JOURNAL OF
CHEMICAL &
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Influence of Anion Structure on the Liquid−Liquid Equilibria of 1-Ethyl-3-methyl-imidazolium Cation Based Ionic Liquid-Hydrocarbon Binary Systems

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S *Supporting Information*

ABSTRACT: Binary liquid−liquid phase equilibria for 15 systems containing an ionic liquid (1-ethyl-3-methyl-imidazolium thiocyanate, 1-ethyl-3-methyl-imidazolium trifluoroacetate, 1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate) with a hydrocarbon (*n*-hexane, *n*-heptane, cyclohexane, benzene, toluene) were measured using dynamic method. The influence of the anion structure of 1-ethyl-3-methyl-imidazolium cation based ionic liquids on solubility of aliphatic and aromatic hydrocarbons is discussed. The liquid−liquid solubility data are reported only for the ionic-liquid-rich side of the phase diagram. It was found that the solubility of investigated hydrocarbons is the highest for ionic liquid with trifluoromethanesulfonate anion and the lowest for 1-ethyl-3-methyl-imidazolium thiocyanate.

■ INTRODUCTION

Dearomatization processes play key role in chemical industry and are used, inter alia, to produce kerosene with a better smoke point, diesel oil with a higher cetane number or a mineral oil with a better viscosity index. In industrial processes different types of entrainers are used, namely, di-, tri-, and tetra-ethyleneglycols (abbreviations: DEG, TEG and TETRA respectively), *N*-methylpyrrolidone (NMP), *N*-formylmorpholine (NFM), dimethylsulfoxide (DMSO), tetramethylenesulfone (sulfolane).[1] Although the processes based on these solvents are well-known, there is still need to find environmentally friendly solvents with better selectivity and capacity. From the activity coefficients at infinite dilution measurements, it was shown that a large number of ionic liquids (ILs) exhibit selectivity and capacity in extraction of aromatics from aromatic/aliphatic mixtures higher than typical solvents such as sulfolane and NMP.[2] Ionic liquids are relatively new class of salts with melting temperature below 373.15 K.[3] In general, ILs are composed of organic cations with either inorganic or organic anions. Additionally, ionic liquids have other important properties required for entrainers, namely, negligible vapor pressure, a wide liquid range and stability at high temperatures. Ionic liquids are also considered as extractants in separation of sulfur compounds from fuels;[4−8] therefore, the solubility of aromatic and aliphatic hydrocarbons in ionic liquids for this problem are very useful and important. To design an ionic liquid for specific separation problem the knowledge of influence of cation and anion structure on solubility of interest compounds is required.

In this work, the influence of anion structure of 1-ethyl-3-methyl-imidazolium cation based ionic liquids on solubility of aliphatic and aromatic hydrocarbons is presented. Binary liquid−liquid phase equilibria (LLE) for 15 systems containing an ionic liquid (1-ethyl-3-methyl-imidazolium thiocyanate, [emim][SCN], 1-ethyl-3-methyl-imidazolium trifluoroacetate, [emim][TFA], 1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate, [emim][CF_3SO_3]) with a hydrocarbon (*n*-hexane, *n*-heptane, cyclohexane, benzene, toluene) were measured by the dynamic method. Because of the method limitations the liquid−liquid solubility data are reported only for the ionic-liquid-rich side of the phase diagram. The potentials of 1-ethyl-3-methyl-imidazolium cation based ionic liquids as extractants for the separation of aromatic hydrocarbons from aromatic/aliphatic mixtures have been already studied in a few papers by measuring liquid−liquid equilibrium for IL + hydrocarbon systems: [emim][$EtSO_4$], 1-ethyl-3-methyl-imidazolium ethyl sulfate;[9−14] [emim][NTf_2], 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide;[15−19] [emim][$OcSO_4$], 1-ethyl-3-methyl-imidazolium octyl sulfate;[20] [emim][PF_6], 1-ethyl-3-methyl-imidazolium hexafluorophosphate;[21,22] [emim][I_3], 1-ethyl-3-methyl-imidazolium triiodide,[23] and activity coefficients at infinite dilution, γ^∞.[24−35]

■ EXPERIMENTAL METHOD

Materials. The ionic liquid [emim][SCN] had a mass purity of > 0.99 and was supplied by Merck (Germany). The ionic liquid [emim][TFA] had a mass purity of > 0.996 and was supplied by Merck (Germany). The ionic liquid [emim][CF_3SO_3] had a mass purity of > 0.998 and was supplied by Merck (Germany). The ionic liquids were further purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at a temperature about 368 K for ca. 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The list of hydrocarbons used in this study including source and grade is as follows: *n*-hexane, Fluka (Germany), w>0.997; *n*-heptane, Sigma-Aldrich (Germany), w >0.995; cyclohexane, Sigma-Aldrich (Germany), w >0.997; benzene, Sigma-Aldrich (Germany), w ≥0.999; toluene, Sigma-Aldrich (Germany), w ≥0.999. While the purity of hydrocarbons was high all hydrocarbons were used without further purification.

Received: May 26, 2010
Accepted: January 5, 2011
Published: January 13, 2011

dx.doi.org/10.1021/je101114r | *J. Chem. Eng. Data* 2011, 56, 368–374

Water Content. The water content was analyzed by Karl Fischer titration technique (model SCHOTT Instruments Titro-Line KF). A sample of IL was dissolved in methanol and titrated with steps of 2.5 μL. The results obtained have shown the water content to be less than 100 ppm. The titrant CombiTitrant 5 no. 1.8805.1000 Merck one-component reagent for volumetric Karl Fischer titration was used. The lower determination limit of this technique is approximately 50 to 100 ppm H_2O.

