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Ionic Liquids' Cation and Anion Influence on Aromatic Amine Solubility

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ABSTRACT: The mutual solubility of aniline and a series of imidazolium based ionic liquids with bis(trifluoromethylsulfonyl)-amide, chloride, dicyanamide, tetrafluoroborate, and hexafluorophosphate anions were studied. The produced results show the potential in the new solvent systems which can be used in amine chemistry. The liquid–liquid equilibrium (LLE) and solid–liquid equilibrium (SLE) measurements were performed using a dynamic (synthetic) method. The mutual solubility of aniline in bis(trifluoromethylsulfonyl)amide and hexafluorophosphate ionic liquids was complete in the examined range of temperatures. The solubility of remaining studied ionic liquids decreases with the decrease of Kamlet–Taft basicity of ionic liquid anion. In other words, the solubility was the lowest for a chloride ionic liquid and increases for dicyanamide and for tetrafluoroborate ionic liquids. Additionally, the increase of the alkyl chain length of the IL cation effects negatively the solubility of aniline in the investigated ionic liquids.

1. INTRODUCTION

Ionic liquids are chemicals that are broadly used in wide range of applications.^{1–3} Ionic liquids, together with other alternative solvents such as water and CO₂,⁴ have proven their sustainable applications in catalysis,² reactions,⁵ and separations.⁶ The continuous discovery of new ionic liquids makes them an interesting group of solvents for many applications^{7,8} especially due to their interesting solvent power^{9,10} and easily and widely tunable physicochemical properties.¹¹ Other important issue is the toxicity and biodegradability of ionic liquids.^{12,13} An often claimed disadvantage of ionic liquids is also their prices. However, the most recent achievements demonstrate that ionic liquid price can be as low as the price of classical solvents¹⁴ and still the possibility of reuse of ILs make them an excellent alternative for classical organic solvents.¹⁵ Therefore, ionic liquids as designer solvents having excellent properties and low price are an excellent medium for any reaction. Nevertheless, before any chemicals including ionic liquids can be used in the reactions their potential as solvent must be scrutinized. Thus, simple although very useful study permits the examination of the solubility of chemical compounds in ionic liquids. In particular, the knowledge about interactions existing between ionic liquids and other chemicals is exceptionally important, as it allows designing greener and more sustainable chemical processes.

One of the simplest primary aromatic amines is aniline. It is constituted by a phenyl ring and an amino group. Aniline, due to a high reactivity of the amine group present in the chemical structure, is broadly used in synthesis of various industrial products. The major application of aniline is directed to production of methylene diphenylene isocyanate which is commonly used to form polyurethanes, rubber processing chemicals, dyes and pigments, pharmaceuticals, and so on.¹⁶ Aniline is one of the chemicals produced worldwide on the

scale of megatons, and aniline consumption by 2015 is foreseen to reach 6.2 Mtons.¹⁷

This work is focused on mapping the solubility of aniline in several imidazolium based ionic liquids. The major aim of this work is to study the interactions that govern the solubility of aniline in a series of imidazolium ionic liquids. To the best of our knowledge, until now there are very scarce studies about the solubility of aniline in ionic liquids. Santos et al. examined the solubility of aniline in five bis(trifluoromethylsulfonyl)-amide based and five trifluoromethanesulfonate based ionic liquids. They discovered that aniline as a weak hydrophobic base is completely soluble in the [NTf₂] ionic liquids. Contrary to this discovery, hydrophilic [OTf] ionic liquids are rather poor solvents for aniline and solubility is strongly reliant on the alkyl chain length in the IL cation. The miscibility gap of systems containing aniline and trifluoromethanesulfonate shrinks with the decrease of the alkyl chain length of the cation.¹⁸ Other work shows that for the (ionic liquids + aromatic compounds) solutions the mutual solubility increases as the cation alkyl chain becomes longer and, compared to the [OTf], the [NTf₂] anion guarantees much better mutual solubility of the studied ionic liquids and the aromatic compounds.¹⁹ These contradictory results especially on the influence of alkyl chain length of ionic liquid cation guided the study presented in this work. In particular, the following ionic liquids were used: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [C₄mim][NTf₂], 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆], 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄], 1-butyl-3-methylimidazolium dicyanamide [C₄mim][N(CN)₂],

