Miscibility Phenomena in Systems Containing Polyhydroxy Alcohols and Ionic Liquids

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ABSTRACT: Ionic liquids are innovative media for applications, which offer large advantages over common chemicals, such a negligible vapor pressure, and thus, no air pollution potential, and comparative thermal stability. All these properties make them good solvents compared to the classical volatile chemicals and allow for their employment in reactions, extractions, and material processing. For this reason investigations into phase equilibria in many systems with ionic liquids are essential. This paper focuses on the liquid−liquid equilibria of twenty binary mixtures composed of the imidazolium based ionic liquids with dicyanamide ($[C_n\text{mim}][DCA]$) or bistriflamide($[C_n\text{mim}][NTf_2]$)anions and glycols, or glycerol, or butan-1-ol. In this study, the following glycols were tested: (ethylene glycol (ethane-1,2-diol); propylene glycol (propane-1,2-diol); propane-1,3-diol; butylene glycols (butane-1,2-diol; butane-1,3-diol, butane-1,4-diol; butane-2,3-diol); diethylene glycol (2,2'-oxydiethanol); dipropylene glycol (4-oxaheptane-1,7-diol). The systems containing hydrophilic dicyanamide ionic liquid exhibit complete miscibility with the studied polyhydroxy alcohols. Solutions containing bis(trifluoromethylsulfonyl)amide ionic liquids demonstrate limited solubility with the investigated butane-1,2-diol and its isomers. It was found that miscibility of $[C_n\text{mim}][NTf_2]$ with butanediols depends on the choice of the cation and the arrangement of hydroxyl groups in the alcohol structure.

■ INTRODUCTION

Ionic liquids (ILs) exhibit intriguing properties that make them a good replacement of volatile compounds in many chemical processes. ILs are characterized by negligible vapor pressure,[1] comparative thermal stability,[2] and great solvent abilities to dissolve various chemicals[3] and raw materials.[4] Their very low vapor pressure reduces the risk of exposure that is a clear advantage over the use of the classical volatile solvents. Nevertheless, it is important to underline that the basic properties in the environmental risk assessment of ILs are scarce,[5] albeit mostly ILs are touted as "green solvents".

ILs have attracted much attention and been a subject of numerous studies leading to the understanding of their physicochemical and thermodynamic properties, in particular the phase behavior.[6−11] Such knowledge is essential for the employment of ILs as solvents in liquid−liquid extraction[12] and additionally for understanding the solute−solvent interactions existing in the mixture.[6−8,12]

Among the several applications predictable for ionic liquids the most popular is their employment in chemical reactions,[13,14] homogeneous,[15] and heterogeneous[16] catalysis, and separation processes.[17,18] Since the beginning of ionic liquids, the imidazolium based ILs have been ones most studied. Studies of other ionic liquids, such as phosphonium, pyridinium, pyrazolium, ammonium, etc., are still rare.

The solubility of organic compounds in ionic liquids is an important feature, which is very often underestimated but limits employment of a certain system in a designed process. Liquid−liquid equilibria (LLE) of (ionic liquid + alcohol) solutions have called significant scientific attention over the last years. Effects of temperature, anion, both alcohol and the ionic liquid alkyl chain

length, or alcohol branching[8,10,12,17,19,20] on solubility, as well as cosolvent effects in aqueous (ionic liquid + alcohol) solutions[7,21] have been investigated broadly. However, to the best of our knowledge, studies that include ionic liquid solutions with glycols or glycerol are still scarce.[12,15,22,23] In fact, these compounds are very attractive, both from fundamental and application points of view. They possess the same similar alkyl backbone and the number or the position of their OH groups is different. They have the possibility to form both inter- and intramolecular hydrogen bonds. Driven by the aforementioned reasons, we have set up investigation focused on solubility of polyols in ionic liquids.

Polyhydroxy alcohols are compounds broadly produced in the natural processes[24] and used in chemical reactions, such as telomerization,[25] esterification,[26] etc. For example, the telomerization of ethylene glycol with butadiene performed in ionic liquids can be used to improve the product extraction to the organic phase and catalyst recycling within the aqueous phase.[27] Another example is the telomerization of nucleophile glycerol because it is cheap and versatile byproduct of biodiesel production.[25] Furthermore, the phase equilibria are the critical information for the potential extraction and separation of the products of the aforementioned and other chemical processes.

