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Phase Equilibria of an Ammonium Ionic Liquid with Organic Solvents and Water

Urszula Domańska* and Izabella Bąkała

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

Juliusz Pernak

Faculty of Chemical Technology, Poznań University of Technology, Poznań, Poland

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We report the phase diagrams of an ammonium ionic liquid: (benzyl)dimethylalkylammonium nitrate, [BA][NO_3], where the alkyl is {$C_{12}H_{25}$ ($w = 0.4$) or $C_{14}H_{29}$ ($w = 0.6$)} with alcohols (propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol); with hydrocarbons (benzene, toluene, hexane, and hexadecane); and with water. The phase equilibria were measured by a synthetic method from 220 K to the melting point of the ionic liquid or to the normal boiling temperature of the solvent. Simple eutectic systems were observed for binary mixtures of [BA][NO_3] with propan-1-ol and with butan-1-ol. The solid−liquid equilibria with immiscibility in the liquid phase for the ([BA][NO_3] + water, hexan-1-ol, octan-1-ol, decan-1-ol, benzene, toluene, hexane, or hexadecane) are described. The difference of the solubility of the ionic liquid with longer chain alcohols is significant, a simple eutectic system was observed with immiscibility in the liquid phase for low mass fraction of the solvent. The upper critical solution temperature in binary mixtures of {[BA][NO_3] + heptane or hexadecane} was limited by the boiling temperature of the solvent. For the systems evaluated, immiscibility of the liquid mixtures was observed up to a very high mass fraction of the ionic liquid.

Introduction

Ionic liquids (ILs) are a new generation of organic salts that are in the liquid state up to 373 K. They have unusual chemical and physical properties and have unique applications for catalysis and synthesis due, in part, to their extremely low vapor pressures. During the past 10 years ILs have been recognized as important novel solvents showing specific properties including high heat capacity, high density, non-flammability, high thermal stability, and extremely low volatility. ILs are in the liquid state over a wide temperature range and have a large number of possible variations in cation and anion combination.[1−7] ILs with their promising physical and chemical properties are versatile electrolytes for such diverse technologies as photoelectrical cells, batteries, and other electrochemical devices.[8] The solid−liquid and liquid−liquid phase equilibria measurements of ILs systems based on 1,3-dialkylimidazolium or ammonium cations have attracted increased attention for applications in liquid−liquid extraction.[5,9−19] Knowledge of solid−liquid equilibria is of crucial importance for the successful implementation of separation processes, especially anti-solvent crystallization. There is a pressing need to develop more advanced solvents for separation techniques, especially in the case of nonideal complexing mixtures. Numerous papers concerning the suitability of ionic liquids as entrainers for extractive distillation and as extraction solvents for liquid−liquid extraction have been published.[5,11] With increasing awareness as to how the structure of an IL affects its physical properties, it becomes possible to be able to predict which IL would be the most suitable to replace the various volatile organic solvents currently in use. ILs display enhanced selective properties when utilized in the separation of aliphatics from aromatics than do 1-methyl-2-pyrrolidinone (NMP), (NMP + water), or sulfolane.[20−25]

The majority of previous studies have focused on the solid−liquid or liquid−liquid phase behavior of ionic liquids with alcohols and the subsequent determination of their upper critical solution temperatures (UCST).

Information pertaining to ammonium ILs is not widely available despite their interesting physical properties, which make them suitable not only as green solvents but also as high-performance fluids for use in a wide range of technological applications including, wood,[26,27] paper[28] and tissue preservatives,[29] and antistatic agents.[30] Recently data comparing pyridinium ILs with imidazolium ILs[31] and comparing ammonium ILs with imidazolium ILs were published.[32] An extensive review by Hu and Xu considers the influence that the structure of an ionic liquid has upon its physiochemical properties and phase behavior.[33]

This paper is a continuation of our systematic study of the solubility of ionic liquids and includes discussion of the effects of the strong interaction of the polar anion $[NO_3]^-$ with alcohols, hydrocarbons, and water.[17,19,32,34]