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1-butyl-3-methylimidazolium chloride $[\text{C}_4\text{mim}][\text{Cl}]$, 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)amide $[\text{C}_8\text{mim}][\text{NTf}_2]$, 1-methyl-3-octylimidazolium hexafluorophosphate $[\text{C}_8\text{mim}][\text{PF}_6]$, 1-methyl-3-octylimidazolium tetrafluoroborate $[\text{C}_8\text{mim}][\text{BF}_4]$, 1-methyl-3-octylimidazolium dicyanamide $[\text{C}_8\text{mim}][\text{N}(\text{CN})_2]$, 1-methyl-3-octylimidazolium chloride $[\text{C}_8\text{mim}][\text{Cl}]$. The chemical structures of all examined ionic liquids and aniline are presented in Figure 1.

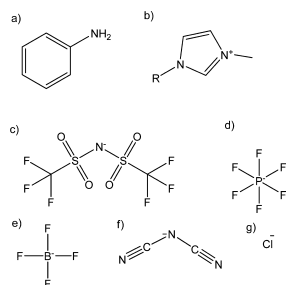


Figure 1. Chemical structure of substances studied in this work: (a) aniline; (b) 1-alkyl-3-methylimidazolium cation, where R = butyl- or octyl- (c) bis(trifluoromethylsulfonyl)amide anion; (d) hexafluorophosphate; (e) tetrafluoroborate; (f) dicyanamide; (g) chloride.

2. EXPERIMENTAL METHODS

2.1. Materials. Aniline with the stated purity of ≥ 99.5 mass % was purchased from Sigma-Aldrich. All used ionic liquids were bought from Iolitec, Germany, with the stated purity ≥ 99 mass %. All ionic liquids were degassed, dried, and freed from residues of volatile compounds by applying a vacuum 0.1 Pa at moderate temperature of 60 °C. All the drying techniques were carried out for 48 h prior to the preparation of new solutions. The mass fraction of water remaining in the dried samples was analyzed by the coulometric Karl Fischer titration and showed the following amount of water in the pure compounds: $[\text{C}_4\text{mim}][\text{NTf}_2] = 1.1 \times 10^{-4}$, $[\text{C}_4\text{mim}][\text{PF}_6] = 0.9 \times 10^{-4}$, $[\text{C}_4\text{mim}][\text{BF}_4] = 2.3 \times 10^{-4}$, $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2] = 2.1 \times 10^{-4}$, $[\text{C}_4\text{mim}][\text{Cl}] = 3.9 \times 10^{-4}$, $[\text{C}_8\text{mim}][\text{NTf}_2] = 1.2 \times 10^{-4}$, $[\text{C}_8\text{mim}][\text{PF}_6] = 1.1 \times 10^{-4}$, $[\text{C}_8\text{mim}][\text{BF}_4] = 2.2 \times 10^{-4}$, $[\text{C}_8\text{mim}][\text{N}(\text{CN})_2] = 2.0 \times 10^{-4}$, $[\text{C}_8\text{mim}][\text{Cl}] = 3.7 \times 10^{-4}$.

2.2. Experimental Procedure. A detailed description of experimental procedure utilized in this work was presented previously.²⁰ The solid–liquid equilibrium (SLE) and liquid–

liquid equilibrium (LLE) of studied systems were obtained at pressure of 0.1 MPa and a temperature ranging from 271.01 to 418.10 K using a dynamic (synthetic) method. The Pyrex glass cell equipped with stirring bar was used to perform experiments. The long capillary neck allowed to introduce samples by syringe and at the same time diminishes losses of aniline due to evaporation. The solution compositions were measured gravimetrically, using with a Mettler AT201 analytical semi-microbalance with a stated accuracy (repeatability) of $\pm 2 \times 10^{-5}$ in mass fraction. The experiments were carried out in cell deeply immersed in a temperature-controlled bath. The mixture of solute and solvent was heated very slowly (at less 2 K h⁻¹ near the equilibrium temperature) with continuous stirring inside the Pyrex glass cell, placed in a thermostatic bath with acetone (260–278 K) water, (278–333 K), or silicon (333–423 K). The cloud point for LLE and last crystal disappearance for SLE were detected visually and temperature was measured by a calibrated DOSTMANN electronic P600 thermometer equipped in a Pt 100 probe totally immersed in the thermostatic liquid. The uncertainty of the temperature measurements was ± 0.03 K and mole fraction composition was ± 0.0005 .

