Phase equilibria of binary mixtures (ionic liquid + aromatic hydrocarbon): Effect of the structure of the components on the solubility

Emilio J. González [a], Patricia F. Requejo [b], Ángeles Domínguez [b], Eugénia A. Macedo [a],*

[a] LSRE-Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, Porto 4200-465, Portugal
[b] Advanced Separation Processes Group, Department of Chemical Engineering, University of Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

ABSTRACT

In this work, mutual solubilities of 24 binary mixtures containing ionic liquids (1-ethyl-3-methylpyridinium ethylsulfate, 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-3-methylimidazolium dicyanamide and 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide) with aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene) were determined in the range $T = (293.15–333.15)$ K and at atmospheric pressure, and the corresponding temperature-composition phase diagrams were obtained from the density of the equilibrium phases. From the experimental data, the effect of the structure of the ionic liquid and the aromatic hydrocarbon on the solubility was analyzed and discussed. The ionic liquids reported in this work show a negligible solubility in the studied aromatic hydrocarbons and the solubility of the aromatic compounds in the ionic liquids decreases in the order benzene > toluene > ethylbenzene > xylene isomers. The experimental results show that solubility is also affected by the ionic liquid structure while the temperature has a very little effect on the phase equilibria. Finally, experimental liquid–liquid equilibrium data were satisfactorily correlated using the Non-Random Two-Liquid (NRTL) model.

© 2013 Published by Elsevier B.V.

1. Introduction

In the last decade, the study of ionic liquids (ILs) as replacements for traditional organic solvents and their application in extraction processes has grown considerably [1–6]. One of the most studied processes is the liquid extraction of aromatic hydrocarbons from aliphatic compounds using ILs as solvents, as it is shown by the large number of articles cited in a recent review published by Meindersma et al. [3]. This trend is mainly due to the specific properties of the ILs, especially their non-volatile nature and easy recovery, making the global process easier and cheaper.

In order to apply ILs as potential solvents in the extraction of aromatic compounds, the knowledge of mutual solubility of binary mixtures (ionic liquid + aromatic hydrocarbon) has a crucial importance. Moreover, this information is also necessary to design any process involving ILs on an industrial scale. As shown by Ferreira et al. [7] in a recent article, a large database of experimental LLE data of several ILs with a broad range of hydrocarbons

was already reported. Most of these data refer to mixtures containing imidazolium-based ILs [8–21], while only few publications on phase behavior of binary mixtures with aromatic hydrocarbons and ILs based on other cations (such as ammonium, phosphonium, pyridinium, pyrrolidinium, or isoquinolinium) were found in the literature [22–28].

Taking into account the large number of (ionic liquid + aromatic hydrocarbon) potential mixtures, new solubility studies are always necessary. In this study, liquid–liquid equilibria (LLE) data of 24 new binary mixtures (ionic liquid + aromatic hydrocarbon) are reported at $T = (293.15–333.15)$ K and atmospheric pressure. Aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene) were mixed with several ILs (1-ethyl-3-methylpyridinium ethylsulfate, 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-3-methylimidazolium dicyanamide and 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide), and the composition of the two-phase equilibrium mixtures was determined by measuring the density.

The experimental LLE data obtained in this work and other results found in the literature for other ILs [9,13,16,19,21] were used to analyze and discuss the effect of the ionic liquid structure

* Corresponding author. Tel.: +351 225081653; fax: +351 225081674.
E-mail address: eamacedo@fe.up.pt (E.A. Macedo).

and aromatic hydrocarbon on the solubility. Finally, experimental liquid–liquid equilibrium data were satisfactorily correlated using the Non-Random Two-Liquid (NRTL) model [29].

To our knowledge, no measurements of LLE data for the binary mixtures studied in this work were previously published.

2. Experimental

2.1. Chemicals

Benzene, toluene, ethylbenzene, and xylene isomers were purchased from a commercial supplier, degassed ultrasonically and dried over molecular sieves of 4×10^{-8} cm, supplied by *Aldrich*. Then, they were kept in bottles under inert atmosphere (using argon gas) without further treatment.

All the ILs used in this work were supplied by *Iolitec GmbH* (Germany) with a high purity, except the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate, [EMpy][ESO$_4$], which was synthesized and purified in our laboratory following the procedure previously published [30]. Its purity was checked by nuclear magnetic resonance (NMR) spectroscopy. Prior to their use, ILs were subjected to vacuum ($p = 2 \times 10^{-1}$ Pa) and moderate temperature ($T = 343.15$ K) for several days in order to reduce moisture and any residual solvent. Then, they were also kept under argon gas.

The full name, abbreviation and purity of each component used in this work are reported in Table 1, together with the water content of the ILs. The water content of the pure ILs was determined using a Metrohm 870 KF Titrino using Titran 2, supplied by Merck, as titrant.

