at room temperature. Water was removed by evaporation under reduced pressure. After removing the solvent, 100 mL of CH_2Cl_2 (POCH, 99 % in mass fraction) was added. Then, the mixture was filtered and was left up to the evaporation of the solvent. Product was dried in vacuum for 24 h at 300 K (yield 95 %). NMR, differential scanning calorimetry (DSC), and elemental analysis identified the obtained IL.

All solvents were fractionally distilled over different drying reagents until a mass fraction purity better than 99.8 % was obtained and were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by gas−liquid chromatography (GLC) analysis, and no significant impurities were found. The physicochemical characterization of the IL is presented in Table 1.

Nuclear Magnetic Resonance. ^{1}HNMR and ^{13}CNMR spectra in $CDCl_3$ solutions were recorded on a Varian Gemini 2000 spectrometer. The uncertainty was estimated to be on the level of 5 %. A description of the spectra is presented in Graphs 1 and 2 of the Supporting Information.

Water Content. Water content was analyzed by Karl Fischer titration (with TitroLine Method). Samples of [HMIM][SCN] and the solvents were dissolved in dry methanol and titrated with steps of 2.5 μL. The analysis showed that the water mass fraction in the solvents and in the mixtures with the IL was less than $(250 \cdot 10^{-6} \pm 10 \cdot 10^{-6})$.

Differential Scanning Microcalorimetry. Basic thermal characteristics of the IL, that is, glass transition temperature ($T_{g,1}$) and change of heat capacity at the glass transition temperature, $T_{g,1}$ ($\Delta C_{p(g),1}$), have been measured using a differential scanning microcalorimetry technique at the 5 $K \cdot min^{-1}$ scan rate with the power sensitivity of 16 $mJ \cdot s^{-1}$ and with the recorder sensitivity of 5 mV. The instrument (Perkin-Elmer Pyris 1) was each time calibrated with the indium sample, which purity was 99.9999 in mole fraction. The calorimetric accuracy was ± 3 %. The thermophysical properties (average over three scans) are shown in Table 1, and the DSC diagram is shown as Graph 3 in the Supporting Information. The average value of the glass transition temperature was $T_{g,1}$ was (189.9 ± 0.1) K with $\Delta C_{p(g),1}$ of (118 ± 3) $J \cdot mol^{-1} \cdot K^{-1}$ (average over three scans).

Table 2. Experimental SLE Data for the Binary System {[HMIM][SCN] (1) + Water (2)}: the Mole Fraction (x_1), Temperature (T^{SLE}), and Activity Coefficient of the Solvent (γ_2)

x_1	T^{SLE}/K	γ_2	x_1	T^{SLE}/K	γ_2
0.2950	235.0[a]	1.67	0.0832	267.0	2.20
0.2566	244.6	1.90	0.0566	271.1	2.26
0.2089	254.9	1.98	0.0304	272.2	2.32
0.1495	264.2	2.08	0.0005	272.9	2.39
0.1088	268.5	2.15	0.0000	273.1	2.39

[a] The results are, for example, (235.0 ± 0.1) K.

Decomposition of Compound. Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) experiments was performed using a MOM Hungary derivatograph PC. In general, runs were carried out using matched labyrinth platinic crucibles with Al_2O_3 in the reference pan. The crucible design hampered the migration of the volatile decomposition products, reducing the rate of gas evolution and, in turn, increasing the contact time of the reactants. All of the TG/DTA curves were obtained at 5 $K \cdot min^{-1}$ heating rate with a nitrogen dynamic atmosphere (flow rate 20 $dm^3 \cdot h^{-1}$). Temperature of decomposition is presented in Graph 4 in the Supporting Information. We can see that up to 511 K the decomposition is not observed and at temperature (535 ± 3) K the decomposition is 20 %.