3. RESULTS AND DISCUSSION

The (liquid + liquid) phase diagrams for aniline in series of 1-butyl-3-methylimidazolium and 1-methyl-3-octylimidazolium ionic liquids have been measured by a dynamic method in the range of temperature from 271.01 to 418.10 K. The obtained data are reported in Tables 1 and 2 and are also presented in Figures 2 and 3, respectively. The SLE phase envelope for system $[\text{C}_4\text{mim}][\text{Cl}]$ + aniline has been determined using the analogous method in the temperature range from 284.05 K to melting point of IL (341.94 K).²¹ The SLE and LLE diagram for this system is depicted in Figure 4.

The examined systems with studied $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$, $[\text{C}_4\text{mim}][\text{Cl}]$, $[\text{C}_8\text{mim}][\text{BF}_4]$, $[\text{C}_8\text{mim}][\text{N}(\text{CN})_2]$ and $[\text{C}_8\text{mim}][\text{Cl}]$ ionic liquids and aniline are described by the classical liquid–liquid phase envelopes with the upper critical solution temperature (UCST) in the range of the studied temperatures. The T – x projection of these binary phase diagrams depicts characteristic tilt toward low ionic liquid mole fraction. The asymmetry versus the equimolar composition was observed for obtained LLE phase envelopes. Such an

Table 1. Experimental (Solid + Liquid) or (Liquid + Liquid) Equilibrium Temperatures T and Liquid Mole Fractions x for the System Ionic Liquid (1) and Aniline (2) at Pressure $p = 0.1$ MPa^a

$[\text{C}_4\text{mim}][\text{BF}_4]$ (1)		$[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (1)		$[\text{C}_4\text{mim}][\text{Cl}]$ (1)					
				+ aniline (2)					
x_1	T/K	x_1	T/K	x_1^{LLE}	T/K	x_1^{SLE}	T/K	x_1^{SLE}	T/K
0.2099	311.73	0.1513	291.19	0.1135	295.16	0.0000 ^b	266.85	0.7018	284.05
0.2411	331.51	0.1745	318.15	0.1309	329.76	0.1135	284.09	0.7135	286.12
0.2894	341.48	0.1839	332.54	0.1379	354.12	0.1309	284.03	0.7319	292.87
0.3489	340.94	0.2157	378.29	0.1618	396.82	0.1379	284.11	0.7498	301.19
0.4101	329.65	0.2546	411.47	0.1910	417.08	0.1618	284.03	0.7623	308.10
0.4499	313.68	0.4715	410.00	0.5815	418.10	0.1910	284.07	0.8122	323.87
0.4975	285.79	0.5212	374.74	0.6155	381.35	0.5815	284.03	0.8815	337.19
		0.5739	331.29	0.6572	341.84	0.6155	284.01	0.9365	340.12
		0.6315	284.15	0.6915	290.14	0.6572	284.09	1.0000 ^c	341.94
						0.6915	284.03		

^aStandard uncertainties u are $u(T) = 0.03$ K, $u_r(p) = 0.005$ MPa, $u_r(x) = 0.0005$. ^b16. ^c21.

Table 2. Experimental (Liquid + Liquid) Equilibrium Temperatures T and Liquid Mole Fractions x for the System Ionic Liquid (1) and Aniline (2) at Pressure $p = 0.1$ MPa^a

[C ₈ mim][BF ₄] (1)		[C ₈ mim][N(CN) ₂] (1)		[C ₈ mim][Cl] (1)	
		+ aniline (2)			
x_1	T/K	x_1	T/K	x_1	T/K
0.0770	301.23	0.0500	292.19	0.0175	295.12
0.0891	338.15	0.0579	328.01	0.0203	331.29
0.0941	351.56	0.0612	341.01	0.0214	344.42
0.1064	374.39	0.0692	363.16	0.0242	366.79
0.1194	390.67	0.0776	378.95	0.0272	382.74
0.1260	406.94	0.0819	394.73	0.0287	398.68
0.6210	398.55	0.0900	404.90	0.0315	408.95
0.6543	374.95	0.7452	394.56	0.8097	409.51
0.6815	342.48	0.7851	371.20	0.8636	374.91
0.6995	326.12	0.8178	342.10	0.8996	345.52
0.7123	314.01	0.8393	322.86	0.9233	326.09
0.7214	294.10	0.8548	310.87	0.9403	313.98
0.7350	276.74	0.8657	291.16	0.9522	288.07
		0.8820	273.97	0.9702	271.01

^aStandard uncertainties u are $u(T) = 0.03$ K, $u(p) = 0.005$ MPa, $u(x) = 0.0005$.