In this work, studies on the solubility of series of ionic liquids in various diols, glycerol or an alcohol are presented. The influence of aliphatic alkyl chain length in the cation of IL on the solubility of polyalcohols was investigated. The liquid−liquid equilibrium experiments were performed using the following
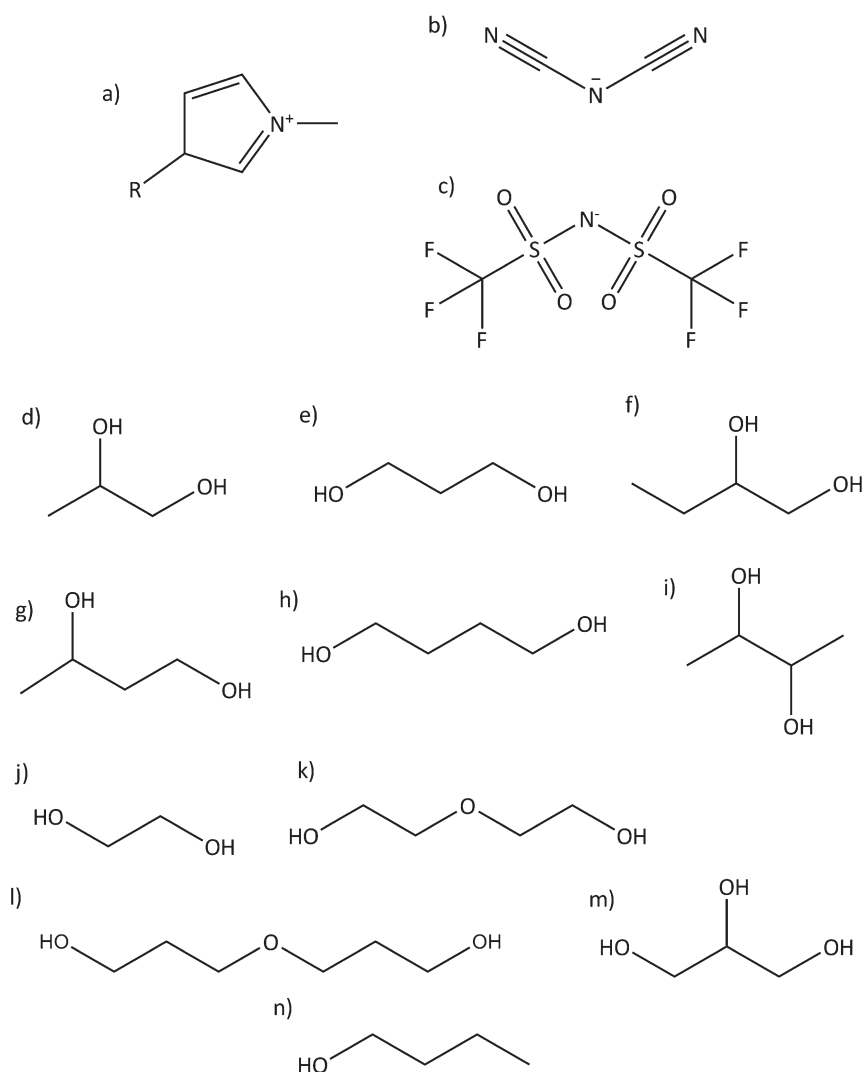
Figure 1. Structure of studied ionic liquids and polyhydroxy alcohols: (a) 1-alkyl-3-methylimidazolium cation, where R = ethyl-, butyl-, octyl-, decyl-; (b) dicyanamide anion; (c) bis(trifluoromethylsulfonyl)amide anion; (d) propane-1,2-diol; (e) propane-1,3-diol; (f) butane-1,2-diol; (g) butane-1,3-diol; (h) butane-1,4-diol; (i) butane-2,3-diol; (j) ethylene glycol; (k) diethylene glycol; (l) dipropylene glycol; (m) glycerol; (n) butan-1-ol.

