# Phase Equilibria Study of the Binary Systems (*N*-Hexylisoquinolinium Thiocyanate Ionic Liquid + Organic Solvent or Water)

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S *Supporting Information*

ABSTRACT: Liquid−liquid phase equilibria (LLE) of binary mixtures containing a room-temperature ionic liquid *N*-hexylisoquinolinium thiocyanate, [HiQuin][SCN] with an aliphatic hydrocarbon (*n*-hexane, *n*-heptane), aromatic hydrocarbon (benzene, toluene, ethylbenzene, *n*-propylbenzene), cyclohexane, thiophene, water, and 1-alcohol (1-ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol) have been determined using a dynamic method from room temperature to the boiling-point of the solvent at ambient pressure. *N*-hexylisoquinolinium thiocyanate, [HiQuin][SCN] has been synthesized from *N*-hexyl-isoquinolinium bromide as a substrate. Specific basic characterization of the new compound including NMR spectra, elementary analysis, and water content have been done. The density and viscosity of pure ionic liquid were determined over a wide temperature range from 298.15 to 348.15 K. The mutual immiscibility with an upper critical solution temperature (UCST) for the binary systems {IL + aliphatic hydrocarbon, cyclohexane, or water} was detected. In the systems of {IL + aromatic hydrocarbon or thiophene} an immiscibility gap with a lower critical solution temperature (LCST) was observed. Complete miscibility in the liquid phase, over a whole range of ionic liquid mole fraction, was observed for the binary mixtures containing IL and an 1-alcohol. For the tested binary systems with immiscibility gap {IL + aliphatic hydrocarbon, aromatic hydrocarbon, cyclohexane, thiophene, or water}, the parameters of the LLE correlation have been derived using the NRTL equation. The basic thermal properties of the pure IL, that is, the glass-transition temperature as well as the heat capacity at the glass-transition temperature, have been measured using a differential scanning microcalorimetry technique (DSC). Decomposition of the IL was detected by simultaneous thermogravimetric/differential thermal analysis (TG/DTA) experiments.
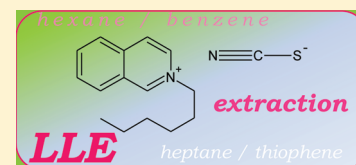
INTRODUCTION

Liquid−liquid extraction is a technique commonly used on an industrial scale in the processes of separating mixtures. The high efficiency of this method largely depends on precisely selecting the most suitable solvent for specific separation process. Commonly used on an industrial scale, organic solvents are very volatile, flammable, and often toxic. Currently, the chemical industry is widely regarded as the main factor having a deleterious effect on the environment. This view became the basis for development activities, environmental programs, modernization of chemical plants, and replacement of hazardous chemicals with safe materials.

Good candidates from this point of view are ionic liquids (ILs), which are a family of low melting salts[1] with very interesting properties. The negligible vapor pressure under normal operating conditions, a wide temperature range for the liquid state, and high selectivity in many separation processes makes them attractive for a number of applications.[2−4]

The knowledge of physicochemical and thermodynamic properties, including density, viscosity, and liquid + liquid phase equilibrium (LLE) of IL binary mixtures with traditional organic solvents is essential to determine their potential applications as solvents in extraction processes.[4−15]

This paper in a continuation of our systematic work on thiocyanate-based ionic liquids to investigate the physicochemical properties[16,17] and possibility of using them as an effective

solvent for the separation of aromatic from aliphatic hydrocarbons and in the desulphurization process.[14,18−23] The liquid + liquid phase equilibrium data of new isoquinolinium-based ionic liquid in binary mixtures with aliphatic and aromatic hydrocarbons, cyclohexane, thiophene, water, and 1-alcohols will be discussed in terms of the applicability of the *N*-hexyl-isoquinoliunium thiocyanate, [HiQuin][SCN], as an efficient solvent for extraction of aromatic hydrocarbons from aliphatics and release sulfur compounds from fuels.

As far as quinolinium-based ILs are concerned, there are still a small number of publications available in the open literature.[24−28]

Because of the polyaromatic structure of the quinolinium cation of ILs, they indicate the good solubility of the aromatic hydrocarbons and thiophene in quinolinium-based ionic liquid compared to the solubility of aliphatic hydrocarbons. This fact creates a hope for the possibility of using quinolinium-based ionic liquids as a solvent in this kind of separation process.

It has been shown that quinolinium-based ionic liquid possesses great potential in the desulfurization of oils (extraction of dibenzothiophene from *n*-dodecane)[5] and was

also used in the selection of entrainers in the 1-hexene/n-hexane separation problem with moderate results.[24]

In order to select the best ionic liquid for a specific separation problem, the knowledge of the influence of cation and anion structure of the ionic liquids is required. Due to the large number of prospective ILs, the choice of the best one is not easy to make and an overview of the literature is necessary. The solubilities of N-butylquinolinium bis{(trifluoro-methyl)-sulfonyl}imide [BQuin][NTf₂],[25] N-butylisoquinolinium bis-{(trifluoromethyl)-sulfonyl}imide [BiQuin][NTf₂],[26] N-hexyl-quinolinium bis{(trifluoromethyl)sulfonyl}imide[HQuin]-[NTf₂],[27] and N-hexylisoquinolinium bis{(trifluoromethyl)sulfonyl}imide[HiQuin][NTf₂][28] with aromatic hydrocarbons (benzene, toluene, ethylbenzene, propylbenzene, or thiophene) and 1-alcohols (1-butanol, 1-hexanol, 1-octanol, or 1-decanol) have been measured in our laboratory.