Phase Equilibria Measurements. Solubilities have been determined using a dynamic method that has been described in detail previously.[11] Appropriate mixtures of IL and solvent placed under the nitrogen in a drybox into a Pyrex glass cell were heated very slowly (less than 2 $K \cdot h^{-1}$ near the equilibrium temperature) with continuous stirring inside a cell. The sample was placed in a glass thermostat filled with silicone oil, water, or acetone with dry ice. The temperature of the liquid bath was varied slowly until one phase was obtained. The two phase disappearance temperatures in the liquid phase were detected visually during an increasing temperature regime. The temperature was measured with an electronic thermometer P550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostatting liquid. The thermometer was calibrated on the basis of ITS-90. Mixtures were prepared by mass, and the uncertainty was estimated to be better than ± 0.0002 and ± 0.1 K in the mole fraction and temperature, respectively. The results of the SLE/LLE measurements for the binary systems of {[HMIM][SCN] (1) + water or hydrocarbons (2)} are presented in Tables 2, 3, 4, and 5. The tables include the direct experimental results of the SLE/LLE temperatures, T^{SLE} or T^{LLE} versus x_1, the mole fraction of the IL at the equilibrium temperatures for the investigated systems.

Results and Discussion

The formula of the IL, the abbreviation, and the physicochemical properties are presented in Table 1 and in Figure 1.

The thiocyanate anion, $[SCN]^-$, is less viscous, more hydrolytically stable, and more environmentally friendly than other popular anions such as bis{(trifluoromethyl)sulfonyl}imide $[NTf_2]^-$, hexafluorophosphate, $[PF_6]^-$, or tetrafluoroborate, $[BF_4]^-$. Unfortunately, the [HMIM][SCN] is thermally less stable than [BMIM][SCN]. The IL investigated in this work has revealed the first decomposition temperature at 511 K, while [BMIM][SCN] is at 523 K. The compound has been decomposed in one step.

The experimental data of SLE/LLE of the measured binary systems of [HMIM][SCN] are shown in Figures 2, 3, 4, and 5.

Table 3. Experimental LLE in the {[HMIM][SCN] (1) + Aliphatic Hydrocarbon (2)} Binary Systems

x_1	T^{LLE}/K	x_1	T^{LLE}/K
	n-Hexane		
0.9755	286.6[a]	0.9418	324.3
0.9629	299.6	0.9397	329.9
0.9529	308.3	0.9362	333.5
0.9497	313.0	0.9288	341.1
0.9477	316.3	0.9177	351.2
0.9453	320.6	0.9061	359.4
0.9444	321.1	0.8962	367.3
	n-Heptane		
0.9839	282.6	0.9279	376.0
0.9673	325.9	0.9140	395.0
0.9535	348.6	0.9012	408.8
0.9401	363.2		
	n-Octane		
0.9906	284.7	0.9676	359.2
0.9843	302.2	0.9651	363.2
0.9820	310.1	0.9537	377.5
0.9793	318.1	0.9481	389.1
0.9732	331.4	0.9402	402.3
0.9703	339.2		
	n-Nonane		
0.9901	312.15	0.9684	396.4
0.9866	341.85	0.9613	416.8
0.9769	368.69		
	n-Decane		
0.9941	310.4	0.9829	369.3
0.9903	328.2	0.9802	384.0
0.9873	346.5	0.9740	410.6

[a] The results are, for example, (286.6 ± 0.1) K.

Table 4. Experimental LLE in the {[HMIM][SCN] (1) + Aromatic Hydrocarbon (2)} Binary Systems

x_1	T^{LLE}/K	x_1	T^{LLE}/K
	Benzene		
0.2824	346.3[a]	0.2643	294.7
0.2784	332.3	0.2609	284.4
0.2734	319.3	0.2598	279.2
0.2694	306.9		
	Toluene		
0.4356	355.7	0.3799	248.9
0.4184	313.7	0.3758	245.0
0.4137	292.7	0.3719	240.1
0.4092	282.1	0.3684	239.6
0.4047	272.6	0.3648	236.8
0.4003	267.7	0.3612	233.9
0.3960	262.9	0.3576	229.6
0.3920	259.6	0.3541	226.1
0.3880	255.9	0.3509	221.8
0.3839	252.8		
	Ethylbenzene		
0.5835	359.0	0.5033	227.0
0.5662	332.7	0.4968	223.1
0.5524	300.4	0.4867	220.9
0.5398	272.7	0.4790	219.2
0.5310	261.0	0.4698	217.7
0.5222	250.7	0.4642	216.3
0.5161	242.1	0.4471	214.2
0.5101	232.6	0.4305	211.7

[a] The results are, for example, (346.3 ± 0.1) K.