ionic liquids: 1-butyl-3-methylimidazolium dicyanamide, 1-methyl-3-octylimidazolium dicyanamide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, 1-methyl-3-octylimidazolium bis-(trifluoromethylsulfonyl)amide, and 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide. Among polyhydroxy alcohols the following were tested: propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, butane-2,3-diol, ethylene glycol, diethylene glycol, dipropylene glycol, glycerol, and butan-1-ol. Structures of ionic liquids and alcohols used in this work are presented in Figure 1. The aim of this investigation was to explore the effect of structure of ionic liquids and mono- and polyhydroxy alcohols on the mutual solubility.

■ MATERIALS AND METHODS

Polyhydroxy alcohols were purchased from Sigma: propane-1,2-diol, CAS 57-55-6. 99.5 % (mass); propane-1,3-diol, CAS 504-63-2, 99.6 % (mass); butane-1,2-diol, CAS, 584-03-2, 98 % (mass); butane-1,3-diol, CAS 107-88-0, 99 % (mass); butane-1,4-diol, CAS 110-63-4, 99 % (mass); butane-2,3-diol, CAS 513-85-9, 98 % (mass); ethane-1,2-diol (ethylene glycol), CAS 107-21-1, 99 % (mass); 2,2′-oxydiethanol (diethylene glycol), CAS 111-46-6, 99 % (mass); 4-oxaheptane-1,7-diol (dipropylene glycol), CAS 25265-71-8 % to 99 % (mass); propan-1,2,3-triol (glycerol), CAS 56-81-5, 99.5 % (mass); butan-1-ol, CAS 71-36-3, 99.5 % (mass). All alcohols have been dried using molecular sieves of 3 Å. Ionic liquids $[C_n\text{mim}][NTf_2]$ (n = 2, 4, 8, 10) and $[C_n\text{mim}][DCA]$ (n = 4, 8) were obtained from Solchemar, Portugal with a stated purity of 98 % (mass). All ionic liquids were degassed, dried, and freed from residues of volatile compounds by applying a vacuum 0.1 Pa at moderate temperature, 60 °C. All the drying techniques were carried out for 48 h prior to new solutions were prepared. The mass fraction of water remaining in the dried samples were analyzed by the coulometric Karl Fischer titration and showed the following amount of water in pure compounds: $[C_2\text{mim}][NTf_2]$, 70 ppm; $[C_4\text{mim}][NTf_2]$, 50 ppm; $[C_8\text{mim}][NTf_2]$, 80 ppm; $[C_{10}\text{mim}]$-$[NTf_2]$, 40 ppm; $[C_4\text{mim}][DCA]$, 280 ppm; $[C_8\text{mim}][DCA]$, 310 ppm; propane-1,2-diol, 210 ppm; propane-1,3-diol, 250 ppm; butane-1,2-diol, 390 ppm; butane-1,3-diol, 410 ppm; butane-1,4-diol, 400 ppm; butane-2,3-diol, 390 ppm; ethylene

glycol, 320 ppm; diethylene glycol, 280 ppm; dipropylene glycol, 320 ppm; glycerol, 520 ppm; butan-1-ol, 320 ppm.

The solubilities have been determined using a dynamic (synthetic) method, described in detail previously.[7] The liquid–liquid equilibrium temperature–composition phase diagrams were obtained at an ambient pressure (0.1 MPa) and in a temperature range of 273 K to 458 K. A glass beaker of 2 L was used as a thermostat bath and was filled with ethanol (273 K to 293 K), water (293 K to 333 K), or silicon oil (333 K to 458 K) as a thermostatic liquid. A method of visual observation of the turbidity–cloud point, indicating phase separation, was used in the solubility measurements. Experiments were carried out in a Pyrex-glass cell equipped with a magnetic stirrer. The cell was possible to open and close through a Teflon valve, allowing it to remain immersed in the temperature controlled oil bath without any evaporation losses. Temperature was monitored using a Pt100 temperature probe (DOSTMANN electronic GmbH Serie P600), which had an accuracy of ±0.03 K. The uncertainty of the temperature measurements was 0.5 K. It was confirmed by the repeatability of the experimental points that was better than 0.5 K.[12] Solutions of ionic liquid and alcohol were prepared gravimetrically using a Mettler Model AT201 analytical semi microbalance with a stated accuracy of $2 \cdot 10^{-5}$ g. Depending on the composition of the sample, the mass was in the range 0.5 g to 2.5 g. The repeatability of mole fraction was better than ± 0.0005.