2.2. Apparatus and procedure

2.2.1. Density

As commented above, the determination of the composition of the two-phase equilibrium mixtures was carried out by measuring the densities and correlating these values versus the composition. Therefore, the first part of this work was to determine the calibration curves by measuring the density of miscible (ionic liquid + hydrocarbon) mixtures with known composition. Since preliminary solubility studies have shown that the solubility of the aromatic hydrocarbons in the studied ILs decreases when the temperature is increased, these calibration curves were determined at $T = 283.15$ K. For each system, several binary mixtures (sample volume: 2.5 mL) were prepared by weighing over the whole miscible composition range, and their densities were measured. Then, density and mole fraction data were fitted to polynomial expressions by least square method:

$$\rho = \sum_{p=0}^{M} A_p x_1^p \qquad (1)$$

where ρ is the density (in g cm^{-3}), x_1 is the mole fraction of the ionic liquid, A_p (in g cm^{-3}) are the adjustable parameters, and M is the polynomial degree. The corresponding fitting parameters, together with the standard relative deviation, σ, are given in Table S1, available as Supporting Information. The choice of the polynomial degree (second or third order) was based on the values obtained for the standard relative deviation, σ, which was calculated as:

$$\sigma = \left\{ \frac{\sum_{i}^{n_{dat}} ((\rho - \rho_{cal})/\rho_{cal})^2}{n_{dat}} \right\}^{1/2} \qquad (2)$$

where ρ_{cal} are the calculated density values, and n_{dat} is the number of experimental points.

The samples were prepared using a Mettler AX – 205 Delta Range balance with an uncertainty of $\pm 3 \times 10^{-4}$ g, and the density was determined using an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm 3 \times 10^{-5}$ g cm^{-3}. The densimeter has a temperature controller that keeps the samples at working temperature with an uncertainty of ± 0.01 K. In order to avoid moisture absorption by the mixtures, all the samples were prepared into a glove box which is under argon atmosphere.

2.2.2. Liquid–liquid equilibrium (LLE)

For the determination of the experimental LLE, an immiscible (ionic liquid + hydrocarbon) binary mixture was placed inside a glass cell in a glove box under argon atmosphere, and sealed using a silicon cover. The total volume of each sample was 12 mL (4 mL of ionic liquid + 8 mL of aromatic hydrocarbon). In order to ensure an intimate contact between both phases, the mixture was stirred using a magnetic stirrer for 3 h, and then it was left for at least 3 h in a thermostatic bath (PoliScience digital temperature controller, with a stability of ± 0.01 K) to ensure a complete phase separation. The temperature was controlled using a digital thermometer (ASL model F200) with an uncertainty of ± 0.01 K. Next, a sample from each phase was withdrawn using a syringe and the density of both phases was measured at $T = 283.15$ K. This procedure was repeated for each studied temperature. From density data, phase compositions were determined using the reverses of the above mentioned calibration curves (Eq. (1)). The expression and parameters of these reverse functions are reported in Table S2, available as Supporting Information.

Samples were prepared in duplicate in order to calculate the uncertainty in the determination of the composition. The obtained results show that the estimated error for the mole fraction is less than 0.005.

3. Results and discussion

3.1. Experimental data

The experimental LLE data in mole fraction for the binary mixtures (ionic liquid (1) + benzene, or toluene, or ethylbenzene (2)) and (ionic liquid (1) + o-xylene, m-xylene, or p-xylene (2)) in the ionic liquid-rich phase are shown in Tables 2 and 3, respectively. The corresponding temperature-composition phase diagrams for the studied binary systems are shown in Fig. 1.

Usually, the solubility of ILs in the aromatics is very low, in the order of 1×10^{-3} in mole fraction [7]. In this work, the studied ionic liquids were assumed as practically immiscible in all the tested aromatic hydrocarbons at the studied temperature range. Therefore, Fig. 1 only shows the compositions of the ionic liquid-rich phase. As indicated below, in order to apply the NRTL model, the solubility of the ILs in the hydrocarbon-rich phase was assumed to be $x_1^* = 0.0001$.

From Fig. 1 it is also possible to analyze the effect of the temperature on the solubility. For the mixtures reported in this work, the experimental data show that the temperature has small effect on the phase behavior. In general, a slight decrease of the solubility of the aromatic in the studied ILs with an increase of the temperature was observed at the studied temperature range, as it can be seen in Tables 2 and 3. Similar results were obtained by Marcianiak [31] studying the LLE for binary systems containing ILs based on trifluoromethanesulfonate anion with aromatics. Although this behavior is not typical, as commented by Marcianiak [31], several LLE diagrams for binary mixtures (ionic liquid + aromatic hydrocarbon) can be found in literature in which this trend is also observed [9,15,19,32].

Table 1
List of the pure components used in this work.