The solubilities of these ionic liquids in aromatic hydrocarbons and 1-alcohols decreased with an increase of the molecular weight of the solvent. For all binary mixtures of {IL + aromatic hydrocarbon}, eutectic systems with an immiscibility gap with upper critical solution temperature (UCST) in the liquid phase were observed. The immiscibility in the liquid phase in aromatic hydrocarbons was detected over a narrow region of the ionic liquid concentration.

The current study focuses on solutions of N-hexylisoquinolinium thiocyanate, [HiQuin][SCN] with aliphatic hydrocarbon (n-hexane, n-heptane), aromatic hydrocarbon (benzene, toluene, ethylbenzene, n-propylbenzene), cyclohexane, thiophene, water, and/or 1-alcohol (1-ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol) at ambient pressure.

The experimental data presented in this work were compared to those ILs with quinolinium cation, or different ILs with thiocyanate anion, available in the open literature. The effect of the alkyl chain length of the solvent and the effect of the cation and anion structure will be discussed.

From the standpoint of the use of ionic liquids in a real industrial process, the knowledge of physicochemical properties such as density and viscosity is also required. Herein, the densities and dynamic and kinematic viscosities were determined at a wide range of the temperatures from 298.15 to 348.15 K.

The data presented here will make a valuable information on the technological applicability of presented ionic liquid.

■ EXPERIMENTAL METHODS

Materials. The ionic liquid named N-hexylisoquinolinium thiocyanate, [HiQuin][SCN], was synthesized in our laboratory from N-hexylisoquinolinium bromide, [HiQuin][Br], as a substrate. Synthesis of 1-hexylisoquinolinium bromide, [HiQuin][Br], have been described in our previous paper.[28]

For synthesis of [HiQuin][SCN], a 500 cm³ flask was used. To a solution of 24.01 g N-hexylisoquinolinium bromide (synthesized) (0.0816 mol) in 150 cm³ water, 8.16 g sodium thiocyanate (as received, Aldrich 98%) (0.1007 mol, 1.23 equivalents) was added. Solution became darker in color. Next 100 mL of dichloromethane was added, and the mixture was stirred for 24 h, afterward phases were separated. The water phase was extracted 10 times with 25 mL of dichloromethane, then, the organic phase was extracted 4 times with distilled water to remove sodium bromide and excess of sodium thiocyanate. Dichloromethane was removed in vacuum, and the product was dried under vacuum at 333.15 K for 72 h. The

yield was: 19.93 g (89.7% of theoretical value). The following information was determined for our sample.

¹H NMR (400 MHz, CDCl₃): δ = 0.433 (t, 3H, J = 7.2); 0.948 (m, 4H); 1.092 (quint, 2H, J = 6.4); 1.835 (quint, 2H, J = 7.2); 4.665 (t, 2H, J = 7.2); 7.626 (m, 1H); 7.833 (m, 1H); 7.893 (m, 1H); 8.180 (d, 1H, J = 6.8); 8.297 (d, 1H, J = 8.4); 8.508 (m, 1H); 9.976 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ = 12.926; 21.253; 24.749; 30.004; 30,687; 61.021; 125.778; 126.377; 126.749; 129.812; 130.563; 133.566; 136.274; 136.342; 148.529.

Elementary Microanalysis. Found: C 70.40%, N 10.30%, H 7.32%, S 11.81%. Theory: C 70.55%, N 10.28%, H 7.40%, S 11.77%.

The NMR spectra for [HiQuin][SCN] are shown as GRS 1−4 in the Supporting Information.

To diminish the volatile chemical and water content, the ionic liquid was further purified by subjecting the liquid to a very low pressure of about 5×10^{-3} Pa at a temperature of about 300 K for approximately 5 h. The structure of the investigated ionic liquid and the different physicochemical properties are listed in Tables 1 and 2.

Table 1. Investigated Ionic Liquid: Chemical Structure, Name, Abbreviation, and Measured Thermophysical Properties: Density (ρ), Dynamic Viscosity (η) at 298.15 K, Glass Transition Temperature ($T_{g,1}$), and Heat Capacity Change at $T_{g,1}$ ($\Delta C_{p(g),1}$) and Decomposition Temperature (T_d)
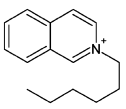
Structure	Name, Abbreviation		
	N-hexylisoquinolinium thiocyanate, [HiQuin][SCN]		
	M / (g mol⁻¹)	$\rho^{298.15}$ / (kg m⁻³)	$\eta^{298.15}$ / (Pa s)
	272.41	1081.34	0.74513
	$T_{g,1}$ / (K)	$\Delta C_{p(g),1}$ / (J mol⁻¹ K⁻¹)	T_d / (K)
	216.4	124.1	531

Table 2. Density and Viscosity (Dynamic and Kinematic) for [HiQuin][SCN]