In our recent work the solid−liquid equilibria (SLE) and the liquid−liquid (LLE) of many binary systems consisting of quaternary ammonium ILs with alcohols, hydrocarbons, and water were presented.[19,32,34] The experimental SLE phase diagrams investigated for the four quaternary ammonium salts (ethyl(2-hydroxyethyl)dimethylammonium bromide, C_2Br; (2-hydroxyethyl)dimethylpropylammonium bromide, C_3Br; butyl-(2-hydroxyethyl)dimethylammonium bromide, C_4Br; and hexyl-(2-hydroxyethyl)dimethylammonium bromide, C_6Br) in alcohol and in water were published previously,[19,34] and the influence of the anions BF_4^-, PF_6^-, $(CN)_2N^-$, and NTf_2^- have been discussed.[32]

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* Corresponding author. Tel: +4822-6213115. E-mail: ula@ch.pw.edu.pl.

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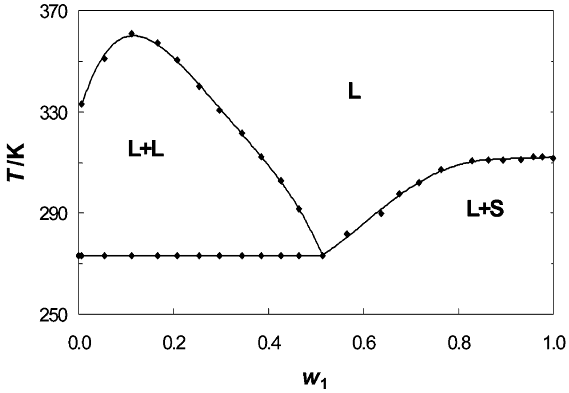


Figure 1. $T-w$ diagram for [BA][NO_3] (1) in water: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

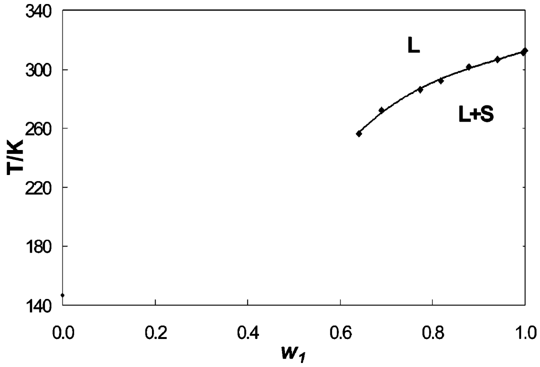


Figure 2. Liquidus curve for [BA][NO_3] (1) in propan-1-ol: ◆, experimental points; full line drawn to guide the eye; L and S, liquid and solid phase, respectively.

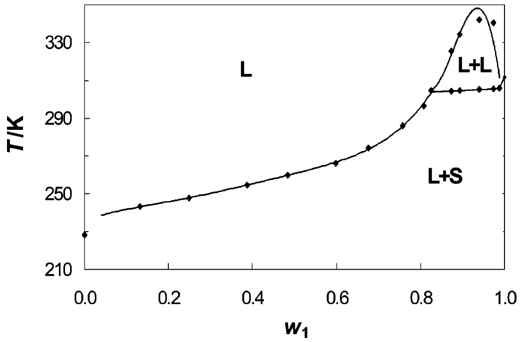


Figure 3. $T-w$ diagram for [BA][NO_3] (1) in hexan-1-ol: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

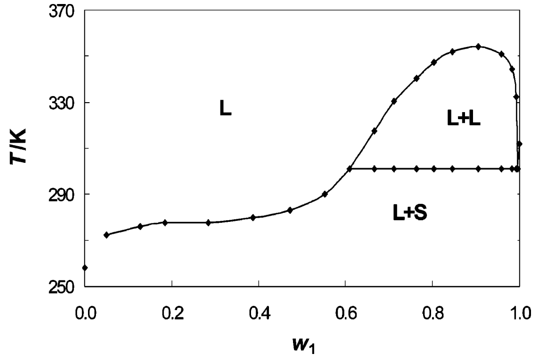


Figure 4. $T-w$ diagram for [BA][NO_3] (1) in octan-1-ol: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