Component	Abbreviation	CAS no.	Supplier	Purity (% mass fraction)	Water content (ppm)
Benzene	–	71-43-2	Aldrich	≥99.9	–
Toluene	–	108-88-3	Sigma–Aldrich	99.8	–
Ethylbenzene	–	100-41-4	Sigma–Aldrich	99.8	–
o-Xylene	–	95-47-6	Fluka	≥99	–
m-Xylene	–	108-38-3	Fluka	≥99	–
p-Xylene	–	106-42-3	Fluka	≥99	–
1-Ethyl-3-methylpyridinium ethylsulfate	[EMpy][ESO$_4$]	872672-50-9	–	>98	502
1-Ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[EMpy][NTf$_2$]	841251-37-4	Iolitec	99	305
1-Hexyl-3-methylimidazolium dicyanamide	[HMim][dca]	n.a.	Iolitec	>98	1150
1-Propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[PMpy][NTf$_2$]	817575-06-7	Iolitec	99	434

n.a., not available.

Table 2
Experimental liquid–liquid equilibrium for binary mixtures (ionic liquid (1) + benzene, or toluene, or ethylbenzene (2)) at different temperatures, expressed as mole fraction of ionic liquid, x_1.

x_1	T (K)	x_1	T (K)	x_1	T (K)
[EMpy][ESO$_4$] + benzene		[EMpy][ESO$_4$] + toluene		[EMpy][ESO$_4$] + ethylbenzene	
0.408	293.15	0.645	293.15	0.806	293.15
0.412	298.15	0.649	298.15	0.804	298.15
0.412	303.15	0.649	303.15	0.805	303.15
0.418	308.15	0.652	308.15	0.807	308.15
0.423	313.15	0.652	313.15	0.805	313.15
0.424	318.15	0.656	318.15	0.807	318.15
0.432	323.15	0.660	323.15	0.808	323.15
0.439	328.15	0.660	328.15	0.808	328.15
0.437	333.15	0.657	333.15	0.806	333.15

x_1	T (K)	x_1	T (K)	x_1	T (K)
[EMpy][NTf$_2$] + benzene		[EMpy][NTf$_2$] + toluene		[EMpy][NTf$_2$] + ethylbenzene	
0.204	293.15	0.295	293.15	0.409	293.15
0.205	298.15	0.296	298.15	0.410	298.15
0.207	303.15	0.298	303.15	0.414	303.15
0.205	308.15	0.297	308.15	0.413	308.15
0.207	313.15	0.300	313.15	0.417	313.15
0.208	318.15	0.302	318.15	0.419	318.15
0.211	323.15	0.295	323.15	0.421	323.15
0.209	328.15	0.301	328.15	0.416	328.15
0.210	333.15	0.300	333.15	0.425	333.15

x_1	T (K)	x_1	T (K)	x_1	T (K)
[HMim][dca] + benzene		[HMim][dca] + toluene		[HMim][dca] + ethylbenzene	
0.230	293.15	0.354	293.15	0.494	293.15
0.231	298.15	0.358	298.15	0.496	298.15
0.228	303.15	0.366	303.15	0.494	303.15
0.230	308.15	0.356	308.15	0.502	308.15
0.233	313.15	0.363	313.15	0.503	313.15
0.240	318.15	0.374	318.15	0.511	318.15
0.243	323.15	0.378	323.15	0.511	323.15
0.245	328.15	0.374	328.15	0.507	333.15
0.242	333.15	0.370	333.15		

x_1	T (K)	x_1	T (K)	x_1	T (K)
[PMpy][NTf$_2$] + benzene		[PMpy][NTf$_2$] + toluene		[PMpy][NTf$_2$] + ethylbenzene	
0.194	293.15	0.268	293.15	0.367	293.15
0.196	298.15	0.270	298.15	0.371	298.15
0.193	303.15	0.269	303.15	0.369	303.15
0.194	308.15	0.271	308.15	0.371	308.15
0.193	313.15	0.270	313.15	0.374	313.15
0.196	318.15	0.272	318.15	0.377	318.15
0.195	323.15	0.274	323.15	0.375	323.15
0.194	328.15	0.271	328.15	0.376	328.15
0.195	333.15	0.272	333.15	0.372	333.15

Table 3
Experimental liquid–liquid equilibrium for binary mixtures (ionic liquid (1) + o-xylene, or m-xylene, or p-xylene (2)) at different temperatures, expressed as mole fraction of ionic liquid, x_1.