The two-phase solutions were heated with a constant stirrer (Bibby Scientific Ltd., Stuart SB161) until they showed a uniform/homogeneous appearance: one phase. Subsequently, the solution was cooled until becoming turbid again. The temperature at which this happened is called "cloud point". Experiments were performed in 2 runs, with the last run being performed very slowly (the rate of temperature change near the expected cloud point was no more than 5 K·h^{-1}).

■ RESULTS AND DISCUSSION

The liquid–liquid phase equilibria for the following binary systems were determined: $[C_4mim][DCA]$ + propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, butane-1,3-diol, butane-2,3-diol, butane-1,2-diol, ethylene glycol, diethylene glycol, or dipropylene glycol; $[C_8mim][DCA]$ + propane-1,3-diol, butane-1,4-diol, glycerol, or butan-1-ol; $[C_2mim][NTf_2]$ + butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, or butane-2,3-diol; $[C_4mim][NTf_2]$ + butane-1,2-diol; $[C_8mim][NTf_2]$ + butane-1,2-diol; $[C_{10}mim][NTf_2]$ + butane-1,2-diol. The systems containing hydrophilic dicyanamide ionic liquid exhibit complete miscibility with the studied polyhydroxy alcohols. The solutions containing bis(trifluoromethylsulfonyl)amide ionic liquids demonstrate limited solubility with the studied butane-1,2-diol and its structural isomers.

The T–x diagrams of systems containing bis(trifluoromethylsulfonyl)amide ionic liquids and structural isomers of butane-1,2-diol exhibit phase separation at an ambient pressure and in the range of temperature being of interest of this work are presented in Figures 2 and 3. The experimental results in the form of T–x data for each binary system are also given in Table 1.

To rationalize the data with the aim of permitting interpolation or extrapolation of the phase diagrams and approximate determination of the critical coordinates, T_c, x_c, the scaling-type equations[28–30] of the type $|x - x_c| = A[(T_c - T)/T_c]^\delta$ were applied to systems presenting limited miscibility in the investigated range of temperature. The scaling equation arises from the regular solution theory and aims description of the critical
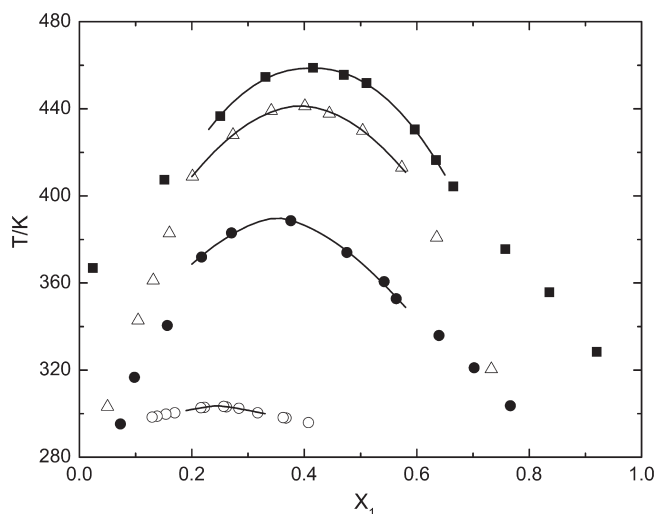