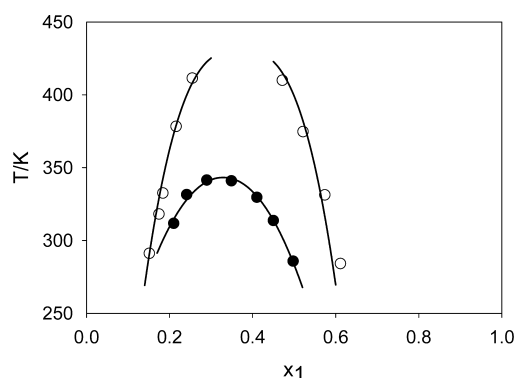


Figure 2. Liquid–liquid phase equilibria of systems consisting of (○) [C₄mim][BF₄] or (●) [C₄mim][N(CN)₂] (1) + aniline (2). Points represent the experimental results and solid lines have been obtained using the scaling equations.

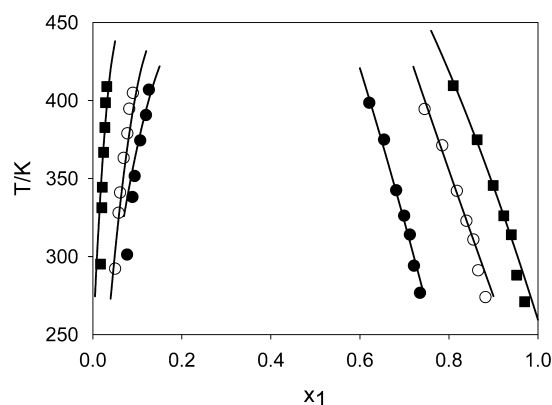


Figure 3. Liquid–liquid phase equilibria of systems consisting of (○) [C₈mim][BF₄], (●) [C₈mim][N(CN)₂], or (■) [C₈mim][Cl] (1) + aniline (2). Points represent the experimental results and solid lines have been obtained using the scaling equations.

asymmetry is caused by a much higher molar volume of the ionic liquids in comparison to aniline.^{18,19}

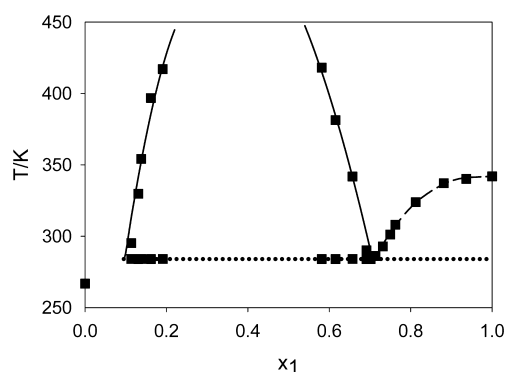


Figure 4. Phase equilibria of systems containing [C₄mim][Cl] (1) + aniline (2). Points represent the experimental results, and solid lines have been obtained using the scaling equations. The dashed line was designated by NRTL correlation equation. The dotted line depicts the phase transition between phases represented by crystals of ionic liquid + liquid saturated with crystals of ionic liquid (below dotted line) and two liquids (above dotted line but in the range of miscibility gap).

The systems with less basic anions such as bis-(trifluoromethylsulfonyl)amide and hexafluorophosphate exhibit complete miscibility with aniline. The basic ionic liquids with [BF₄], [N(CN)₂], and [Cl] anions reveal the miscibility gap that depends on the anion as well as on the alkyl chain in the IL cation. For the studied ionic liquids, the miscibility gap decreases in the following order: [C₈mim][Cl] > [C₈mim][N(CN)₂] > [C₈mim][BF₄] > [C₄mim][Cl] > [C₄mim][N(CN)₂] > [C₄mim][BF₄].