x_1	T (K)	x_1	T (K)	x_1	T (K)
[EMpy][ESO$_4$] + o-xylene		[EMpy][ESO$_4$] + m-xylene		[EMpy][ESO$_4$] + p-xylene	
0.755	293.15	0.812	293.15	0.811	293.15
0.755	298.15	0.811	303.15	0.810	298.15
0.761	303.15	0.813	308.15	0.813	303.15
0.763	308.15	0.812	313.15	0.811	308.15
0.763	313.15	0.816	318.15	0.815	313.15
0.762	318.15	0.821	323.15	0.814	318.15
0.766	323.15	0.821	328.15	0.815	323.15
0.768	328.15			0.816	328.15
0.766	333.15			0.815	333.15

x_1	T (K)	x_1	T (K)	x_1	T (K)
[EMpy][NTf$_2$] + o-xylene		[EMpy][NTf$_2$] + m-xylene		[EMpy][NTf$_2$] + p-xylene	
0.366	293.15	0.410	293.15	0.411	293.15
0.366	298.15	0.409	298.15	0.416	298.15
0.366	303.15	0.413	303.15	0.418	303.15
0.368	308.15	0.409	308.15	0.417	308.15
0.372	313.15	0.416	313.15	0.422	313.15
0.368	318.15	0.417	318.15	0.424	318.15
0.376	323.15	0.420	323.15	0.427	323.15
0.370	328.15	0.417	328.15	0.421	328.15
0.377	333.15			0.429	333.15

x_1	T (K)	x_1	T (K)	x_1	T (K)
[HMim][dca] + o-xylene		[HMim][dca] + m-xylene		[HMim][dca] + p-xylene	
0.453	293.15	0.500	293.15	0.508	293.15
0.458	298.15	0.507	298.15	0.513	298.15
0.451	303.15	0.503	303.15	0.517	303.15
0.460	308.15	0.512	308.15	0.515	308.15
0.467	313.15	0.509	313.15	0.516	313.15
0.472	318.15	0.502	318.15	0.523	318.15
0.469	323.15	0.503	323.15	0.524	323.15
0.471	328.15	0.511	328.15	0.520	328.15
		0.515	333.15		

x_1	T (K)	x_1	T (K)	x_1	T (K)
[PMpy][NTf$_2$] + o-xylene		[PMpy][NTf$_2$] + m-xylene		[PMpy][NTf$_2$] + p-xylene	
0.331	293.15	0.367	293.15	0.371	293.15
0.333	298.15	0.371	298.15	0.373	298.15
0.328	303.15	0.368	303.15	0.370	303.15
0.333	308.15	0.374	308.15	0.378	308.15
0.343	318.15	0.363	313.15	0.374	313.15
0.343	323.15	0.364	318.15	0.381	318.15
0.339	328.15	0.377	323.15	0.373	323.15
0.339	333.15	0.372	328.15	0.379	328.15
		0.377	333.15	0.379	333.15

3.1.1. Influence of the structure of the ionic liquid on the solubility

As it can be seen in Fig. 1, the solubility values of the aromatic hydrocarbons in the studied ILs are strongly affected by the structure of the ionic liquid, and they increase in the order: [EMpy][ESO$_4$] < [HMim][dca] < [EMpy][NTf$_2$] < [PMpy][NTf$_2$]. From this figure it is possible to analyze the effect of the ionic alkyl chain length and anion structure on the solubility values. As it can be observed, an increase of the alkyl chain length of the ionic liquid ([EMpy][NTf$_2$]/[PMpy][NTf$_2$]) leads to an increase of the solubility of the aromatic compound in the studied ionic liquid. The same effect was already observed for other binary mixtures containing ILs mixed with aromatic hydrocarbons [9,16,21]. Ferreira et al. [7] comment that the increase of the alkyl chain length leads to a lower polarity of the ionic cation which enhances interactions with the aromatic. Moreover, a longer chain increases the entropic effects that contribute to enhance the solubility, such as the asymmetry and the free volume of the ionic liquid.

The anion of the ionic liquid also has an important influence on the solubility data. The experimental LLE data for the binary mixtures containing benzene with [EMpy][NTf$_2$] and [EMpy][ESO$_4$] show that the solubility of the studied aromatic hydrocarbons in the NTf$_2$-based IL is much higher than in the ionic liquid with sulfate anion. Similar conclusions were obtained by Ferreira et al. [7] comparing binary mixtures with imidazolium-based ILs. These authors suggest that solubility increases because the polarity of the anion decreases which facilitates interactions with the aromatic hydrocarbon, although van der Waals interaction and packing effect also play a key role on the solubility, as discussed by Marciniak [31].