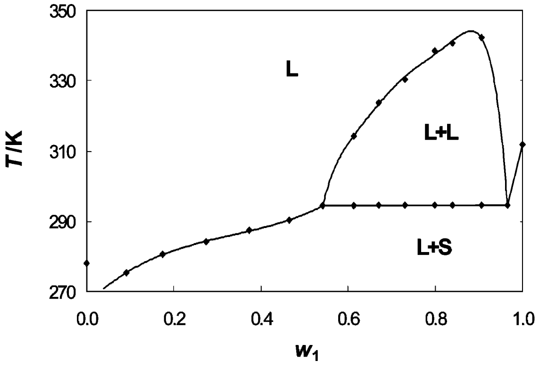


Figure 5. $T-w$ diagram for [BA][NO_3] (1) in decan-1-ol: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

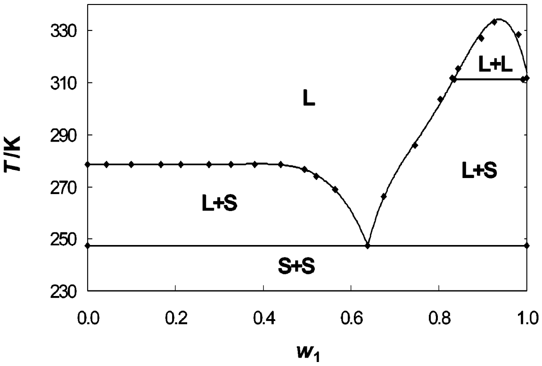


Figure 6. $T-w$ diagram for [BA][NO_3] (1) in benzene: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

Quaternary ammonium salts are well-known cationic surfactants and useful phase-transfer catalysts; these salts exhibit anti-microbial activity, anti-fungal activity, and anti-electrostatic effects.[28,29] Recently, ammonium nitrate ILs have also been assessed as to their suitability as wood preservation agents, encouraging results ensued especially for mixtures of two different ILs.[29] Anti-microbial activity of the ammonium salt, benzalkonium chloride, [BA][Cl] (which is a mixture of homologues of alkylbenzyl dimethylammonium chlorides, with alkyl groups ranging between n-C_8H_{17} and n-$C_{18}H_{37}$), has been assessed.[29] Another compound belonging to the ammonium salt group is chinoline chloride also known as vitamin B_4. It is an essential component that ensures the correct functioning of the nervous system and is used widely as a feed additive for livestock.[34]

In this work, the melting temperature, the enthalpy of fusion, and the glass transition temperature of [BA][NO_3] were determined by differential scanning calorimetry (DSC). The phase diagrams of the ammonium IL, benzalkonium nitrate [BA][NO_3], with two substituent alkyl groups, n-$C_{12}H_{25}$ and n-$C_{14}H_{29}$, combined with an alcohol (propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol); with a hydrocarbon (benzene, toluene, hexane, and hexadecane); and with water are reported. It has previously been shown that the alkyl chain has a large influence on the phase equilibria for the imidazolium, pyridynium, and ammonium salts.[4,5,17,19,30−32,34−36]

Experimental Section

Materials. Benzalkonium nitrate [BA][NO_3] was synthesized by an anion exchange reaction at room temperature in water from [BA][Cl].[27] The prepared ILs were characterized by their ^1H NMR and ^{13}C NMR spectra. ^1H NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz with

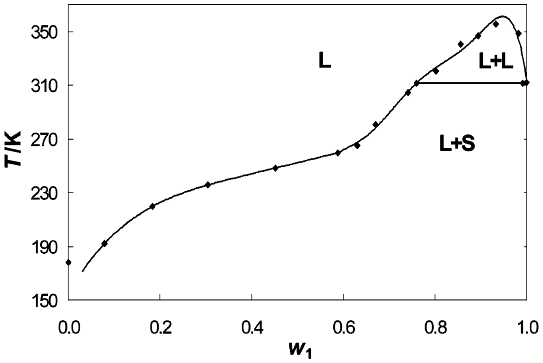


Figure 7. *T*−*w* diagram for [BA][NO_3] (1) in toluene: ◆, experimental points; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