T/K	ρ/kg m⁻³	η_{dyn}/Pa s	$10^4 \eta_{kin}$/m² s⁻¹
298.2	1081.34	0.74513	6.8911
303.2	1078.42	0.50118	4.6474
308.2	1075.51	0.32767	3.0466
313.2	1072.58	0.23478	2.1889
318.2	1069.64	0.17225	1.6104
323.2	1066.86	0.12964	1.2151
328.2	1064.05	0.09943	0.93444
333.2	1061.23	0.07790	0.73402
338.2	1058.42	0.06209	0.58661
343.2	1055.61	0.05022	0.47573
348.2	1052.81	0.04132	0.39247

The purity in mass fraction and supplier of each of the solvents were as follows: n-hexane (CAS No. 110-54-3, Fluka, ≥99%), n-heptane (CAS No. 142-82-5, Fluka, 99.5%), benzene (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%); n-propylbenzene (CAS No. 103-65-1, Sigma-Aldrich, 98%), cyclohexane (CAS No. 110-83-8, Fluka, 99.5%), ethanol (CAS No. 64-17-5, POCH, 99.8%), 1-butanol (CAS No. 71-36-3, Sigma-Aldrich, 99.8%), 1-hexanol (CAS No. 111-27-3, Sigma-Aldrich, 99%), 1-octanol (CAS No. 11-87-5,

Sigma-Aldrich, 99%), 1-decanol (CAS No. 112-30-1, Sigma-Aldrich, 99%), thiophene (CAS No. 110-02-1, Sigma-Aldrich, 99%). All utilized solvents before use were fractionally distilled over different drying reagents to the mass fraction purity of ≥0.998. They were each stored over freshly activated molecular sieves of type 4 Å (Union Carbide).

Water Content. The water content was analyzed by Karl Fischer titration (method TitroLine KF). Samples of [HiQuin]-[SCN] and the solvents were dissolved in dry methanol and titrated with steps of 2.5 μL. The analysis have shown that the water content was less than 230 ppm.

Density Measurements. The Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria) was used to determined the density of pure IL over the temperature range 298.15−348.15 K. Two integrated Pt 100 platinum thermometers provided good precision in temperature control internally ($T \pm 0.01$ K). Densimeter includes an automatic correction for the viscosity of the sample. The calibration for temperature and pressure was made by the producer. The apparatus is precise to within 1×10^{-2} kg m^{-3}, and the uncertainty of the measurements was estimated to be better than ± 0.1 kg m^{-3}. Table 2 and Figure 1 show the density of pure ionic liquid as a function of temperature
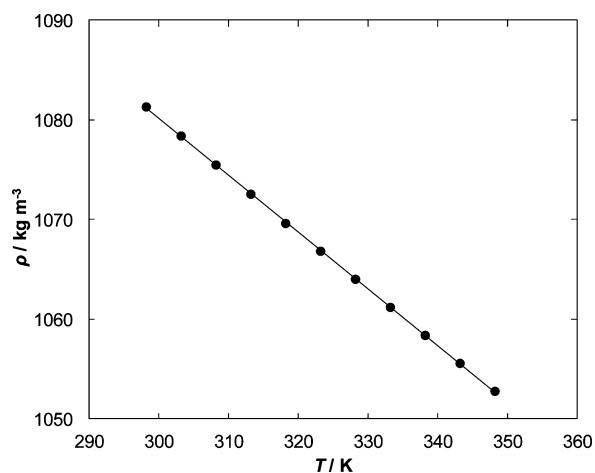

Figure 1. Plot of the density as a function of temperature for [HiQuin][SCN]. The solid line represents the linear approximation.

Viscosity Measurements. Viscosity measurements for pure IL were carried out using an Anton Paar BmbH AMVn (Graz, Austria) programmable rheometer, with a nominal uncertainty of $\pm 0.1\%$ and reproducibility <0.05% for viscosities from $(3 \times 10^{-4}$ to 2.5) Pa s. Temperature was controlled internally with a precision of ± 0.01 K in a range from 298.15 to 348.15 K. In this range of viscosity values, the diameter of the capillary was 3.0 mm and the error for this capillary was <0.01%. The values of the dynamic and kinematic viscosities of pure ionic liquid as a function of temperature are collected in Table 2 and shown in Figure 2.

Differential Scanning Microcalorimetry (DSC). Basic thermal characteristics of the ionic liquid, that is, the glass transition temperature ($T_{g,1}$) and the change of heat capacity at the glass-transition temperature ($\Delta C_{p(g),1}$) have been measured using a differential scanning microcalorimetry technique (DSC) at the 5 K min^{-1} scan rate. The instrument (Perkin-Elmer Pyris 1) was calibrated with the 99.9999 mol % purity indium sample. The calorimetric accuracy was $\pm 3\%$, and the calorimetric
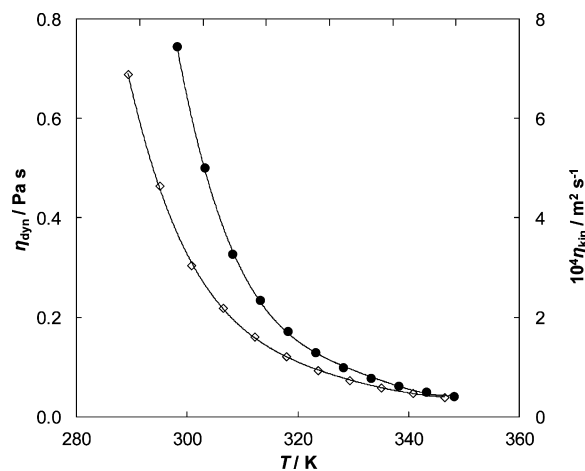