In Fig. 2, the experimental LLE data obtained in this work for the binary systems ([EMpy][ESO$_4$], or [[EMpy]][NTf$_2$], or [HMim][dca] (1) + benzene (2)) are compared with those found in literature for the mixtures containing the ionic liquids 1-ethyl-3-methylimidazolium bis{(trifluoromethy)lsulfonyl}amide, [EMim][NTf$_2$], or 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO$_4$], or 1-hexyl-3-methylimidazolium thiocyanate, [HMim][SCN], or 1-hexyl-3-methylimidazolium triflate, [HMim][TfO] with benzene [9,13,16,19,21]. From this figure it is possible to observe that: (i) benzene is more soluble in
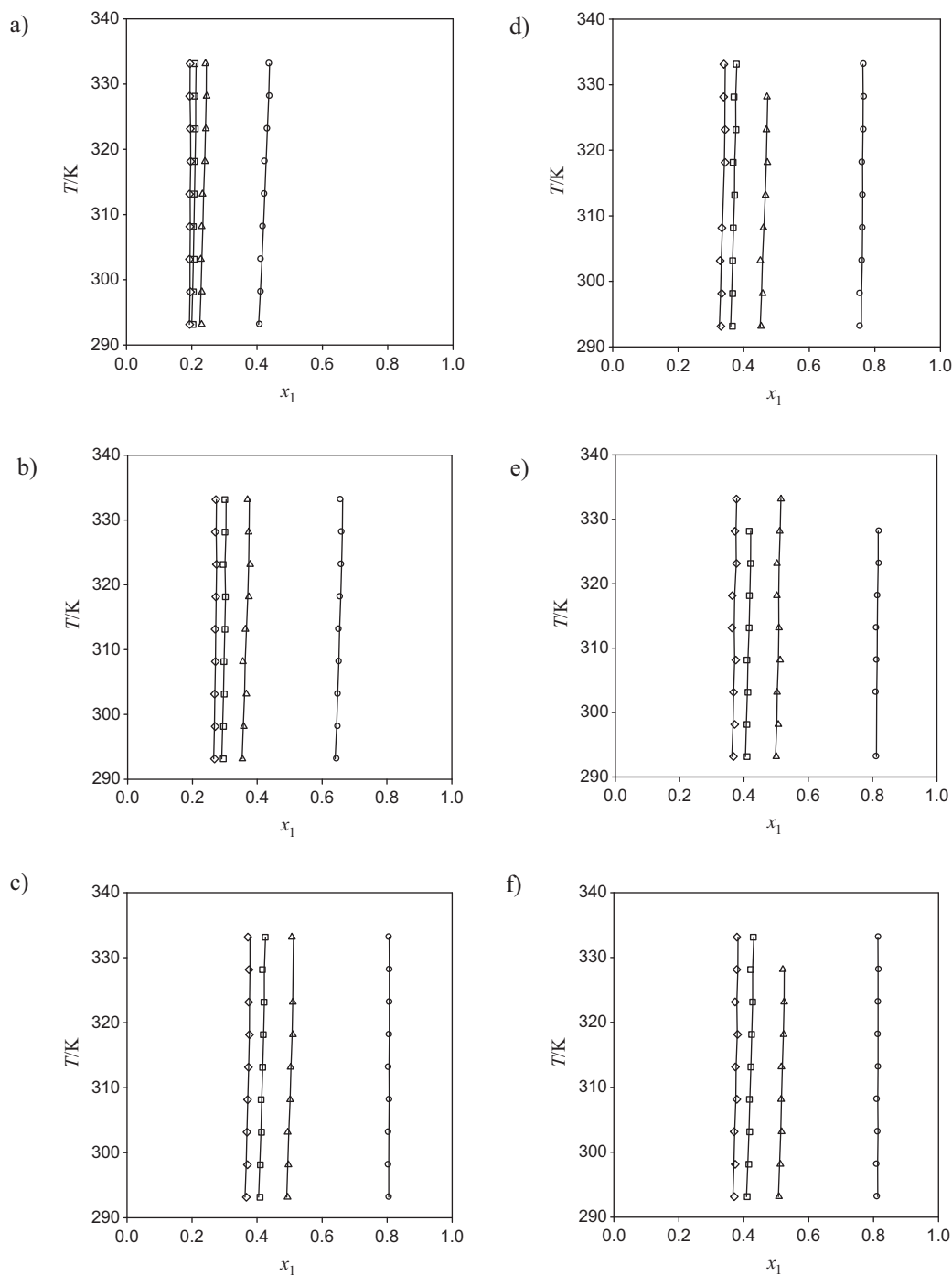
Fig. 1. Experimental LLE data of the binary systems (a) ionic liquid (1) + benzene (2); (b) ionic liquid (1) + toluene (2); (c) ionic liquid (1) + ethylbenzene (2); (d) ionic liquid (1) + o-xylene (2); (e) ionic liquid (1) + m-xylene (2); and (f) ionic liquid (1) + p-xylene (2). Lines indicate calculated data from NRTL model. Symbols: (○) [EMpy][ESO$_4$]; (□) [EMpy]][NTf$_2$]; (△) [HMim][dca] and (◇) [PMpy][NTf$_2$].

[EMim][NTf$_2$] than in [EMim][ESO$_4$], which agrees with the results above mentioned for the mixtures with pyridinium-based ILs; (ii) the solubility of benzene in pyridinium-based ILs ([EMpy][ESO$_4$] and [EMpy][NTf$_2$]) is higher than in the corresponding imidazolium-based ILs ([EMim][ESO$_4$] and [EMim][NTF$_2$]), which can be explained from the higher aromatic character of the pyridinium cation and the similar structure of this cation to the benzene structure [32]; and (iii) for the studied temperature range, the solubility of benzene in the ILs increases in the following order: [TfO]$^-$ > [dca]$^-$ > [SCN]$^-$.