Liquid−Liquid Phase Equilibria Apparatus and Measurements. Two phases disappearance observed with an increasing temperature have been determined using a dynamic (synthetic) method. The schematic diagram of apparatus is shown on Supporting Information Figure 1S. Mixtures of solute and solvent were prepared under the nitrogen atmosphere in a drybox by weighing pure components to within 10^{-4} g. For systems with aliphatic hydrocarbons about 5 to 6 g of an ionic liquid and about 0.01 to 0.07 g of a solvent were used. For systems with aromatic hydrocarbons about 2.5 to 4 g of an ionic liquid and about 0.7 to 1.3 g of a solvent were used. All ionic liquids were used in the liquid state. The sample of solute and solvent was heated very slowly (at less than 2 $K \cdot h^{-1}$ near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell, placed in a thermostat. The dimensions of the cell are: internal diameter 2 cm^3 and height 2 cm. The foggy solution disappearance temperature detected visually was measured by calibrated electronic thermometer P 550 (DOSTMANN electronic GmbH, Germany). The measurements were carried out over a wide range of solute mole fraction ranging from 10^{-4} to 1. For each system the reproducibility was tested once. For selected mole fraction the temperature of two phases disappearance was observed. The uncertainty of temperature measurements was ± 0.05 K. For the investigated aliphatic solvents the relative error was 0.1 to 1% mole fraction. The reproducibility of the LLE experimental points was ± 0.1 K. The experimental results are listed in Table 1.

RESULTS

For this study, the liquid-phase behavior was determined for the 15 binary ionic liquid-hydrocarbon systems. Results are presented in the Table 1 and on Figures 1 to 3. To visualize difference in anion structure of investigated ionic liquids, anions and cation structures are presented in the Table 2. Additionally results are compared to other ionic liquid based on 1-ethyl-3-methyl-imidazolium cation: [emim][$EtSO_4$], [emim][NTf_2], [emim][$OcSO_4$], [emim][PF_6], [emim][I_3]. The anion structures of mentioned ionic liquids are presented in the Table 2.

An increase of solubility with an increase of the temperature is observed for the systems: [emim][TFA] + (*n*-hexane or *n*-heptane or cyclohexane or benzene or toluene) and for ([emim][SCN] or [emim][CF_3SO_3])+(*n*-hexane or *n*-heptane or cyclohexane). These types of diagrams for systems ionic liquid + aliphatic hydrocarbon are typical and were reported in literature.[22,36−39] With an increase of the alkane chain length the increase of miscibility gap is observed. This tendency is consistent with other ionic liquid-alkane binary systems.[9,13,15,17] Cyclohexane comparing to *n*-hexane shows better solubility in all investigated ionic liquids. This stands that aliphatic hydrocarbons with cyclic structure, analogous to imidazolium structure, reveal better solubility than linear alkanes (*similia similibus solvuntur*). Moreover the molar volume of cycloalkanes ($1.089 \cdot 10^{-4}$ $m^3 \cdot mol^{-1}$ for cyclohexane)[40] is smaller than that for linear alkanes ($1.314 \cdot 10^{-4}$ $m^3 \cdot mol^{-1}$ for *n*-hexane);[40] therefore, the

Table 1. Experimental Binary Liquid−Liquid Equilibria for Systems {Ionic Liquid (1) + Hydrocarbon (2)}

x_1	T/K	x_1	T/K	x_1	T/K
		[emim][SCN] + *n*-hexane			
0.9962	298.7	0.9946	335.4	0.9929	340.6
0.9958	324.1				
		[emim][SCN] + *n*-heptane			
0.9993	307.5	0.9974	336.4	0.9957	350.3
0.9988	313.3	0.9965	345.0	0.9942	358.6
		[emim][SCN] + cyclohexane			
0.9898	300.7	0.9834	331.6	0.9774	353.8
0.9876	311.8	0.9804	346.4		
0.9856	319.7	0.9788	350.4		
		[emim][SCN] + benzene			
0.5453	289.5	0.5634	312.3	0.5861	348.8
0.5488	294.6	0.5709	322.2	0.5888	353.2
0.5539	300.0	0.5752	328.2		
0.5585	306.3	0.5833	343.5		
		[emim][SCN] + toluene			
0.7793	296.0	0.7834	329.6	0.7844	342.5
0.7811	312.9				
		[emim][TFA] + *n*-hexane			
0.9894	297.8	0.9809	320.5	0.9713	341.1
0.9854	306.3	0.9754	335.7		
		[emim][TFA] + *n*-heptane			
0.9885	321.3	0.9842	344.2	0.9786	360.3
0.9860	334.1	0.9808	353.9		
0.9850	340.3	0.9798	358.1		
		[emim][TFA] + cyclohexane			
0.9646	305.1	0.9525	328.9	0.9410	353.7
0.9597	314.6	0.9476	340.4		
0.9552	324.3	0.9440	349.2		
		[emim][TFA] + benzene			
0.4863	286.1	0.4841	323.2	0.4803	353.2
0.4856	305.7	0.4822	338.8		
		[emim][TFA] + toluene			
0.6693	298.3	0.6655	331.7	0.6612	355.4
0.6678	317.7	0.6621	352.8	0.6564	366.5
		[emim][CF_3SO_3] + *n*-hexane			
0.9842	304.1	0.9772	321.5	0.9673	338.5
0.9822	310.3	0.9746	326.5	0.9646	341.4
0.9798	316.7	0.9716	331.4		
		[emim][CF_3SO_3] + *n*-heptane			
0.9924	298.2	0.9877	325.6	0.9787	356.2
0.9903	309.2	0.9843	337.2	0.9739	367.2
0.9891	316.2	0.9816	345.7		
		[emim][CF_3SO_3] + cyclohexane			
0.9685	295.8	0.9606	317.7	0.9494	340.4
0.9649	306.5	0.9558	328.7	0.9433	352.0