Figure 2. Plot of the viscosity (dynamic and kinematic) as a function of temperature for [HiQuin][SCN]. Points are the experimental results: ●, dynamic viscosity; ◇, kinematic viscosity. Solid lines represent polynomial approximation.

precision was $\pm 0.5\%$. The thermophysical properties are collected in Table 1, and the DSC diagram is shown as GRS 5 in the Supporting Information. The average value of the glass-transition temperature, $T_{g,1}$, was 216.4 K with a $\Delta C_{p(g),1}$ of 124.1 J mol^{-1} K^{-1}.

Decomposition of Compounds. Simultaneous TG/DTA experiments were performed using a MOM Derivatograph PC (Hungary). In general, runs were carried out using matched labyrinth platinic crucibles with Al$_2$O$_3$ in the reference pan. The crucible design hampered the migration of volatile decomposition products, reducing the rate of gas evolution and, in turn, increasing the contact time of the reactants. All TG/DTA curves were obtained at a 5 K min^{-1} heating rate with an argon dynamic atmosphere. The decomposition temperature of [HiQuin][SCN] is presented in GRS 6 in the Supporting Information. It is easy to detect that the decomposition was not observed up to 531 K.

Phase Equilibria Apparatus and Measurements. A dynamic method was used to determined the temperature of the two-phase disappearance in the present work. Mixtures of IL and solvent were prepared by weighing with accuracy ± 0.0001 g in the drybox under the nitrogen atmosphere, then placed into a Pyrex glass cell, and heated very slowly (less than 2 K h^{-1} near the equilibrium temperature) with continuous stirring inside the cell, placed in the thermostat. The temperature of the two-phase disappearance during an increasing temperature period was detected visually and controlled by calibrated electronic thermometer P550 (DOS-TMANN electronic GmbH) with uncertainty ± 0.05 K. The experiments have been carried out over a wide range of the ionic liquid mole fraction (x_1). The liquid−liquid phase equilibrium data for the binary systems of {[HiQuin][SCN] (1) + organic solvent or water (2)} are collected in Tables 3−7. Experimental results have been correlated by means of the NRTL equation. The parameters of these calculation are collected in Table 8.

■ RESULTS AND DISCUSSION

The main objective of this study is to determine the potential application of studied ionic liquid in the extraction of aromatics from aliphatic hydrocarbons and in the desulphurization processes.

Table 3. Experimental (Liquid + Liquid) Phase Equilibrium of the {[HiQuin][SCN] (1) + Aliphatic Hydrocarbon (2)} Binary Systems

x_1	T^{LLE}/K	x_1	T^{LLE}/K
		n-hexane	
0.9500	321.6	0.9365	334.6
0.9473	324.0	0.9350	338.0
0.9437	327.0	0.9339	341.4
0.9386	331.3	0.9319	345.0
		n-heptane	
0.9660	315.1	0.9540	338.2
0.9644	318.7	0.9494	341.0
0.9622	325.8	0.9446	345.3
0.9613	330.1	0.9424	350.7
0.9570	335.1		

Table 4. Experimental (Liquid + Liquid) Phase Equilibrium of the {[HiQuin][SCN] (1) + Aromatic Hydrocarbon (2)} Binary Systems

x_1	T^{LLE}/K	x_1	T^{LLE}/K
		benzene	
0.2416	325.0	0.2342	302.4
0.2407	319.4	0.2332	299.1
0.2398	317.8	0.2312	295.3
0.2390	316.8	0.2304	291.0
0.2380	314.1	0.2295	288.8
0.2371	310.7	0.2282	285.3
0.2350	304.9		
		toluene	
0.4000	334.2	0.3851	305.5
0.3991	326.5	0.3810	300.5
0.3976	320.7	0.3715	290.8
0.3937	316.1	0.3615	281.3
0.3886	310.8		
		ethylbenzene	
0.5247	316.7	0.5073	296.0
0.5203	309.9	0.5034	289.1
0.5112	302.5	0.4961	281.8
		n-propylbenzene	
0.6553	327.1	0.6329	303.0
0.6497	320.4	0.6276	294.2
0.6452	314.1	0.6130	279.7

This paper focuses on presenting the experimental data of liquid + liquid phase equilibria for binary mixtures of [HiQuin][SCN] with organic solvents and water over the whole range of composition. In order to determine the effect of the cation and anion structure on phase equilibria, experimental results were compared to the literature data for other thiocyanate-based ionic liquids[18–23] and [HiQuin][NTF$_2$].[28]

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

Table 2 presents the experimental values of the density and viscosity (dynamic and kinematic) of pure ionic liquid over a wide temperature range from 298.15 to 348.15 K. The density of [HiQuin][SCN] at T = 298.15 K is low and is equal to 1081.34 kg m^{-3} which is similar to the rest of the thiocyanate-based ionic liquids.[17,19–21] The comparison with [HiQuin]-[NTf$_2$][28] shows that [HiQuin][SCN] has lower density and much higher viscosity.