The difference in solubility has an origin in the hydrophilicity/hydrophobicity as well as in the basicity of ionic liquid. The basicity of IL governs the solubility showing that more basic ionic liquid demonstrate larger miscibility gap with aniline. According to so-called empirical solvent polarity Kamlet–Taft scale,²² the IL basicity is described by β parameter that is almost solely dependent on the anion of IL. The values of β parameter for examined ionic liquids are as follows: [C₄mim][Cl] = 0.96,²³ [C₄mim][N(CN)₂] = 0.708,²⁴ [C₄mim][BF₄] = 0.376,²⁵ [C₄mim][NTf₂] = 0.243,²⁵ [C₄mim][PF₆] = 0.207.²⁵ These data clearly confirm the observed trend and prove that basicity of ionic liquid is a key factor driving the solubility of weak base ($pK_a = 4.6$)¹⁶ such as aniline.

Other important characteristic of the studied system is the increase of the miscibility gap with the increase of the alkyl chain size in the imidazolium cation. This can be explained by the chemical interactions established in the studied systems. Ionic liquids with more acidic proton in C-2 position especially in basic conditions formed by aniline²⁶ are able to form much easier “carbene solution”²⁷ enhancing the hydrogen bond formation between weak base such as aniline and more acidic [C₄mim] ionic liquids. For comparison, the hydrogen bond acidity described as α Kamlet–Taft parameter²⁸ of [C₄mim]-[Cl] is at the level of 0.41²³ while for [C₈mim][Cl] this value is only 0.33.²³ Therefore, larger miscibility gap in case of ionic liquids with longer alkyl chain is an effect of lower acidity that lowers the potential to create carbene solution reducing effectively the solubility of weak aromatic base such as aniline. Similar conclusions were drawn for other aromatic compounds, e.g. benzene.^{29,30} It is worth stressing that aniline is benzene derived amine (phenylamine); thus, the solubility of aniline should exhibit a similar tendency to that of benzene. In general,

Table 3. Critical Parameter for Scaling Equation (Critical Composition x_c , Critical Temperature T_c , Critical Amplitude A , Critical Exponent δ , and Root-Mean-Square Deviation σ)

system	x_c		T_c/K		A		δ	
	value	σ	value	σ	value	σ	value	σ
[C ₄ mim][BF ₄] + aniline	0.3292	0.0034	343.24	2.68	0.398	0.054	0.485	0.072
[C ₄ mim][N(CN) ₂] + aniline	0.3701	0.0036	430.65	2.18	0.324	0.061	0.350	0.016
[C ₄ mim][Cl] + aniline	0.3834	0.0033	508.76	3.97	0.509	0.0945	0.557	0.053
[C ₈ mim][BF ₄] + aniline	0.3795	0.0042	573.55	5.12	0.597	0.069	0.753	0.028
[C ₈ mim][N(CN) ₂] + aniline	0.4213	0.0056	708.90	10.47	0.837	0.092	1.141	0.048
[C ₈ mim][Cl] + aniline	0.4349	0.0091	565.36	6.44	0.814	0.068	0.595	0.099

the solubility of benzene decreases with the increase of the alkyl chain length in the ionic liquid cation. Hence, the reported trend for nicotine in the literature¹⁹ must be an effect of temperature reversible reaction of carbene–nicotine ylid formation in the presence of base as it was also reported for many other carbenes as well.³¹ In addition, the increase of temperature promotes reversible reaction; thus, the cloud point observation does not demonstrate any significant differences between freshly prepared solution of nicotine–ionic liquid and the previously examined one. Furthermore, Calado et al.¹⁹ discusses the NMR results of ylid of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate) carbene and nicotine complex while de facto the work shows the NMR of ylid of 1-ethyl-3-methylimidazolium methanesulfonate carbene–nicotine.¹⁹

The upper critical solution temperature (UCST) has been determined experimentally in the case of a system constituted by [C₄mim][BF₄] + aniline. The UCST was detected at $x_c = 0.3292$ and $T_c = 343.29$ K. For the remaining systems, the UCST was out of the detection limit either due to too high or too low critical temperature.