Table 1. Continued

x_1	T/K	x_1	T/K	x_1	T/K
		[emim][CF$_3$SO$_3$] + benzene			
0.4106	289.2	0.4264	311.3	0.4349	348.2
0.4194	298.7	0.4316	324.2		
0.4230	304.7	0.4329	332.2		
		[emim][CF$_3$SO$_3$] + toluene			
0.6231	283.4	0.6294	292.6	0.6417	356.5
0.6250	286.0	0.6312	295.8		
0.6268	288.9	0.6332	299.6		

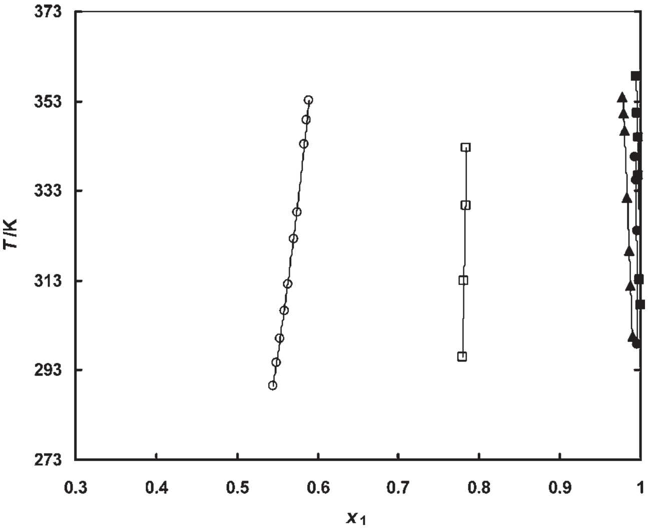


Figure 1. Liquid−liquid phase equilibria of {[emim][SCN] (1) + hydrocarbon (2)} binary systems: ●, *n*-hexane; ■, *n*-heptane; ▲, cyclohexane; ○, benzene; □, toluene. Solid lines are drawn to guide the eye with use of the polynomial regression.

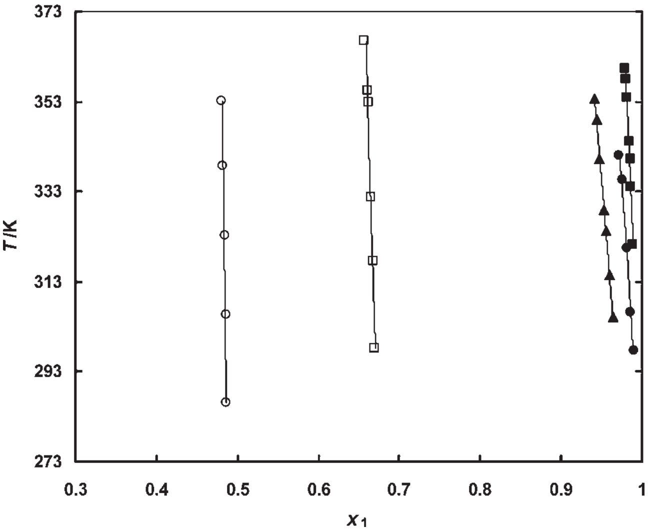


Figure 2. Liquid−liquid phase equilibria of {[emim][TFA] (1) + hydrocarbon (2)} binary systems: ●, *n*-hexane; ■, *n*-heptane; ▲, cyclohexane; ○, benzene; □, toluene. Solid lines are drawn to guide the eye with use of the polynomial regression.

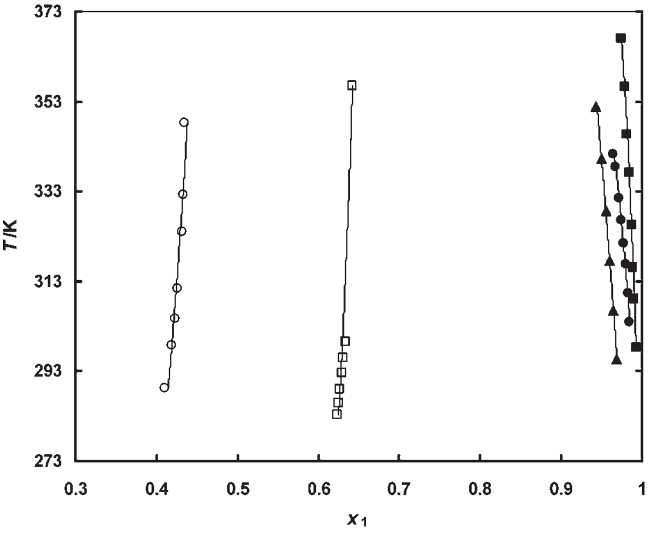


Figure 3. Liquid−liquid phase equilibria of {[emim][CF$_3$SO$_3$] (1) + hydrocarbon (2)} binary systems: ●, *n*-hexane; ■, *n*-heptane; ▲, cyclohexane; ○, benzene; □, toluene. Solid lines are drawn to guide the eye with use of the polynomial regression.