The UCSTs of the curves were not observed because the boiling temperatures of solvents were much lower. For the investigated mixtures, it was impossible to detect, by the visual method, the mutual solubility of the IL in the solvent-rich phase. However, it was measured with UV−vis spectroscopy for a similar IL, [BMIM][SCN], and the solubility was in a range of $x_1 = 1.7 \cdot 10^{-5}$ to $3.5 \cdot 10^{-5}$ for *n*-hexane; $x_1 = 1.7 \cdot 10^{-3}$ to $2.2 \cdot 10^{-3}$ for benzene; and $x_1 = 2.1 \cdot 10^{-5}$ to $4.3 \cdot 10^{-5}$ for cyclohexane.[10]

Table 5. Experimental LLE in the {[HMIM][SCN] (1) + Cycloalkane (2)} Binary Systems

x_1	T^{LLE}/K	x_1	T^{LLE}/K
	Cyclohexane		
0.9727	289.1[a]	0.8468	376.5
0.9269	305.6	0.8346	380.8
0.9150	318.6	0.8191	386.6
0.9022	332.5	0.8012	392.8
0.8927	341.5	0.7911	397.2
0.8817	354.7	0.7815	400.3
0.8685	364.9	0.7613	407.8
0.8553	373.1		
	Cycloheptane		
0.9698	279.6	0.9096	353.6
0.9573	291.9	0.8995	367.3
0.9455	309.8	0.8885	381.7
0.9330	324.0	0.8755	397.0
0.9203	342.3	0.8640	411.1

[a] The results are, for example, (289.1 ± 0.1) K.

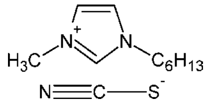

Figure 1. Formula of the 1-hexyl-3-methylimidazolium thiocyanate.

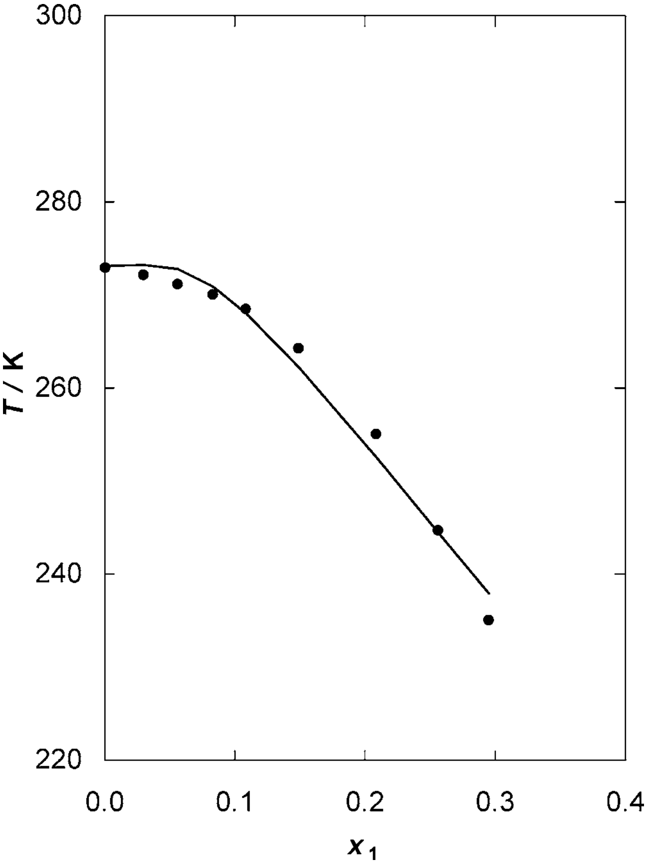

Figure 2. SLE diagram of the binary system {[HMIM][SCN] (1) + water (2)}: ●, experimental points; solid line, calculated by the UNIQUAC equation.

For the shorter chains of an *n*-alkane[10] and the alkyl substituent at the benzene ring,[7] the area of the immiscibility is always lower than that for the longer *n*-alkane chains. In fact, this is typical solution behavior, observed for every IL measured by us.