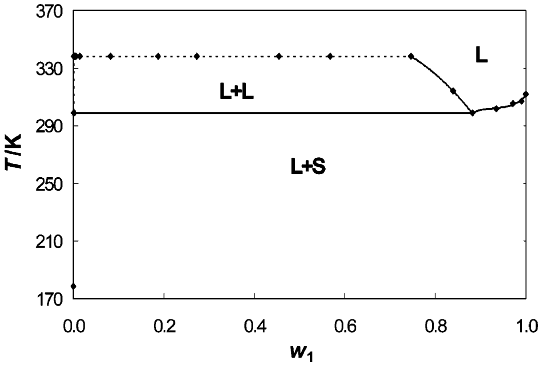


Figure 8. *T*−*w* diagram for [BA][NO_3] (1) in hexane: ◆, experimental points; full lines drawn to guide the eye; dotted line, the boiling temperature of the solvent; L and S, liquid and solid phase, respectively.

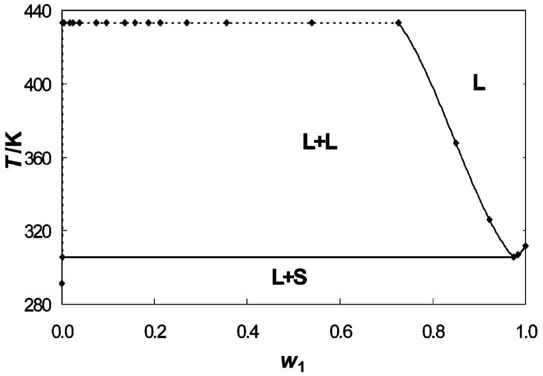


Figure 9. *T*−*w* diagram for [BA][NO_3] (1) in hexadecane: ◆, experimental points; left-facing solid triangle, points showing the maximum measured temperature; full lines drawn to guide the eye; L and S, liquid and solid phase, respectively.

tetramethylsilane as the standard. ^{13}C NMR spectra were recorded on the same instrument at 75 MHz to detect the presence of any impurities. Activated charcoal was used to remove any colored compounds from the IL, which was subsequently dried under vacuum at 290.15 K for 48 h to remove any organic solvent or water contamination. Analysis for water using the Karl Fischer technique for the solvents and for the IL showed that the mass fraction of the water content was < 0.02. All solvents were obtained from Sigma−Aldrich Chemie GmbH, Stenheim, Germany. Before direct use, they were fractionally distilled over several drying reagents to ensure a mass fraction purity ≥ 99.8 %. The solvents were stored over freshly activated molecular sieves of type 4 Å (Union Carbide).

The mixture of the two [BA][NO_3] compounds contained a 0.40 mass fraction of the substituted alkyl chain $C_{12}H_{25}$ and a 0.60 mass fraction of the substituted alkyl chain $C_{14}H_{29}$, which was analyzed by HPLC using methanol as the solvent was used in the experiment.

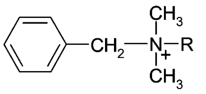
Differential Scanning Microcalorimetry (DSC). The melting temperature and the enthalpy of fusion were measured by a Perkin-Elmer Pyris 1 DSC. The measurements were carried out at a scan rate of 10 K·min^{-1} with a power sensitivity of 16 mJ·s^{-1} and with a recorder sensitivity of 5 mV. Each time the instrument was used, it was calibrated with a 99.9999 % pure indium sample. The uncertainty of the calorimetric measurements was estimated to be ± 1.5 %. The average melting temperature was (311.8 ± 1) K (lit. 309.4 K)[27] for [BA][NO_3] with alkyl groups ranging between *n*-C_8H_{17} and *n*-$C_{18}H_{37}$ as measured by the DSO technique. The repeatability of the measured melting temperature (visual method as for SLE) was ± 0.1 K. The enthalpy of melting was found to be (1.35 ± 0.02) J·g^{-1}, and the glass transition temperature was determined to be (196.1 ± 0.2) K (lit. 216.3 K).[27]