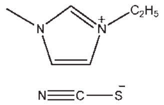
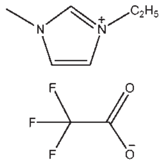
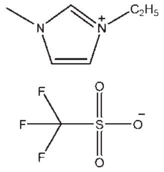
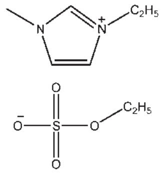
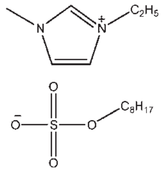
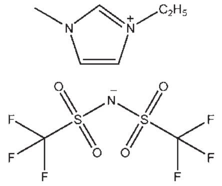
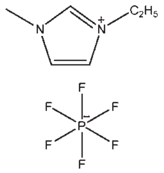
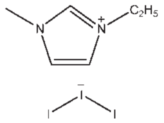
packing effect additionally increases solubility. Benzene and toluene, due to aromatic nature, exhibit much better solubility in ionic liquids than aliphatic hydrocarbons. Strong interaction between six π-delocalized electrons in the aromatic structure with the polar ionic liquids causes better solubility. The solubility is lower for toluene than for benzene because of the presence of a methyl group in the toluene structure. More aliphatic character of toluene reduces the solubility in ionic liquids. This trend is consistent with other ionic liquid-aromatic hydrocarbon binary systems.[9,11,21]

A different trend, namely, a decrease of solubility with an increase of the temperature, is observed for four systems ([emim][SCN] or [emim][CF$_3$SO$_3$]) + (benzene or toluene). This behavior is not typical but several analogous LLE diagrams for ionic liquid + aromatic hydrocarbon system can be found in the literature, namely, [bmim][SCN], [hmim][SCN] + benzene, toluene and ethylbenzene;[41,42] [emim][NTf$_2$] + benzene and α-methylstyrene;[19] [1,3bmPY][CF$_3$SO$_3$], [bmPYR][CF$_3$SO$_3$], [bmim][CF$_3$SO$_3$] + benzene and toluene.[37]

Figures 4 to 8 show the influence of an ionic liquid anion structure on the hydrocarbons solubility. On the basis of LLE diagrams for systems containing an ionic liquid based on [emim]$^+$ cation and alkane the following order of solubility for anions is observed (Figures 4 to 6): [OcSO$_4$]$^-$[20] > [PF$_6$]$^-$[22] > [NTf$_2$]$^-$[15,17] >[CF$_3$SO$_3$]$^-$≈[TFA]$^-$>[EtSO$_4$]$^-$[9,12] >[SCN]$^-$. It is obvious that solubility of an alkane is better in ionic liquid with more aliphatic cation, therefore [OcSO$_4$]$^-$ anion has higher ability to dissolve aliphatic hydrocarbons than the [EtSO$_4$]$^-$ one. The difference in solubility of alkanes and cyclohexane is small in case of trifluoromethanesulfonate (CF$_3$-SO$_3$$^-$) and trifluoroacetate (CF$_3$-CO$_2$$^-$) anions. In this case the difference in structure does not influence substantially on solubility. Except interactions between aliphatic groups in anion structure (if present) the van der Waals interaction and packing effects play the key role on solubility of aliphatic hydrocarbons.

For systems containing an ionic liquid based on [emim]$^+$ cation and benzene the following order of solubility for anions is observed

Table 2. Abbreviations, Names, and Structures of Investigated Ionic Liquids

abbreviation	name	structure
[emim][SCN]	1-ethyl-3-methyl-imidazolium thiocyanate	
[emim][TFA]	1-ethyl-3-methyl-imidazolium trifluoroacetate	
[emim][CF_3SO_3]	1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate	
[emim][$EtSO_4$]	1-ethyl-3-methyl-imidazolium ethyl sulfate	
[emim][$OcSO_4$]	1-ethyl-3-methyl-imidazolium octyl sulfate	
[emim][NTf_2]	1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-amide	
[emim][PF_6]	1-ethyl-3-methyl-imidazolium hexafluorophosphate	
[emim][I_3]	1-ethyl-3-methyl-imidazolium triiodide	

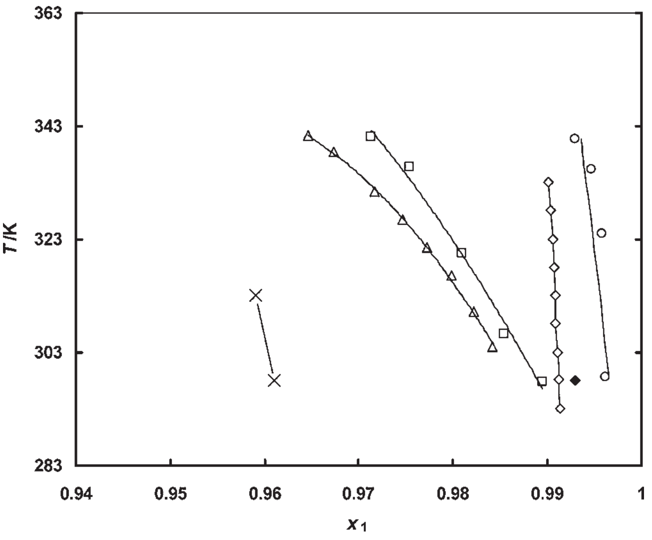


Figure 4. Liquid–liquid phase equilibria of {ionic liquid (1) + *n*-hexane (2)} binary systems: ○, [emim][SCN]; □, [emim][TFA]; Δ, [emim][CF_3SO_3]; ◇, [emim][$EtSO_4$];[9] ♦, [emim][$EtSO_4$];[13] ×, [emim][NTf_2].[17] Solid lines are drawn to guide the eye with use of the polynomial regression.