Figure 2 shows the experimental liquidus curve of water in the IL. Figure 3 presents the equilibrium curves of solubility of the IL in five *n*-hydrocarbons. Equilibrium curves for the three

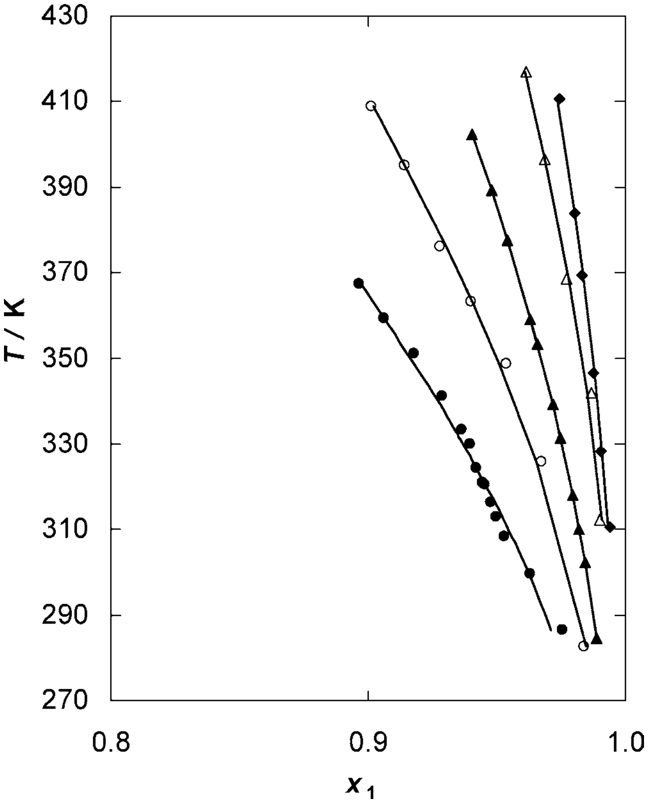

Figure 3. LLE diagrams for the binary systems {[HMIM][SCN] (1) + *n*-alkane (2)}: ●, *n*-hexane; ○, *n*-heptane; ▲, *n*-octane; △, *n*-nonane; ◆, *n*-decane; solid lines, calculated using the nonrandom two-liquid (NRTL) equation.

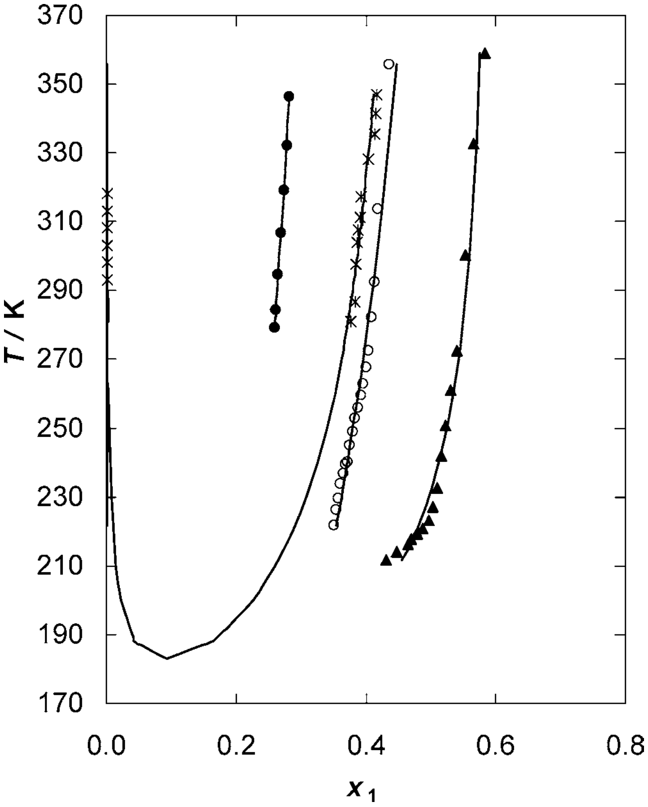

Figure 4. LLE diagrams for the binary systems {[HMIM][SCN] (1) + an aromatic hydrocarbon (2)}: ●, benzene; ○, toluene; ▲, ethylbenzene; ×, comparison with the system {[BMIM][SCN] (1) + benzene (2)}.[10] Solid lines, calculated using the NRTL equation.