This article focuses on the solubility of [HiQuin][SCN] in binary mixtures with organic solvents in comparison with

different thiocyanate-based ionic liquids with imidazolium, pirydynium, pyrolidynium, and piperidinium cation and with [HiQuin][NTf$_2$].

The experimental results for binary mixtures of {[HiQuin]-[SCN] (1) + aliphatic hydrocarbon (2)} are presented in Table 3 and in the Figure 3. The table includes the direct experimental results of the LLE temperatures, T/K versus x_1, the mole fraction of the IL at the equilibrium temperatures for
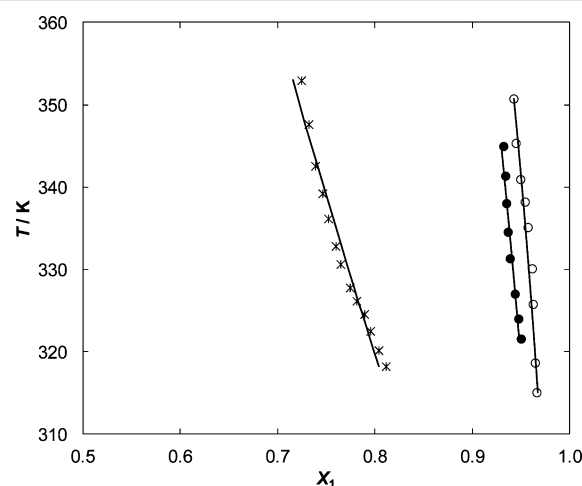
Figure 3. Experimental and calculated liquid + liquid phase equilibria of {[HiQuin][SCN] (1) + aliphatic hydrocarbon (2)} binary systems: ●, *n*-hexane; ○, *n*-heptane; ∗, cyclohexane. Solid lines have been calculated using the NRTL equation.

the investigated systems. As usual, the liquid + liquid phase equilibria with upper critical solution temperature (UCST) were observed for these systems. The maximum of the curves were not observed because the boiling point of the solvent was lower.

The solubility of *n*-alkane in the tested IL is very low; the miscibility gap started from mole fraction x_1 = 0.95 for *n*-hexane and x_1 = 0.96 for *n*-heptane. It was also observed that the solubility decreases with an increase of the alkyl chain length of the solvent. This tendency is consistent with other ionic liquid-*n*-alkane binary systems.[11,13,18] These experimental results are compared to the previously measured binary systems with thiocyanate-based ionic liquids. For all binary mixtures of thiocyanate-based ionic liquids with aliphatic hydrocarbons, very low solubility and a nearly complete immiscibility gap in the liquid phase were observed.

The solubility of *n*-hexane in the thiocyanate-based ionic liquids increases in the order [EMIM][SCN] < [BMIM][SCN] < [BMPYR][SCN] < [BMPIP][SCN] ∼ [HiQuin][SCN] < [HMIM][SCN]. The comparison of the solubility of *n*-hexane in the ILs with the same anion is presented in Figure 4.

Equilibrium curves for the four binary systems of [HiQuin]-[SCN] with aromatic hydrocarbons as a function of temperature for different compositions are shown in Figure 5. These systems exhibit much better solubility of aromatic hydrocarbons than that with aliphatic hydrocarbons, because of the aromatic nature of the solvent and polyaromatic structure of quinolinium cation of the IL. Strong interaction between six π-delocalized electrons in the aromatic structure of the solvent and ionic liquid structure is the cause of greater solubility in these systems. Furthermore, it was observed that the solubility decreases with an increase of the alkyl chain length of the
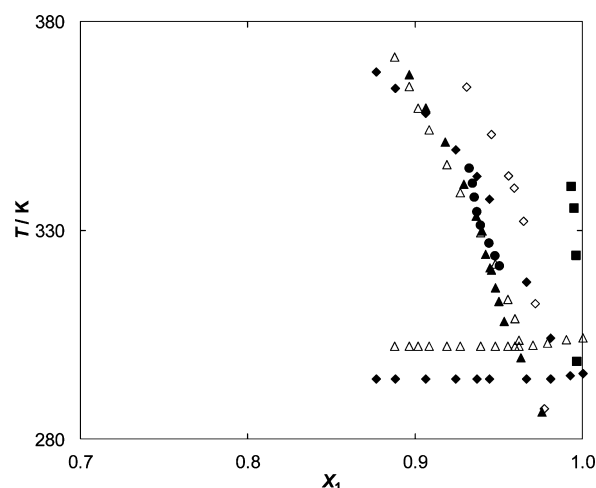
Figure 4. Experimental solid + liquid and liquid + liquid phase equilibria of the {IL (1) + *n*-hexane (2)} binary systems: ●, [HiQuin][SCN]; ■, [EMIM][SCN];[18] ◇, [BMIM] [SCN];[19] ▲, [HMIM][SCN];[20] ◆, [BMPYR][SCN];[22] △, [BMPIP][SCN].[21]
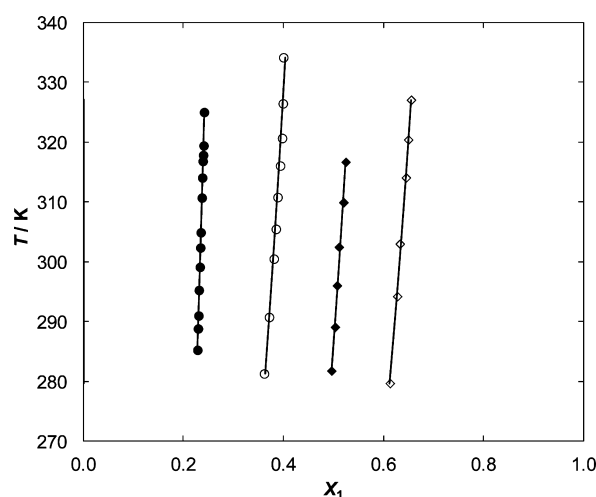