3.1.2. Effect of the structure of the aromatics on the solubility

The effect of the structure of the aromatics on their solubility in ILs can be analyzed from Fig. 3, in which the experimental LLE data for the binary systems ([EMpy][NTf$_2$] (1) + benzene, or toluene, or ethylbenzene, or xylene isomers (2)) are plotted, as example. The same behavior was also observed for the other ILs reported in this work. The solubility of the aromatic compounds in the studied ILs decreases as the alkyl chain in the benzene ring increases. That is, the immiscibility gap increases in the order: benzene < toluene < ethylbenzene < xylene isomers. This
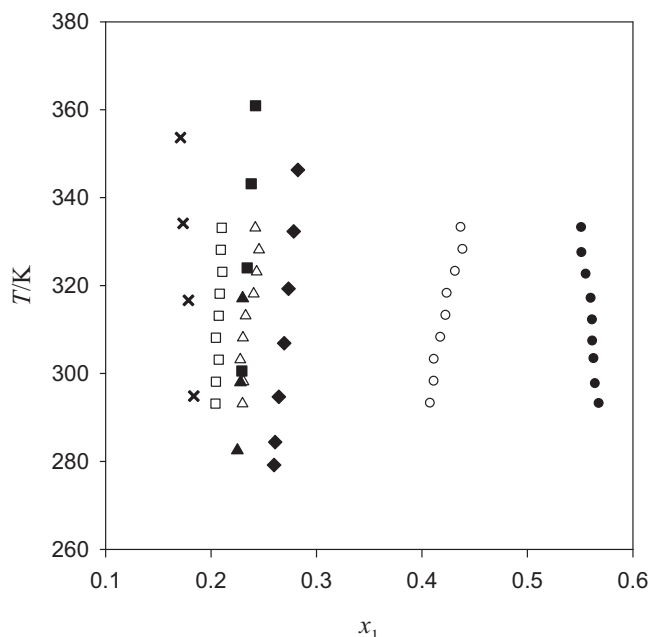
Fig. 2. Experimental LLE data of the binary systems (ionic liquid (1) + benzene (2)). Symbols: (○) [EMpy][ESO₄] (this work); (□) [EMpy]][NTf₂] (this work); (△) [HMim][dca] (this work); (■) [EMim][NTf₂] [9]; (▲) [EMim][NTf₂] [13]; (●) [EMim][ESO₄] [16]; (◆) [HMim][SCN] [19] and (×) [HMim][TfO] [21].

trend is consistent with the results obtained for other (ionic liquid + aromatic hydrocarbon) binary mixtures [12,16,18,21,31,32] confirming that, in general, compounds with a more aliphatic character (due to the presence of alkyl chains) are less soluble in ILs. Shiflett and Niehaus [18] found a trend in the miscibility with the molecular size of the aromatic hydrocarbon studying binary mixtures of aromatic hydrocarbon with [EMim][NTf₂]. These authors suggest that a smaller size allows the aromatic hydrocarbon to exist in localized cavities above and below the imidazolium ring.
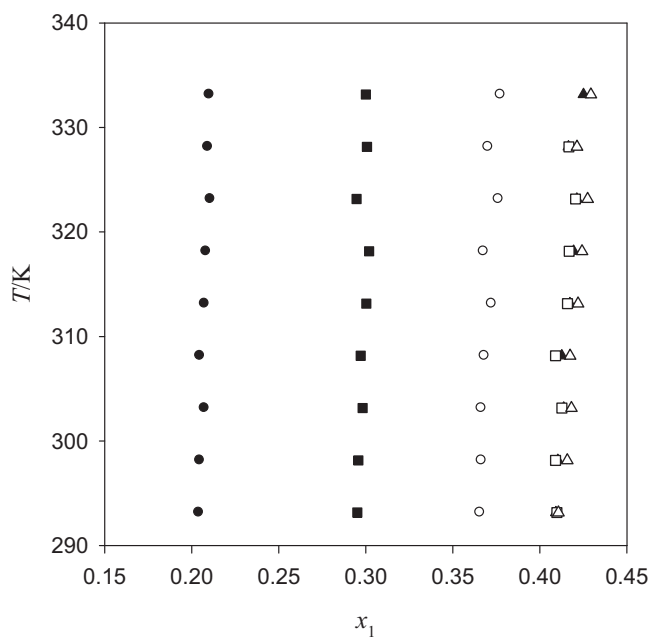

Fig. 3. Experimental LLE data of the binary systems ([EMpy][NTf₂] (1) + aromatic hydrocarbon (2)). Symbols: (●) benzene; (■) toluene; (▲) ethylbenzene; (○) o-xylene; (□) m-xylene and (△) p-xylene.

Table 4
NRTL binary interaction parameters, Δg_{12} and Δg_{21}, and root-mean-square deviations, σ_x ($\alpha = 0.2$).