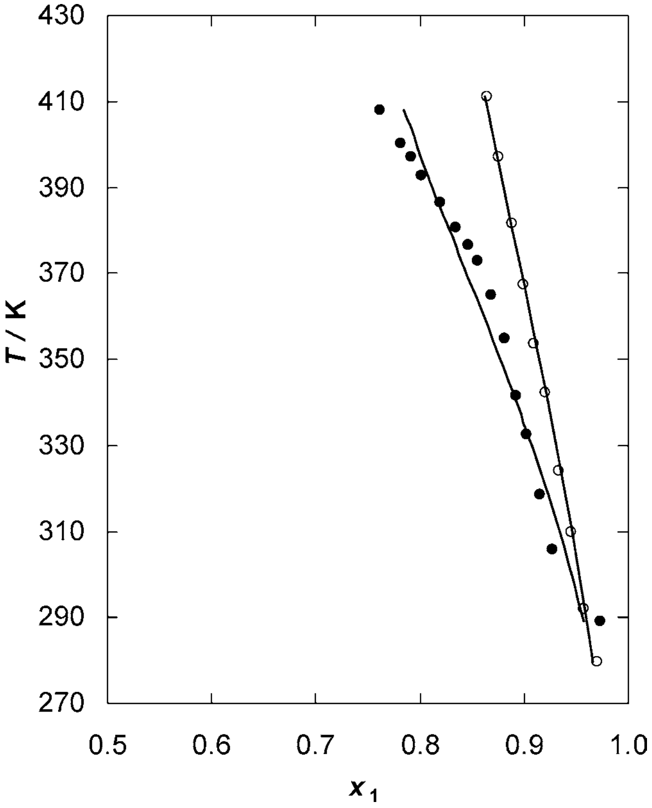

Figure 5. LLE diagrams for the binary systems {[HMIM][SCN] (1) + cycloalkane (2)}: ●, cyclohexane; ○, cycloheptane; solid line, calculated using the NRTL equation.

binary systems studied with aromatic hydrocarbons as a function of temperature for different compositions are shown in Figure 4. As can be observed, the solubility decreases as the alkyl chain at the benzene ring increases. The differences in solubility between the benzene and the toluene in the IL are the same as those for toluene and ethylbenzene in the IL. The same results were presented by us earlier for [BMIM][SCN] in aromatic hydrocarbons.[10] As can be seen from Figure 4, the solubility of benzene in [HMIM][SCN] is much higher than those in [BMIM][SCN].[10]

Experimental phase diagrams with cyclohydrocarbons, investigated in this work, are characterized by the typical order in solubility: cyclohexane > cycloheptane.

The best solubility was observed in water, alcohols, and benzene probably because of the interaction between molecules of the IL (imidazolium ring, thiocyanate anion) and the polar solvent. It can be hydrogen bonding with water and alcohols and n-π and/or π-π interactions with benzene and alkylbenzenes. Packing effects or conformational changes of the investigated molecules in the mixtures are difficult to categorize, especially in comparison with possible hydrogen bonding. All of these interactions have an influence on LLE.

SLE and LLE Correlation

For the correlation of the solubility of water in [HMIM][SCN] and the calculation of the solute activity coefficients γ_1, the UNIQUAC equation[12] was chosen as the better one than the NRTL equation.[13] As a measure of the reliability of the correlations, the root-mean-square deviation of temperature σ_T/K has been calculated according to the following definition:

$$\sigma_T = \left\{ \sum_{i=1}^{n} \frac{(T_{\mathrm{exp},i} - T_{\mathrm{calc},i})^2}{n-2} \right\}^{1/2} \qquad (1)$$

The values of the parameters and the corresponding root-mean-square deviations of temperature are: $\Delta u_{12} = 3528.68\ \mathrm{J \cdot mol^{-1}}$,