Solid−Liquid and Liquid−Liquid Equilibrium Apparatus Measurements. SLE and LLE temperatures were determined using a synthetic method previously described.[19,32,34] Appropriate mixtures of IL and solvent were placed under nitrogen in a dry box into a Pyrex glass cell. The samples were heated very slowly (less than 2 K·h^{-1} near the equilibrium temperature) with continuous stirring; the cell being contained within a glass thermostat filled with either silicone oil or water. The temperature of the liquid bath was varied slowly until the last crystals disappeared. This temperature was taken as the temperature of the SLE of the saturated solution. The crystal disappearance temperatures were detected visually. In LLE measurements, a sample of known composition was heated until one phase was obtained, the equilibrium temperature being subsequently noted. The observation of the “cloud point” with decreasing temperature proved to be exceedingly difficult. The effect of precooling and the kinetics of the phenomenon of binary phase creation were possibly responsible for the non-repeatability of the experimentally obtained cloud point. It was also problematic to detect the temperature of equilibrium because of the very high viscosity of the IL.

Temperatures were measured with an electronic thermometer of the type P 550 (DOSTMANN electronic GmbH), the probe being totally immersed in the thermostating liquid. Mixtures were prepared by mass ratio; the uncertainty in the composition was estimated to be ± 0.0005 and ± 0.1 K for mass fraction and temperature, respectively. For each system, the LLE measurements were limited at the upper temperature by the boiling point of the solvent.

Results and Discussion

The phase diagrams of new binary {ionic liquid + organic solvent or water} systems were determined. The structure of the IL is



NO_3^- R = $C_{12}H_{25}$, or $C_{14}H_{29}$

[$C_{21}H_{38}N$][NO_3](w = 0.4) + [$C_{23}H_{42}N$][NO_3](w = 0.6)

The solubility of [BA][NO_3] in alcohols (propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol); in hydrocarbons (benzene, toluene, hexane, and hexadecane); and in water was measured with the results shown in Figures 1 to 8. The solubilities of [BA][NO_3] in alcohols and water is listed in Table 1, and the solubilities in hydrocarbons is listed in Table 2. These tables include direct experimental results of the equilibrium

Table 1. Experimental SLE and LLE Temperatures for {[BA][NO_3] (1) + Water, or Propan-1-ol, or Butan-1-ol, or Hexan-1-ol, or Octan-1-ol, or Decan-1-ol (2)} Binary Systems[a]