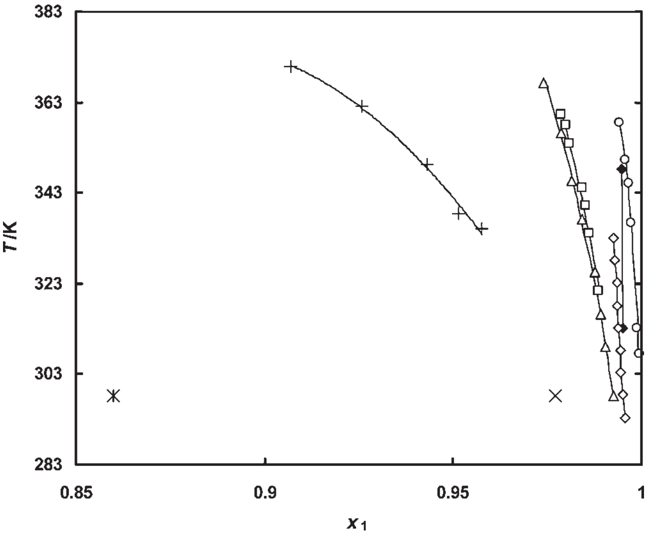


Figure 5. Liquid–liquid phase equilibria of {ionic liquid (1) + *n*-heptane (2)} binary systems: ○, [emim][SCN]; □ [emim][TFA]; Δ, [emim][CF_3SO_3]; ◇, [emim][$EtSO_4$];[9] ♦, [emim][$EtSO_4$];[9] ×, [emim][NTf_2];[15] +, [emim][PF_6];[22] ⋇, [emim][$OcSO_4$].[20] Solid lines are drawn to guide the eye with use of the polynomial regression.

(Figure 7): $[\mathrm{OcSO_4}]^{-20}$>$[\mathrm{NTf_2}]^{-16,17,19}$>$[\mathrm{CF_3SO_3}]^{-}$>$[\mathrm{PF_6}]^{-21}$> $[\mathrm{TFA}]^{-}$ > $[\mathrm{SCN}]^{-}$ > $[\mathrm{EtSO_4}]^{-}$.[9] This order is true only at temperatures below 312 K. Because of different types of LLE diagrams the temperature plays important role for solubility. Above the temperature of about 312 K solubility of benzene is better for [emim][$EtSO_4$] ionic liquid than that for [emim][SCN], and above the temperature of about 344 K solubility of benzene is better for [emim][PF_6] than for [emim][CF_3SO_3]. Interactions of polarizable delocalized bonds in an aromatic hydrocarbon with polar structure of an ionic liquid anion play key role on solubility, apart from van der Waals interactions and packing effects. The strong interactions were observed in system [emim][NTf_2] + benzene, where the congruent melting compound is formed.[43] With an increase of the temperature the interactions in $[\mathrm{NTf_2}]^{-}$, $[\mathrm{CF_3SO_3}]^{-}$, and $[\mathrm{SCN}]^{-}$ anions become weaker giving in result lower solubility. For systems containing an ionic liquid based on $[\mathrm{emim}]^{+}$ cation and toluene the following order of solubility for anions is observed (Figure 8): $[\mathrm{I_3}]^{-23}$>$[\mathrm{NTf_2}]^{-15,18}$>$[\mathrm{CF_3SO_3}]^{-}$> $[\mathrm{PF_6}]^{-21}$≈ $[\mathrm{EtSO_4}]^{-9,11,14}$ > $[\mathrm{TFA}]^{-}$ > $[\mathrm{SCN}]^{-}$ at temperatures below about 350 K and $[\mathrm{I_3}]^{-23}$ > $[\mathrm{NTf_2}]^{-15,18}$ > $[\mathrm{PF_6}]^{-21}$ ≈ $[\mathrm{EtSO_4}]^{-9,11,14}$ > $[\mathrm{CF_3SO_3}]^{-}$ > $[\mathrm{TFA}]^{-}$ > $[\mathrm{SCN}]^{-}$ at temperatures above 350 K. In this case stronger interactions between toluene and $[\mathrm{EtSO_4}]^{-}$ anion is observed than that for benzene.