Table 6. Correlation of the LLE Data by Means of the NRTL Equation: Parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$), ($g_{21} - g_{11} = a_{21} + b_{21}T$), and the Mole Fraction Deviations σ_x

	NRTL parameters[a]				
	($g_{12} - g_{22}$)		($g_{21} - g_{11}$)		
	$J \cdot mol^{-1}$		$J \cdot mol^{-1}$		
solvent	a_{12}	b_{12}	a_{21}	b_{21}	σ_x
n-hexane	14364	−50.16	−889.9	103.7	0.0014
n-heptane	14019	−44.90	−13856	134.7	0.0010
n-octane	13213	−39.15	−6806.4	113.0	0.0013
n-nonane	14500	−37.65	−12881	123.2	0.0006
n-decane	13759	−33.25	−9382.9	111.4	0.0003
benzene	−3087.8	−38.59	4384.8	102.2	0.0003
toluene	−3607	−25.39	5128	83.17	0.0026
ethylbenzene	158.2	−30.06	−12326	131.9	0.0062
cyclohexane	15065	−55.75	−17452	153.8	0.0061
cycloheptane	10520	−39.40	−10430	129.7	0.0011

[a] $\alpha = 0.1$.

$\Delta u_{21} = 480.66 \text{ J} \cdot \text{mol}^{-1}$, and $\sigma_T/\text{K} = 1.7$ K. The resulting curve is presented together with the experimental points in Figure 2.

The LLE was correlated with the NRTL model describing the excess Gibbs energy.[13] The equations were described by us earlier.[10] The NRTL α parameter was set to a value of $\alpha = 0.1$, which has given the best results of the correlations. For LLE, the temperature-dependent model adjustable parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$) and ($g_{21} - g_{11} = a_{21} + b_{21}T$) were found by minimization of the objective function, OF:

$$\text{OF} = \sum_{i=1}^{n} [(\Delta x_1)_i^2 + (\Delta x_1^*)_i^2] \tag{2}$$

where n is the number of experimental points and Δx is defined as

$$\Delta x = x_{\text{calc}} - x_{\text{exp}} \tag{3}$$

The root-mean-square deviation of mole fraction for the LLE calculations was defined as follows:

$$\sigma_x = \left(\frac{\sum_{i=1}^{n} (\Delta x_1)_i^2 + \sum_{i=1}^{n} (\Delta x_1^*)_i^2}{2n - 2} \right)^{1/2} \tag{4}$$

By analogy to [BMIM][SCN], it was assumed in this work that the solubility at the solvent-rich phase was in the range of $x_1 = 2 \cdot 10^{-5}$ in *n*-alkanes, $x_1 = 2 \cdot 10^{-3}$ in benzene and alkylbenzenes, and $x_1 = 2 \cdot 10^{-5}$ in cyclohydrocarbons.

The results of the correlations, values of model parameters and the corresponding standard deviations, are given in Table 6. For the systems presented in this work the average root-mean square deviation σ_x equals 0.0021. The results of the correlations are presented in Figures 3 to 5. Positive deviations from ideality were found. The values of activity coefficients of the IL in the saturated solution, coming from the correlation data, were higher than one ($\gamma_1 > 1$).

Conclusion

The SLE for one and LLE for 10 new binary IL + organic solvent systems were determined. Complete miscibility in the liquid phase was observed with water and 1-alcohols. The experimental data of LLE in binary systems of [HMIM][SCN] with *n*-hydrocarbons and cyclohydrocarbons demonstrate typical behavior: the miscibility gap in the liquid phase increases with an increase of the chain length of the alkane and of the ring of cycloalkane. In the systems with aromatic hydrocarbons, the LCST was noted as it was for the previously published results for the [BMIM][SCN].[10] The solubility of every tested solvent in [HMIM][SCN] was higher than those observed in [BMIM][SCN].[10]

The existence of the liquid−liquid equilibria is the evidence that the interaction between the IL and the solvent is not significant (besides the water and alcohol solutions).

Knowledge of the impact of different factors on the liquid-phase behavior of IL in comparison with other traditional liquids is useful for developing IL as designer solvents. The presented results may give new possibilities in extraction processes.