System	Δg_{12} (J mol⁻¹)	Δg_{21} (J mol⁻¹)	σ_x
Benzene + [EMpy][ESO₄]	−4430.38	20,189.12	0.002
Toluene + [EMpy][ESO₄]	−1593.75	18,781.35	0.002
Ethylbenzene + [EMpy][ESO₄]	300.89	16,149.37	0.001
o-Xylene + [EMpy][ESO₄]	−319.50	15,468.95	0.003
m-Xylene + [EMpy][ESO₄]	478.68	17,072.43	0.002
p-Xylene + [EMpy][ESO₄]	392.54	15,603.77	0.002
Benzene + [EMpy][NTf₂]	−7456.20	21,193.01	0.004
Toluene + [EMpy][NTf₂]	−5768.18	18,942.54	0.004
Ethylbenzene + [EMpy][NTf₂]	−4310.34	18,096.99	0.003
o-Xylene + [EMpy][NTf₂]	−4846.13	18,312.76	0.004
m-Xylene + [EMpy][NTf₂]	−4301.89	17,943.36	0.004
p-Xylene + [EMpy][NTf₂]	−4278.31	18,229.86	0.003
Benzene + [HMim][dca]	−7087.42	21,271.57	0.003
Toluene + [HMim][dca]	−5019.96	19,103.31	0.004
Ethylbenzene + [HMim][dca]	−3326.96	17,784.36	0.003
o-Xylene + [HMim][dca]	−3814.36	18,423.92	0.003
m-Xylene + [HMim][dca]	−3194.24	16,796.20	0.004
p-Xylene + [HMim][dca]	−3142.09	17,489.61	0.003
Benzene + [PMpy][NTf₂]	−7216.44	19,924.63	0.004
Toluene + [PMpy][NTf₂]	−6034.28	18,796.65	0.004
Ethylbenzene + [PMpy][NTf₂]	−4777.66	18,067.82	0.004
o-Xylene + [PMpy][NTf₂]	−5316.21	18,832.16	0.004
m-Xylene + [PMpy][NTf₂]	−4747.07	17,800.51	0.005
p-Xylene + [PMpy][NTf₂]	−4734.34	18,017.49	0.004

Among the three xylene isomers, o-xylene showed a relatively higher solubility in the studied ILs. This result agrees with those found in literature for this kind of mixtures [16,18,32]. Shang et al. [32] suggest that the different solubility of the xylene isomers in ILs can be associated to the difference in the induced dipole moment related to their molecular structure.

3.2. Thermodynamic correlation

In this study, the experimental LLE data for the studied binary mixtures were correlated using the NRTL model to describe the excess Gibbs energy [29]. Although this model was not originally developed for systems involving electrolytes, it has been successfully used to model systems containing ILs [12,13,16,18].

The binary activity coefficients of the NRTL model are given by

$$\ln(\gamma_1) = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (3)$$

$$\ln(\gamma_2) = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (4)$$

where

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (5)$$

$$G_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (6)$$

$$\alpha_{ij} = \alpha_{21} = \alpha_{21} \quad (7)$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT} = \frac{g_{12} - g_{22}}{RT} \quad (8)$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{g_{21} - g_{11}}{RT} \quad (9)$$

where T is the temperature, α_{ij} is the non-randomness parameter, and τ_{ij} is the interaction parameter.

In this work, Δg_{12}, Δg_{21} were considered as adjustable parameters and α was set to a value of 0.2. In this case, the mole fraction

of ionic liquid in the hydrocarbon-rich phase was assumed to be $x_1^* = 0.0001$. The objective function (OF) is defined as follows:

$$OF = \sum_{i=1}^{n} [(\Delta x_1)_i^2 + (\Delta x_1^*)_i^2] \tag{10}$$

where n is the number of experimental points, the superscript '*' represent the hydrocarbon-rich phase, and Δx is defined as:

$$\Delta x = x_{calc} - x_{exp} \tag{11}$$

The root-mean-square deviation of mole fraction, σ_x was calculated using the following expression:

$$\sigma_x = \left(\frac{\sum_{i=1}^{n} \left[(\Delta x_1)_i^2 + \left(\Delta x_1^* \right)_i^2 \right]}{2n - 2} \right)^{0.5} \tag{12}$$

The adjustable parameters together with the values of the root-mean-square deviation are listed in Table 4. From the σ_x values is possible to conclude that the NRTL model fits satisfactorily the experimental LLE data. The good adjustment of this thermodynamic model can be visually confirmed from Fig. 1 where experimental and calculated data are plotted.