w_1	T_1^{SLE}/K	T_1^{LLE}/K	w_1	T_1^{SLE}/K	T_1^{LLE}/K
Water					
0.0000	273.2		0.5657	281.8	
0.0059	273.2	332.9	0.6373	289.9	
0.0547	273.2	351.1	0.6756	297.5	
0.1112	273.2	360.8	0.7170	302.1	
0.1659	273.2	357.2	0.7635	307.2	
0.2075	273.2	350.4	0.8284	310.6	
0.2543	273.2	340.0	0.8638	310.8	
0.2975	273.2	330.6	0.8938	311.0	
0.3449	273.2	321.5	0.9324	311.2	
0.3845	273.2	312.2	0.9579	312.2	
0.4264	273.2	302.8	0.9773	312.2	
0.4640	273.2	291.7	0.9779	312.1	
0.5140	273.2		1.0000	311.8	
Propan-1-ol					
0.0000	146.7		0.8782	301.5	
0.6412	256.3		0.9401	306.7	
0.6896	272.2		0.9966	311.4	
0.7744	286.1		1.0000	311.8	
0.8180	292.3				
Butan-1-ol					
0.0000	183.7		0.6721	250.0	
0.1738	224.0		0.7498	266.0	
0.2142	227.7		0.9023	295.0	
0.3649	228.8		0.9652	305.0	
0.5058	232.0		0.9843	309.4	
0.5482	234.6		1.0000	311.8	
0.6072	240.4				
Hexan-1-ol					
0.0000	228.2		0.8250	304.5	304.5
0.1318	243.2		0.8730	304.2	325.5
0.2488	247.8		0.8926	304.7	334.4
0.3867	254.9		0.9392	305.2	342.1
0.4830	259.8		0.9733	305.5	340.5
0.5974	266.0		0.9874	306.0	
0.6755	274.4		0.9880	306.0	
0.7576	286.0		1.0000	311.8	
0.8074	296.5				
Octan-1-ol					
0.0000	258.2		0.7117	301.0	330.3
0.0495	272.3		0.7633	301.0	340.5
0.1279	276.1		0.8034	301.0	347.3
0.1842	277.7		0.8455	301.0	352.0
0.2844	277.8		0.9050	301.0	354.2
0.3870	279.8		0.9586	301.0	350.8
0.4721	284.8		0.9825	301.0	344.5
0.5525	290.1		0.9932	301.0	332.4
0.6089	301.0		0.9960	301.0	
0.6594	301.0	317.3	1.0000	311.8	
Decan-1-ol					
0.0000	278.2		0.6699	294.6	323.8
0.0917	275.4		0.7308	294.6	330.4
0.1744	280.6		0.8036	294.6	338.5
0.2744	284.2		0.8393	294.6	340.6
0.3730	287.4		0.9062	294.6	342.2
0.4645	290.3		0.9655	294.6	341.6
0.5417	294.4		1.0000	311.8	
0.6135	294.5	314.3			

[a] T, the equilibrium temperature; w_1, the mass fraction of IL.

Table 2. Experimental SLE and LLE Temperatures for {[BA][NO_3] (1) + Benzene, or Toluene, or Hexane, or Hexadecane (2)} Binary Systems[a]

w_1	T_1^{SLE}/K	T_1^{LLE}/K	w_1	T_1^{SLE}/K	T_1^{LLE}/K
Benzene[b]					
0.0000	278.7		0.5637	269.0	
0.0435	278.7		0.6380	247.5	
0.0989	278.7		0.6750	266.2	
0.1676	278.7		0.7463	285.9	
0.2129	278.7		0.8040	303.5	
0.2759	278.7		0.8442		315.4
0.3266	278.7		0.8966		327.0
0.3806	278.7		0.9260		333.2
0.4399	278.7		0.9817		328.3
0.4934	277.5		1.0000	311.8	
0.5212	274.1				
Toluene					
0.0000	178.2		0.7409	304.4	
0.0793	192.2		0.7660		311.8
0.1832	219.6		0.8025		320.4
0.3042	235.7		0.8569		340.5
0.4517	248.3		0.8944		346.7
0.5879	259.5		0.9335		355.3
0.6300	265.3		0.9826		348.5
0.6709	280.7		1.0000	311.8	
Hexane					
0.0000	178.9		0.4542		
0.0014			0.5674		
0.0015			0.7461		338.2
0.0037			0.8386		314.3
0.0059			0.8818	298.7	
0.0139			0.9340	302.1	
0.0828			0.9715	305.4	
0.1866			0.9906	307.0	
0.2725			1.0000	311.8	
Hexadecane					
0.0000	291.2		0.2125		
0.0009			0.2691		
0.0046			0.3557		
0.0176			0.5394		
0.0246			0.7254		433.2
0.0382			0.8500		367.6
0.0742			0.9217		326.3
0.0966			0.9743	305.6	
0.1363			0.9840	306.9	
0.1577			1.0000	311.8	
0.1869					

[a] T, the equilibrium temperature; w_1, the mass fraction of IL. [b] $T_{1,e}$ = 247.5 K; $w_{1,e}$ = 0.638.

temperatures, T_1^{SLE} or T_1^{LLE}, as a function of w_1, the mass fraction of the IL.