Figure 5. Experimental and calculated liquid + liquid phase equilibria of {[HiQuin][SCN] (1) + aromatic hydrocarbon (2)} binary systems: ●, benzene; ○, toluene; ◆, ethylbenzene; ◇, *n*-propylbenzene. Solid lines have been calculated using the NRTL equation.

substituent at the aromatic ring. These systems exhibit lower critical solution temperature (LCST), which was observed previously for all analized thiocyanate-based ionic liquids.[18−23] The minima of the binodal curves were not detected because they were at very low temperatures, and it was impossible to conduct the experiment, even with the use of acetone/dry ice bath. A comparison of the solubility of benzene in thiocyanate-based ILs, presented in the Figure 6, shows that the solubility decreases in the following series: [HiQuin][SCN] > [HMIM]-[SCN] > [BMPIP][SCN] ∼ [BMPYR][SCN] > [BMIM]-[SCN] > [EMIM][SCN]. The strong interaction between the aromatic ring of benzene and aromatic quinoline cation significantly improves the solubility in ionic liquids compared to the IL with imidazolium, pyrrolidinium, and piperidynium cation.

For ionic liquid tested in this work, the immiscibility gap in the liquid phase with benzene was from the low IL mole fraction 1×10^{-4} to 0.2 while for [HiQuin][NTf$_2$] a twice smaller immiscibility gap was observed, (see Figure 7).
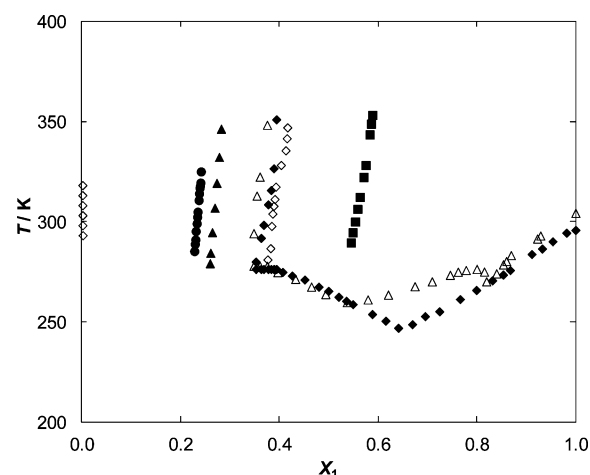

Figure 6. Experimental solid + liquid and liquid + liquid phase equilibria of the {IL (1) + benzene (2)} binary systems: ●, [HiQuin][SCN]; ■, [EMIM][SCN];[18] ◇, [BMIM][SCN];[19] ▲, [HMIM][SCN];[20] ◆, [BMPYR][SCN];[22] △, [BMPIP][SCN].[21]

Improved solubility and therefore greater affinity of [HiQuin]-[NTf$_2$] to aromatic hydrocarbons is due to the presence of
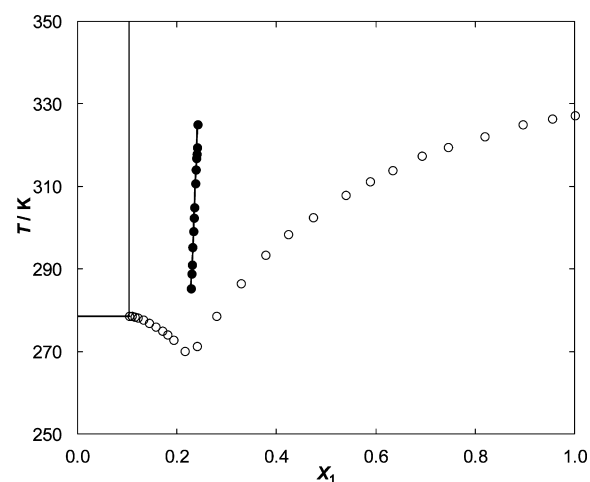

Figure 7. Experimental solid + liquid and liquid + liquid phase equilibria of the {IL (1) + benzene (2)} binary systems: ●, [HiQuin][SCN]; ○ [HiQuin][NTf$_2$].[28]

localized and delocalized electron clouds, permanent dipoles, and lone pair electrons.