4. Conclusions

This work presents new experimental liquid-liquid equilibrium data for 24 binary mixtures containing ionic liquids (ILs) with aromatic hydrocarbons in the range from $T = (293.15–333.15)$ K and atmospheric pressure. From the experimental data, the following conclusions were obtained: (i) the studied ILs show a very low solubility in the aromatic hydrocarbons; (ii) the temperature has a small effect on the phase behavior of the mixtures reported in this work; (iii) an increase of the alkyl chain length of the ionic liquid leads to an increase of the solubility of the aromatic hydrocarbons in ILs; (iv) aromatic hydrocarbons are more soluble in ILs with NTf_2^- anion than in alkylsulfate-based ILs; the solubility of benzene in pyridinium-based ILs is higher than in imidazolium-based ILs; (v) the solubility of the aromatic compounds in ILs decreases in the order benzene > toluene > ethylbenzene > xylene isomers; and (vi) o-xylene is the most soluble isomer in the studied ILs.

Finally, the NRTL thermodynamic model was satisfactorily applied to correlate the experimental LLE data.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fluid.2013.09.044.

References

[1] R.D. Rogers, K.R. Seedon, S. Volkov (Eds.), Green Industrial Applications of Ionic Liquids, Kluwer Academic Publishers, The Netherlands, 2003, pp. 137–156.
[2] H. Zhao, S. Xia, P. Ma, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.
[3] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[4] B. Tang, W. Bi, M. Tian, K.H. Row, J. Chromatogr. B 904 (2012) 1–21.
[5] M.G. Freire, A.F.M. Cláudio, J.M.M. Araújo, J.A.P. Coutinho, I.M. Marucho, J.N.C. Lopes, L.P.N. Rebelo, Chem. Soc. Rev. 41 (2012) 4966–4995.
[6] A. Stojanovic, B.K. Keppler, Sep. Sci. Technol. 47 (2012) 189–203.
[7] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Ind. Eng. Chem. Res. 50 (2011) 5279–5294.
[8] U. Domanska, A. Marcianiak, J. Chem. Eng. Data 48 (2003) 451–456.
[9] J. Lachwa, J. Szydlowski, A. Makowska, K.R. Seddon, J.M.S.S. Esperança, H.J.R. Guedes, L.P.N. Rebelo, Green Chem. 8 (2006) 262–267.
[10] U. Domanska, A. Pobudkowska, F. Eckert, Green Chem. 8 (2006) 268–276.
[11] H.T. Shang, J.S. Wu, Q. Zhou, L.S. Wang, J. Chem. Eng. Data 51 (2006) 1286–1288.
[12] U. Domanska, M. Laskowska, A. Marcianiak, J. Chem. Eng. Data 53 (2008) 498–502.
[13] A. Yokozeki, M.B. Shiflett, Ind. Eng. Chem. Res. 47 (2008) 8389–8395.
[14] M. Bendová, Z. Wagner, Fluid Phase Equilib. 284 (2009) 80–85.
[15] U. Domanska, M. Laskowska, A. Pobudkowska, J. Phys. Chem. B 113 (2009) 6397–6404.
[16] J. García, J.S. Torrecilla, A. Fernández, M. Oliet, F. Rodríguez, J. Chem. Thermodyn. 42 (2010) 144–150.
[17] U. Domanska, M. Królikowska, J. Chem. Thermodyn. 42 (2010) 355–362.
[18] M.B. Shiflett, A.M.S. Niehaus, J. Chem. Eng. Data 55 (2010) 346–353.
[19] U. Domanska, M. Królikowski, M. Arasimowicz, J. Chem. Eng. Data 55 (2010) 773–777.
[20] A. Marciniak, J. Chem. Eng. Data 56 (9) (2011) 368–374.
[21] M.S. Calado, Z. Petrovski, M.S. Manic, V. Najdanovic-Visak, E.A. Macedo, Z.P. Visak, Fluid Phase Equilib. 337 (2013) 67–72.
[22] U. Domanska, A. Marciniak, M. Krolikowski, J. Phys. Chem. B 112 (2008) 1218–1225.
[23] U. Domanska, K. Paduszynski, Fluid Phase Equilib. 278 (2009) 90–96.
[24] U. Domanska, M. Krolikowski, A. Pobudkowska, J. Chem. Eng. Data 54 (2009) 1435–1441.
[25] A. Marciniak, E. Karczemna, J. Phys. Chem. B 114 (2010) 5470–5474.
[26] U. Domanska, M. Królikowski, D. Ramjugernath, T.M. Letcher, K. Tumba, J. Phys. Chem. B 114 (2010) 15011–15017.
[27] J. Dreiseitlová, K. Reháh, R. Vreekamp, J. Chem. Eng. Data 55 (2010) 3051–3054.
[28] M. Królikowski, M. Karpinska, M. Zawadzki, J. Phys. Chem. B 116 (2012) 4292–4299.
[29] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[30] E. Gómez, N. Calvar, A. Domínguez, E.A. Macedo, J. Chem. Thermodyn. 42 (2010) 1324–1329.
[31] A. Marciniak, J. Chem. Eng. Data 56 (2011) 368–374.
[32] H.-T. Shang, J.-S. Wu, Q. Zhou, L.-S. Wang, J. Chem. Eng. Data 51 (2006) 1286–1288.