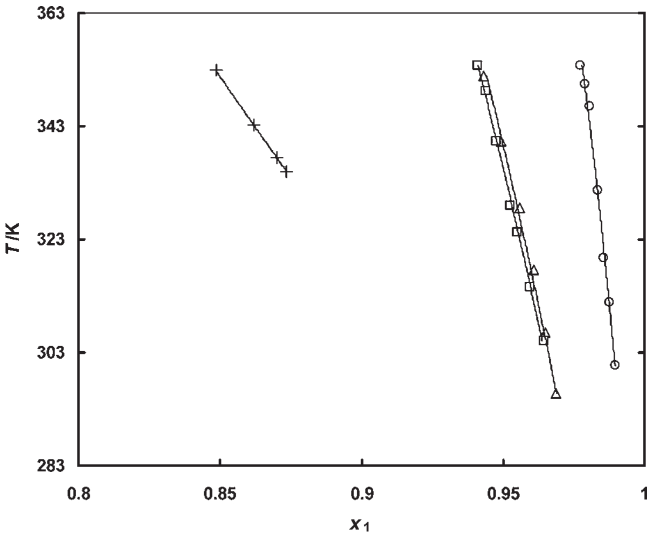


Figure 6. Liquid−liquid phase equilibria of {an ionic liquid (1) + cyclohexane (2)} binary systems: ○, [emim][SCN]; □, [emim][TFA]; Δ, $[emim][CF_3SO_3]$; +, $[emim][PF_6]$.[22] Solid lines are drawn to guide the eye with use of the polynomial regression.

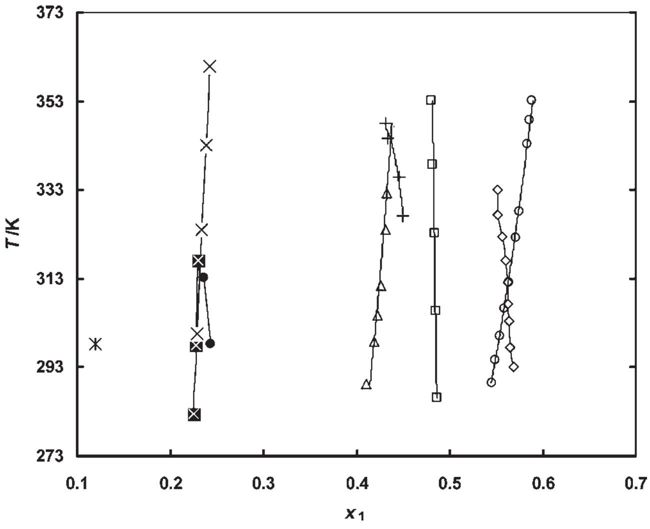


Figure 7. Liquid−liquid phase equilibria of {an ionic liquid (1) + benzene (2)} binary systems: ○, [emim][SCN]; □, [emim][TFA]; Δ, $[emim][CF_3SO_3]$; ◇, $[emim][EtSO_4]$;[9] ×, $[emim][NTf_2]$;[19] × in ■, $[emim][NTf_2]$;[16] ●, $[emim][NTf_2]$;[17] +, $[emim][PF_6]$;[21] ⋇, $[emim][OcSO_4]$.[20] Solid lines are drawn to guide the eye with use of the polynomial regression.

The more aliphatic character of toluene causes better solubility in $[EtSO_4]^-$ anion based ionic liquid where the aliphatic ethyl group is present.

Results obtained from LLE measurements are consistent with those from activity coefficients at infinite dilution. At given temperature, 323.15 K, γ^{∞} take following order for *n*-hexane: $[NTf_2]^-$ (24.2)<$[CF_3SO_3]^-$ (64.0)≈$[TFA]^-$ (68.8) < $[SCN]^-$ (254); benzene: $[NTf_2]^-$ (1.21) < $[CF_3SO_3]^-$ (2.24) < $[TFA]^-$ (2.76) < $[EtSO_4]^-$ (2.84) < $[SCN]^-$ (3.48); toluene: $[NTf_2]^-$ (1.81)< $[CF_3SO_3]^-$ (3.60) < $[TFA]^-$ (4.42)< $[EtSO_4]^-$ (5.60) < $[SCN]^-$ (6.08).[2] The lower values of activity coefficients at infinite dilution the better solubility.

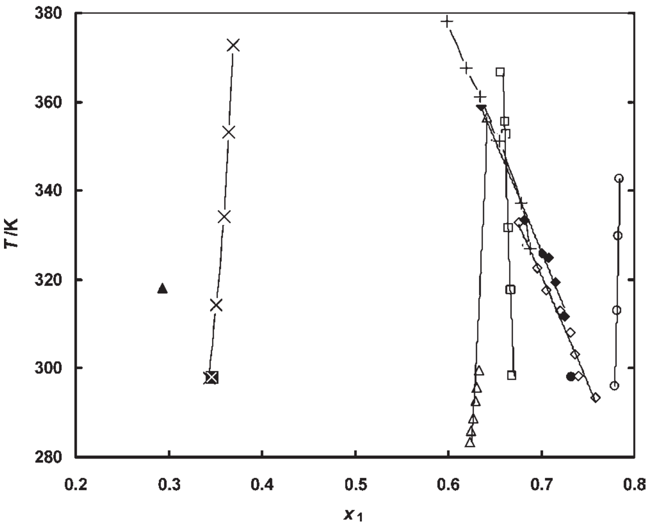


Figure 8. Liquid−liquid phase equilibria of {an ionic liquid (1) + toluene (2)} binary systems: ○, [emim][SCN]; □, [emim][TFA]; Δ, $[emim][CF_3SO_3]$; ◇, $[emim][EtSO_4]$;[9] ♦, $[emim][EtSO_4]$;[11] ●, $[emim][EtSO_4]$;[14] ×, $[emim][NTf_2]$;[18] × in ■, $[emim][NTf_2]$;[15] +, $[emim][PF_6]$;[21] ▲, $[emim][I_3]$.[23] Solid lines are drawn to guide the eye with use of the polynomial regression.