The previously published data shows that among quinolinium-based ionic liquids with bis{(trifluoromethyl)sulfonyl}-imide anion the most optimistic results for the applicability of ionic liquids in separation of aliphatic from aromatic hydrocarbons were obtained for [HiQuin][NTf$_2$],[28] and between thiocyanate-based ionic liquids, the best results were for [BMIM][SCN].[14]

Ionic liquid presented in this work shows a significant difference in the solubility of aromatic and aliphatic hydrocarbons. A small miscibility gap, providing a strong interaction between IL and aromatic hydrocarbons compared to aliphatic hydrocarbon, provides promising information about the applicability of [HiQuin][SCN] in this extraction process. It is possible, however because of the very low solubility of [EMIM][SCN] in aliphatic hydrocarbons, the selectivity of

extraction of aromatic hydrocarbons from aliphatic hydrocarbons may be expected better for [EMIM][SCN].

The liquid + liquid phase equilibria for {[HiQuin][SCN] + cyclohexane} binary mixture is given in Table 5 and in Figure 3. As can be noticed, the solubility of cyclohexane is much higher

Table 5. Experimental Liquid + Liquid Phase Equilibrium of the {[HiQuin][SCN] (1) + Cyclohexane (2)} Binary System

x_1	T^{LLE}/K	x_1	T^{LLE}/K
	cyclohexane		
0.8113	318.2	0.7597	332.8
0.8038	320.2	0.7521	336.2
0.7953	322.5	0.7462	339.2
0.7891	324.6	0.7387	342.6
0.7811	326.2	0.7320	347.6
0.7744	327.8	0.7244	353.0
0.7647	330.6		

than that of *n*-hexane. The solubility of cyclic molecules in ILs is usually higher than those of aliphatic hydrocarbons. Such a relationship is influenced by many factors: the cyclic structure of the cyclohexane, analogous to the structure of ionic liquid, and the smaller molar volume and better packing effect in comparison with *n*-hexane.

In order to determine the potential usefulness of the ionic liquid to fuel desulfurization process, the measurements of liquid + liquid phase equilibria of [HiQuin][SCN] with thiophene, a model sulfur compound have been carried out. Experimental results are presented in Table 6 and in Figure 8. The very good solubility of thiophene in the ILs with LCST

Table 6. Experimental Liquid + Liquid Phase Equilibrium of the {[HiQuin][SCN] (1) + Thiophene (2)} Binary System

x_1	T^{LLE}/K	x_1	T^{LLE}/K
	thiophene		
0.1257	332.2	0.1245	301.0
0.1256	326.1	0.1241	298.6
0.1255	321.7	0.1240	295.3
0.1253	317.5	0.1237	290.9
0.1251	312.6	0.1235	286.9
0.1249	309.1	0.0008	323.1
0.1246	304.8		

was observed as in systems of aromatic hydrocarbons. The immiscibility gap was narrow and in the range of $x_1 = 8 \times 10^{-4}$ to 0.13. This means that the six-π delocalized electrons in aromatic thiophene can strongly interact with the polar cation and anion of the IL tested in this work.

The experiment conducted in this paper shows a large difference in the solubility of aliphatic hydrocarbons and thiophene in [HiQuin][SCN]. This fact gives hope to use the presented IL in the desulfurization process.

The experimental results for systems {[HiQuin][SCN] + water} are given in Table 7 and in Figure 9. In that particular system the strong interaction between polar IL and water has been observed as evidenced by a small immiscibility gap from $x_1 = 1 \times 10^{-4}$ to 0.25. This situation was not observed in systems with thiocyanate-based ILs and water, where complete miscibility in the liquid phase in the whole range of the IL mole fraction were detected.[19,20,22] The occurrence of the miscibility gap in the system {[HiQuin][SCN] + water} may be associated
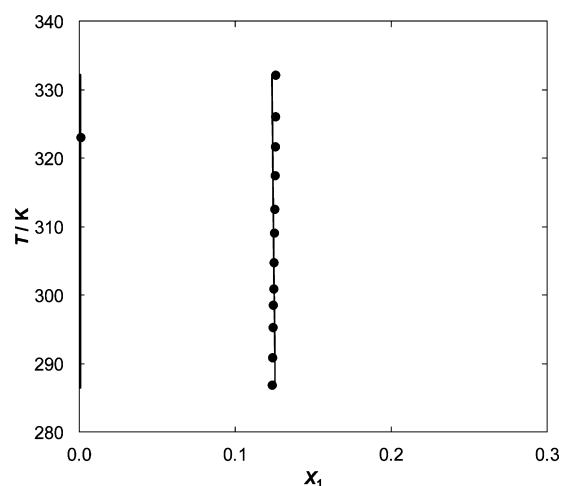

Figure 8. Experimental and calculated liquid + liquid phase equilibria of {[HiQuin][SCN] (1) + thiophene (2)}. Points are the experimental data. Solid lines have been calculated using the NRTL equation.