Supporting Information Available:

^{1}HNMR, ^{13}CNMR, DSC, and TG/DTA graphs of [HMIM][SCN]. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Holbrey, J. D.; López-Martin, I.; Rothenberg, G.; Seddon, K. S.; Silvero, G.; Zheng, X. Desulfurization of Oils Using Ionic Liquids: Selection of Cationic and Anionic Components to Enhance Extraction Efficiency. *Green Chem.* **2008**, *10*, 87–92.

(2) Łachwa, J.; Szydłowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes da Ponte, M.; Esperanca, J. M. S. S.; Guedes, H. J. R. Evidence for Critical Solution Behavior in Ionic Liquid Solution. *J. Am. Chem. Soc.* **2005**, *127*, 6542–6543.

(3) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Phase Behaviour of 1-Methyl-3-octylimidazolium Bis[trifluoromethylsulfonyl]imide with Thiophene and Aliphatic Hydrocarbons: The Influence of *n*-Alkane Chain Length. *Fluid Phase Equilib.* **2008**, *263*, 176–181.

(4) Nebig, S.; Liebert, V.; Gmehling, J. Measurement and Prediction of Activity Coefficients at Infinite Dilution ($\gamma\infty$), Vapor-Liquid equilibria (VLE) and Excess Enthalpies (H^E) of Binary Systems with 1,1-Dialkyl-pyrrolidinium Bis(trifluoromethylsulfonyl)imide Using Modified UNIFAC (Dortmund). *Fluid Phase Equilib.* **2009**, *277*, 61–67.

(5) Neves, C. M. S. S.; Ventura, S. P. M.; Freire, M. G.; Marrucho, I. M.; Coutinho, J. A. P. Evaluation of Cation Influence on the Formation and Extraction Capability of Ionic-Liquid-Based Aqueous Biphasic Systems. *J. Phys. Chem. B* **2009**, *113*, 5194–5199.

(6) Domańska, U.; Marciniak, A. Phase Behaviour of 1-Hexyloxymethyl-3-methyl-imidazolium and 1,3-Dihexyloxymethyl-imidazolium Based Ionic Liquids with Alcohols, Water, Ketones and Hydrocarbons: The Effect of Cation and Anion on Solubility. *Fluid Phase Equilib.* **2007**, *260*, 9–18.

(7) Domańska, U.; Paduszyński, K. Phase Equilibria Study in the Binary Systems (Tetra-*n*-butylphosphonium Tosylate Ionic Liquid + 1-Alcohol, or Benzene, or n-Alkylbenzene). *J. Phys. Chem. B* **2008**, *112*, 11054–11059.

(8) Domańska, U.; Laskowska, M. Measurements of Activity Coefficients at Infinite Dilution of Aliphatic and Aromatic Hydrocarbons, Alcohols, Thiophene, Tetrahydrofuran, MTBE and Water in Ionic Liquid [BMIM][SCN] using GLC. *J. Chem. Thermodyn.* **2009**, *41*, 645–650.

(9) Domańska, U.; Marciniak, A. Measurements of Activity Coefficients at Infinite Dilution of Aromatic and Aliphatic Hydrocarbons, Alcohols, and Water in the New Ionic Liquid [EMIM][SCN] using GLC. *J. Chem. Thermodyn.* **2008**, *40*, 860–866.

(10) Domańska, U.; Laskowska, M.; Pobudkowska, A. Phase Equilibria Study of Their Binary Systems (1-Butyl-3-methylimidazolium Thiocyanate Ionic Liquid + Organic solvent, or Water). *J. Phys. Chem. B* **2009**, *113*, 6397–6404.

(11) Domańska, U. Vapour-Liquid-Solid Equilibrium of Eicosanoic Acid in One- and Two-component Solvents. *Fluid Phase Equilib.* **1986**, *26*, 201–220.

(12) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.

(13) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

Received for review May 28, 2009. Accepted November 1, 2009. This work has been supported by the European Union in the framework of European Social Fund through the Warsaw University of Technology Development Programme. Authors wish to thank Mr. M. Zawadzki for the synthesis of [HMIM][SCN].

JE900460M