CONCLUSIONS

The knowledge of the impact of anion structure on the liquid phase behavior of ionic liquids with hydrocarbons is useful for developing ionic liquids as "designer solvents" for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures. The solubility of aliphatic hydrocarbons is the lowest for [emim][SCN] ionic liquid. Ionic liquids with anions containing long alkyl chains in structure have better ability of solubility of aliphatic hydrocarbons as well as aromatic ones.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Figure 1S, the schematic diagram of LLE apparatus. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Author would like to thank to Warsaw University of Technology.

REFERENCES

(1) Wauquier, J. P. *Petroleum Refining, Vol. 2, Separation Processes*; Editions Technip: Paris, 1995.

(2) Marciniak, A. Influence of cation and anion structure of the ionic liquid on extraction processes based on activity coefficients at infinite dilution. A review. *Fluid Phase Equilib.* **2010**, *294*, 213–233.

(3) Crosthwaite, J. M.; Muldoon, M. J.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid phase behavior of ionic liquids with alcohols: Experimental studies and modeling. *J. Phys. Chem. B* **2006**, *110*, 9354–9361.

(4) Holbrey, J. D.; López-Martin, I.; Rothenberg, G.; Seddon, K. R.; Silvero, G.; Zheng, X. Desulfurisation of oils using ionic liquids:

Selection of cationic and anionic components to enhance extraction efficiency. *Green Chem.* **2008**, *10*, 87–92.

(5) Alonso, L.; Arce, A.; Francisco, M.; Rodríguez, O.; Soto, A. Gasoline desulfurization using extraction with [C$_8$mim][BF$_4$] ionic liquid. *AIChE J.* **2007**, *53*, 3108–3115.

(6) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Solvent extraction of thiophene from *n*-alkanes (C$_7$, C$_{12}$, and C$_{16}$) using the ionic liquid [C$_8$mim][BF$_4$]. *J. Chem. Thermodyn.* **2008**, *40*, 966–972.

(7) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. (Liquid + liquid) equilibria of [C$_8$mim][NTf$_2$] ionic liquid with a sulfur-component and hydrocarbons. *J. Chem. Thermodyn.* **2008**, *40*, 265–270.

(8) Esser, J.; Wasserscheid, P.; Jess, A. Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chem.* **2004**, *6*, 316–322.

(9) García, J.; Torrecilla, J. S.; Fernández, A.; Oliet, M.; Rodríguez, F. (Liquid + liquid) equilibria in the binary systems (aliphatic, or aromatic hydrocarbons + 1-ethyl-3-methylimidazolium ethylsulfate, or 1-butyl-3-methylimidazolium methylsulfate ionic liquids). *J. Chem. Thermodyn.* **2010**, *42*, 144–150.

(10) Domańska, U.; Żołek-Tryznowska, Z.; Królikowski, M. Thermodynamic phase behavior of ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 1872–1880.

(11) Domańska, U.; Laskowska, M.; Marciniak, A. Phase equilibria of (1-ethyl-3-methylimidazolium ethylsulfate + hydrocarbon, + ketone, and + ether) binary systems. *J. Chem. Eng. Data* **2008**, *53*, 498–502.

(12) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary liquid−liquid equilibria for mixtures of toluene + n-heptane + an ionic liquid. *Fluid Phase Equilib.* **2006**, *247*, 158–168.

(13) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Thiophene separation from aliphatic hydrocarbons using the 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. *Fluid Phase Equilib.* **2008**, *270*, 97–102.

(14) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Liquid-liquid equilibria of ([C$_2$mim][EtSO$_4$] + thiophene + 2,2,4-trimethylpentane) and ([C$_2$mim][EtSO$_4$] + thiophene + toluene): Experimental data and correlation. *J. Solution Chem.* **2008**, *37*, 1355–1363.

(15) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. 1-Ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide as solvent for the separation of aromatic and aliphatic hydrocarbons by liquid extraction - Extension to C$_7$- and C$_8$-fractions. *Green Chem.* **2008**, *10*, 1294–1300.

(16) Yokozeki, A.; Shiflett, M. B. Binary and ternary phase diagrams of benzene, hexafluorobenzene, and ionic liquid [emim][Tf$_2$N] using equations of state. *Ind. Eng. Chem. Res.* **2008**, *47*, 8389–8395.

(17) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of aromatic hydrocarbons from alkanes using the ionic liquid 1-ethyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}amide. *Green Chem.* **2007**, *9*, 70–74.

(18) Shiflett, M. B.; Niehaus, A. M. S. Liquid−liquid equilibria in binary mixtures containing substituted benzenes with ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2010**, *55*, 346–353.

(19) Łachwa, J.; Szydłowski, J.; Makowska, A.; Seddon, K. R.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide and arenes. *Green Chem.* **2006**, *8*, 262–267.

(20) Deenadayalu, N.; Ngcongo, K. C.; Letcher, T. M.; Ramjugernath, D. Liquid-liquid equilibria for ternary mixtures (an ionic liquid + benzene + heptane or hexadecane) at T = 298.2 K and atmospheric pressure. *J. Chem. Eng. Data* **2006**, *51*, 988–991.