Table 7. Experimental Liquid + Liquid Phase Equilibrium of the {[HiQuin][SCN] (1) + Water (2)} Binary System

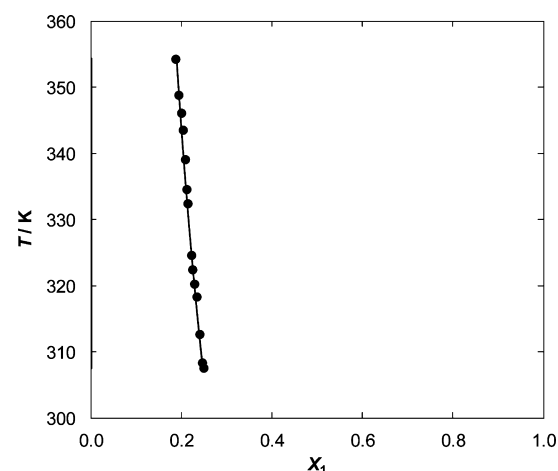| x_1	T^{LLE}/K	x_1	T^{LLE}/K
	water		
0.2489	307.6	0.2137	332.5
0.2458	308.4	0.2114	334.6
0.2400	312.7	0.2082	339.1
0.2336	318.4	0.2032	343.6
0.2284	320.3	0.1997	346.2
0.2242	322.5	0.1936	348.9
0.2219	324.7	0.1868	354.3

Figure 9. Experimental and calculated liquid + liquid phase equilibria of {[HiQuin][SCN] (1) + water (2)}. Points are the experimental data. Solid lines have been calculated using the NRTL equation.

with the occurrence of 6-membered aliphatic chain in the quinoline ring in cation.

Apart from aromatic hydrocarbons, thiophene, and water, the strong interaction was also observed in the systems of [HiQuin][SCN] with 1-alcohols where complete miscibility in the liquid phase was observed from methanol to 1-decanol at room temperature (T = 298.15 K). This may be the result of a strong interaction between the quinolinium cation and/or thiocyanate anion and polar solvent.

■ MODELING

Correlation of Liquid + Liquid Phase Equilibrium. In this paper, the experimental liquid + liquid phase equilibrium data were correlated using the NRTL equation, based on the excess Gibbs free energy defined as follows:[29]

$$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 G_{12} + x_2} \right] \quad (1)$$

The description of this equation and the activity coefficient formula were presented by us earlier.[30]

The model adjustable parameters $g_{12}-g_{22}$ and $g_{21}-g_{11}$ were found by minimization of the objective function (OF)

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

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

$$\Delta x = x_{calc,i} - x_{exp,i} \quad (3)$$

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

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

In this calculation, the parameter α_{12} is a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{12} = \alpha_{21} = 0.2$) and was taken into account by choosing the value that gave the lowest deviation. The calculated values of the NRTL parameters and the corresponding root-mean-square deviations for organic solvent and water are presented in Table 8.

■ CONCLUDING REMARKS

In order to design the best ionic liquid for separation of aromatic hydrocarbons from aliphatic or for the desulphuriza-

tion process, the knowledge about the effects of the ionic liquid structure on phase equilibrium is essential.

Liquid + liquid phase equilibrium data for binary mixtures of N-hexylisoquinolinium thiocyanate [HiQuin][SCN] ionic liquid and n-alkanes, cyclohexane, aromatic hydrocarbons, thiophene, and water have been determined using a dynamic method.

The phase equilibrium diagrams for the binary mixtures with n-alkane, cyclohexane, and water show the immiscibility gap with UCST, while the diagrams with LCST were observed for aromatic hydrocarbon and thiophene. Furthermore, the complete miscibility in the liquid phase, over whole range of ionic liquid mole fraction, was observed for the binary mixtures containing IL and an 1-alcohol.

Due to the polar nature of the [HiQuin][SCN], the high solubility of aromatic hydrocarbons and thiophene in comparison to n-alkanes in the IL were observed. This is an optimistic conclusion, which gives hope to the possible effective application of the ionic liquid in the studied extraction processes.

The results obtained in this work were compared to the data of analogous study of different ionic liquids with the isoquinolinium cation, or thiocyanate anion, and may provide new opportunities for the use of ionic liquids in extraction processes.

The mathematical description of the liquid + liquid phase equilibrium data was carried out by means of the NRTL equation. The results of the correlation were acceptable for all the data.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

GRS 1−4, ^{1}H NMR spectra, and ^{13}C NMR spectra for [HiQuin][SCN]; GRS 5, DSC diagram for [HiQuin][SCN]; GRS 6, TG/DTA diagram for [HiQuin][SCN]. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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Table 8. Correlation of the Liquid + Liquid Phase Equilibrium 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 Deviations σ_x

| | NRTL parameters[a] | | | | |
| | $(g_{12}-g_{12})$/J mol^{-1} | | $(g_{21}-g_{11})$/J mol^{-1} | | |
solvent	a_{12}	b_{12}	a_{21}	b_{21}	$10^4 \times \sigma_x$
n-hexane	10126.34	−15.49	−3895.16	96.58	7.0
n-heptane	12352.04	−19.91	−4270.86	96.89	8.5
benzene	−2577.43	−16.45	2830.85	87.73	1.8
toluene	−3912.91	−1.96	3593.98	79.93	13.2
ethylbenzene	−3265.85	2.40	2675.65	77.32	13.2
n-propylbenzene	−3331.64	7.74	2455.51	74.07	7.1
cyclohexane	12111.52	−32.04	−6822.18	110.47	21.8
thiophene	−318.37	−34.19	−1434.78	99.86	1.0
water	11660.94	−61.80	−13043.54	138.28	11.0

[a]$\alpha = 0.2$. $(g_{12}-g_{22})$/J mol$^{-1} = a_{12} + b_{12}T$/K; $(g_{21}-g_{11})$/J mol$^{-1} = a_{21} + b_{21}T$/K.

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