Figure 1 presents results of the solubility of [BA][NO_3] in water. It is a simple eutectic system with immiscibility in the liquid phase from (0.006 to 0.500) mass fraction of IL. The eutectic point of the system was not observed as it is below 273.15 K and very close to the mass fraction of water being equal to one. Water, a polar solvent, can interact with the anion [NO_3]$^-$, but the substituent of the cation (i.e., the long alkane chain) decreases the interaction between IL and the water and has an adverse influence on packing effects, resulting in immiscibility in the liquid phase. The UCST for the system {[BA][NO_3] + H_2O} was observed at a temperature, T = 360.8 K, and a mass fraction, w_1 = 0.111.

A miscibility gap was not observed for the IL with either propan-1-ol or butan-1-ol. The solubility in propan-1-ol is presented in Figure 2. The ability of a polar anion of the IL to create a hydrogen bond with an alcohol significantly increases the solubility of the IL in the alcohol. The interaction of the methylsulfate, [CH_3SO_4]$^-$, anion with alcohols is so strong that complete miscibility was observed for [BMIM][CH_3SO_4] in alcohols ranging from methanol to undecan-1-ol and with [MMIM][CH_3SO_4] in alcohols ranging from methanol to pentan-1-ol at room temperature.[37] The binary systems of [MMIM][CH_3SO_4] with alcohols from hexan-1-ol to undecan-1-ol were the only mixtures to exhibit upper critical solution temperature behavior.[37] Figures 3 to 5 present the SLE with a miscibility gap in the liquid phase for the binary systems [BA][NO_3] + hexan-1-ol, octan-1-ol, and decan-1-ol, respectively. Immiscibility is observed close to the melting point of the IL, indicating that the self-association between the alcohol molecules is stronger than the IL/alcohol association. The UCST reported here for the {IL + an alcohol} systems agree satisfactorily with results determined by other workers.[16,27,37] In general, the UCST increases with increasing carbon chain length of the alcohol, the maximum being shifted to high solvent mass fraction. It is reasonable to assume that the oxygen atoms of the anion are responsible for the stronger hydrogen bonds formed with an alcohol.

Interactions of IL with aromatic hydrocarbon solvents could result in $\pi-\pi$ interaction between two benzene rings: one from the cation of IL and the second from the solvent. The SLE and LLE for binary mixtures of [BA][NO_3] in benzene and in toluene are presented in Figures 6 and 7. These two systems show that the immiscibility in the liquid phase of the IL is lower in aromatic hydrocarbons than in long chain alcohols, thus indicating that the influence of the cation is stronger that that of the polar anion in the IL. The phase diagrams of LLE for (IL + benzene, or toluene) mixtures discussed in this work were characterized by the following: (1) in both cases miscibility gaps were observed; (2) the mutual solubility of IL decreases with an increase of the alkyl chain of the substituent on the benzene ring. A similar trend has been observed for many ILs in benzene, toluene, and propylbenzene.[17,38]

Inspection of Figures 7 and 8 shows that the solubility of IL in hexadecane is much lower than its solubility in hexane. The UCST temperature increases with an increasing number of carbon atoms on the hydrocarbon. It was noted previously that the solubility of imidazolium ILs show an increasing immiscibility in the liquid phase in the longer chain alkanes.[17,38] The results may suggest that the phenyl substituent in the cation has a much stronger influence on the interaction with solvent than does the alkane chain as immiscibility in the liquid phase is much lower for the aromatic solvents.

Conclusions

Imidazolium and ammonium based ILs are highly ordered hydrogen-bonded substances that may effect many reactions and processes. Greater interaction was observed for [BA][NO_3] with benzene than with alkanols or alkanes; we believe that this was due to a stronger interaction of the phenyl substituent of the cation with the solvent. The specific interaction of the IL with the solvent (association between the oxygen of the anion and the hydroxyl group of an alcohol) increases solubility in low molecular weight alcohols as shown in Figure 2.

ILs have the potential to be used successfully as reagents in separation processes as careful selection of cation, anion, polar, and nonpolar substituents provides an opportunity to enhance the solubility of ILs in various other liquids, hence these novel compounds should have applications in the selective separation of liquids.

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