(21) Domańska, U.; Marciniak, A. Solubility of 1-alkyl-3-methylimidazolium hexafluorophosphate in hydrocarbons. *J. Chem. Eng. Data* **2003**, *48*, 451–456.

(22) Domańska, U.; Marciniak, A.; Bogel-Łukasik, R. Phase equilibria (SLE, LLE) of *N*,*N*-dialkylimidazolium hexafluorophosphate or chloride. *ACS Symp. Ser.* **2005**, *901*, 256–269.

(23) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841–845.

(24) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of activity coefficients at infinite dilution in ionic liquids using the dilutor technique. *J. Chem. Eng. Data* **2002**, *47*, 1411–1417.

(25) Foco, G. M.; Bottini, S. B.; Quezada, N.; de la Fuente, J. C.; Peters, C. J. Activity coefficients at infinite dilution in 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids. *J. Chem. Eng. Data* **2006**, *51*, 1088–1091.

(26) Ge, M.-L.; Wang, L.-S.; Wu, J.-S.; Zhou, Q. Activity coefficients at infinite dilution of organic solutes in 1-ethyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2008**, *53*, 1970–1974.

(27) Sumartschenkowa, I. A.; Verevkin, S. P.; Vasiltsova, T. V.; Bich, E.; Heintz, A.; Shevelyova, M. P.; Kabo, G. J. Experimental study of thermodynamic properties of mixtures containing ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate using gas-liquid chromatography and transpiration method. *J. Chem. Eng. Data* **2006**, *51*, 2138–2144.

(28) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic properties of mixtures containing ionic liquids. 2. Activity coefficients at infinite dilution of hydrocarbons and polar solutes in 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide and in 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide using gas-liquid chromatography. *J. Chem. Eng. Data* **2002**, *47*, 894–899.

(29) Deenadayalu, N.; Letcher, T. M.; Reddy, P. Determination of activity coefficients at infinite dilution of polar and nonpolar solutes in the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl) imidate using gas-liquid chromatography at the temperature 303.15 or 318.15 K. *J. Chem. Eng. Data* **2005**, *50*, 105–108.

(30) 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.

(31) Domańska, U.; Marciniak, A. Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-ethyl-3-methylimidazolium trifluoroacetate. *J. Phys. Chem. B* **2007**, *111*, 11984–11988.

(32) Mutelet, F.; Jaubert, J. N. Accurate measurements of thermodynamic properties of solutes in ionic liquids using inverse gas chromatography. *J. Chromatogr. A* **2006**, *1102*, 256–267.

(33) Olivier, E.; Letcher, T. M.; Naidoo, P.; Ramjugernath, D. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate using gas-liquid chromatography at T = (313.15, 323.15, and 333.15) K. *J. Chem. Thermodyn.* **2010**, *42*, 78–83.

(34) Sobota, M.; Dohnal, V.; Vrbka, P. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methyl-imidazolium nitrate. *J. Phys. Chem. B* **2009**, *113*, 4323–4332.

(35) Mutelet, F.; Revelli, A. L.; Jaubert, J. N.; Sprunger, L. M.; Acree, W. E., Jr.; Baker, G. A. Partition coefficients of organic compounds in new imidazolium and tetralkylammonium based ionic liquids using inverse gas chromatography. *J. Chem. Eng. Data* **2010**, *55*, 234–242.

(36) Domańska, U.; Marciniak, A. Liquid phase behaviour of 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethylsulfate with organic solvents and water. *Green Chem.* **2007**, *9*, 262–266.

(37) Marciniak, A.; Karczemna, E. Influence of cation structure on binary liquid−liquid equilibria for systems containing ionic liquids based on trifluoromethanesulfonate anion with hydrocarbons. *J. Phys. Chem. B* **2010**, *114*, 5470–5474.

(38) Domańska, U.; Królikowski, M. Phase equilibria study of the binary systems (1-butyl-3-methylimidazolium tosylate ionic liquid + water, or organic solvent). *J. Chem. Thermodyn.* **2010**, *42*, 355–362.

(39) Domańska, U.; Marciniak, A. Liquid phase behaviour of 1-hexyloxymethyl-3-methyl-imidazolium-based ionic liquids with hydrocarbons: The influence of anion. *J. Chem. Thermodyn.* **2005**, *37*, 577–585.

(40) Design Institute for Physical Properties, Sponsored by AIChE, *DIPPR Project 801*—*Full Version*; Design Institute for Physical Property Data/AIChE, 2010. http://knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1187&VerticalID=0.

(41) Domańska, U.; Laskowska, M.; Pobudkowska, A. Phase equilibria study of the binary systems (1-butyl-3-methylimidazolium thiocyanate ionic liquid + organic solvent or water). *J. Phys. Chem. B* **2009**, *113*, 6397–6404.

(42) Domańska, U.; Królikowska, M.; Arasimowicz, M. Phase equilibria of (1-hexyl-3-methylimidazolium thiocyanate + water, alcohol, or hydrocarbon) binary systems. *J. Chem. Eng. Data* **2010**, *55*, 773–777.

(43) Łachwa, J.; Bento, I.; Duarte, M. T.; Lopes, J. N. C.; Rebelo, L. P. N. Condensed phase behaviour of ionic liquid−benzene mixtures: Congruent melting of a [emim][NTf$_2$]·C$_6$H$_6$ inclusion crystal. *Chem. Commun.* **2006**, 2445–2447.