The liquid + liquid phase equilibrium for systems ionic liquid + aniline have been correlated using the scaling-type equation:³² $|x - x_c| = A[1 - T/T_c]^\delta$. The critical parameters (A and δ) provide the characteristic data for a specific system as that can be used to characterize and compare systems between each other or can indicate as a factor of the process. The critical parameters were determined using solver add-in to the Office work package to minimize a root-mean-square deviation of temperature and are presented in Table 3.

The solid + liquid phase equilibrium for system [C₄mim][Cl] + aniline has been correlated using the following equation: $-\ln x_1 = (\Delta_{\text{fus}}H_1/R)[(1/T_1) - (1/T_{\text{fus},1})] - (\Delta_{\text{fus}}C_{p1}/R)[\ln(T_1/T_{\text{fus},1}) + (T_{\text{fus},1}/T_1) - 1] + \ln \gamma_1$, where x_1 , γ_1 , $\Delta_{\text{fus}}H_1$, $\Delta_{\text{fus}}C_{p1}$, $T_{\text{fus},1}$, and T_1 stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and liquid at the melting temperature, and melting temperature of the solute and equilibrium temperature, respectively. In this study, the method was used to derive the solute activity coefficients γ_1 from the so-called correlation equation NRTL equation³³ which describes the Gibbs excess energy (G^E). The two adjustable parameters of equations were found by an optimization technique using Rosenbrock's maximum likelihood method of minimization described by the equation: $\Omega = \sum_{i=1}^n [T_i^{\text{exp}} - T_i^{\text{cal}}(x_{1i}, P_1, P_2)]^2$, where Ω is the objective function, n is the number of experimental points, and T_i^{exp} and T_i^{cal} denote respectively experimental and calculated equilibrium temperature corresponding to the concentration. The terms x_1 , P_1 , and P_2 are model parameters resulting from the minimization procedure.

The pure component parameters r (volume parameter) and q (surface parameter) in the NRTL equation were obtained by means of the following simple relationships:³⁴ $r_i = 0.029281V_m$; $q_i = ((Z - 2)r_i/Z) + (2(1 - l_i)/Z)$, where V_m is the molar volume of pure compound i at 298.15 K. The molar volume of solute V_{m1} (298.15 K) was calculated by the group contribution method³⁵ and was assumed to be 186.7 cm³ mol⁻¹, while for the solvent, it was 94.1 cm³ mol⁻¹. The enthalpy of fusion was taken from the literature and is 14.057 kJ mol⁻¹. Values of model parameters obtained by fitting solubility curves are -2847.15 and 687.99 J mol⁻¹ for Δg_{12} and Δg_{21} , respectively. To the best of our knowledge, there are no association data for the studied drugs, thus the calculations were carried out by assuming that at 323.15 K enthalpy of association $-\Delta h_h = 21$ kJ mol⁻¹. For each solute the association constant was optimized and later has been used for optimization of the association constant for [C₄mim][Cl] + aniline was optimized. The Kretschmer–Wiebe model of association for the developing of two adjustable parameters was used.³⁶ In this work, the third nonrandomness parameter $\alpha = 0.45$ was used in calculations for different binary systems. The root-mean-square deviation of temperature equaled 1.84 K.

4. CONCLUSIONS

Data on solubilities of systems involving aniline, a primary aromatic amine, and ionic liquids constituted by imidazolium cations (1-butyl-3-methylimidazolium or 1-methyl-3-octylimidazolium) and bis(trifluoromethylsulfonyl)amide, hexafluorophosphate, tetrafluoroborate, dicyanamide, or chloride anions. The obtained data shows that less basic ionic liquids such as bis(trifluoromethylsulfonyl)amide and hexafluorophosphate are the best solvents for aniline because they are completely miscible in the range of examined temperature and full mole fraction of aniline. The most basic ionic liquids containing tetrafluoroborate, dicyanamide, or chloride are the worst solvents for examined amine and the miscibility gap is increasing with the ionic liquid basicity. Furthermore, the alkyl chain length in the ionic liquid cation plays an important role in the mutual solubility of aniline and ionic liquids. This phenomenon was explained by the ease of carbene formation²⁶ in the basic environment formed by aniline. The acidity of proton in the C2 position affects significantly the potential of carbene formation driving to much lower solubility of aniline in ionic liquids with longer alkyl chain length.

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Notes

The authors declare no competing financial interest.

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