Figure 2. Phase envelope for systems containing {○, $[C_2mim][NTf_2]$; or ■, $[C_4mim][NTf_2]$; △, $[C_8mim][NTf_2]$; ●, $[C_{10}mim][NTf_2]$} (1) + butane-1,2-diol (2). The solid lines designated by the scaling equation.
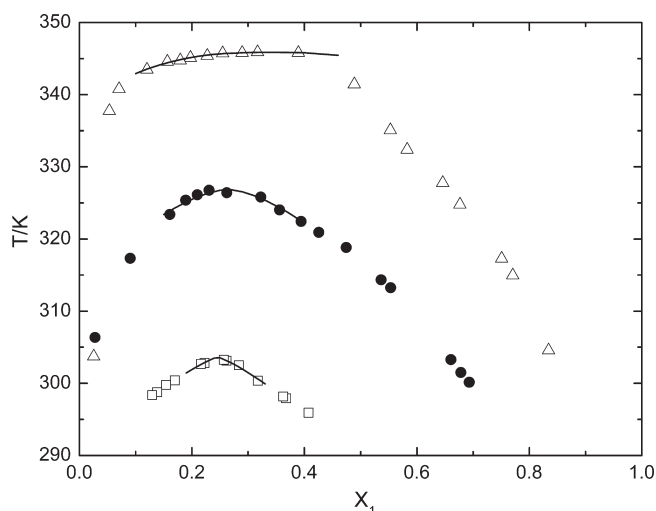
Figure 3. Liquid–liquid phase diagram for systems containing $[C_2mim][NTf_2]$ (1) + {□, butane-1,2-diol; ●, butane-1,3-diol; or △, butane-1,4-diol} (2).The solid lines designated by the scaling equation.

region,[29,31] but not of the whole T–x relation. Parameters for a nominal pressure of 0.1 MPa are reported in Table 2. 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 others or can indicate as a factor of the process, that is, degree of polymerization.[32] The systematic error that comes from the scaling equation is an arbitrary selection of the experimental point in a vicinity of the critical point. That is why in this study the experimental data close to critical region used in scaling equation were selected to minimize a standard deviation of the critical amplitude and a critical exponent; however, the relation $0 < [(T_c - T)/T_c] < 0.1$ was fulfilled. The critical parameters were determined using solver add-in to Office work package to minimize root-mean-square deviation of temperature.

The first conclusion that can be drawn from the obtained results is that the miscibility curves represent the phase diagrams with the upper critical solution temperature (UCST). It can also be seen that the T–x projection of these binary phase diagrams is

Table 1. Liquid—Liquid Equilibrium (LLE) Data for the Binary Mixtures of $[C_n\text{mim}][NTf_2]$ (n = 2, 4, 8, 10) and Butane-1,2-diol, or Butane-1,3-diol, or Butane-1,4-diol; x_1 Refers to Mole Fraction of the Ionic Liquid; T Stands for the Cloud-Point Temperature

x_1	T / K	x_1	T / K	x_1	T / K
		$[C_2\text{mim}][NTf_2]$ (1) +			
butane-1,2-diol (2)		butane-1,3-diol (2)		butane-1,4-diol (2)	
0.4074	295.91	0.6932	300.14	0.8344	304.58
0.3674	297.94	0.6785	301.51	0.7706	314.96
0.3625	298.17	0.6608	303.29	0.7509	317.30
0.3173	300.38	0.5533	313.25	0.6769	324.77
0.2837	302.50	0.5364	314.33	0.6461	327.78
0.2614	303.13	0.4744	318.84	0.5829	332.39
0.2567	303.26	0.4256	320.91	0.5530	335.09
0.2226	302.82	0.3940	322.43	0.4890	341.45
0.2161	302.70	0.3561	324.04	0.3893	345.81
0.1695	300.39	0.3226	325.81	0.3170	345.88
0.1540	299.77	0.2621	326.42	0.2894	345.80
0.1383	298.78	0.2305	326.75	0.2548	345.73
0.1292	298.36	0.2095	326.13	0.2275	345.39
		0.1891	325.36	0.1977	345.11
		0.1610	323.41	0.1793	344.77
		0.0901	317.33	0.1565	344.59
		0.0277	306.36	0.1201	343.48
				0.0706	340.79
				0.0531	337.76
				0.0253	303.73
$[C_4\text{mim}][NTf_2]$ (1) +		$[C_8\text{mim}][NTf_2]$ (1)		$[C_{10}\text{mim}][NTf_2]$ (1) +	
		+ butane-1,2-diol (2)			
0.9204	328.38	0.7326	320.39	0.7666	303.56
0.8361	355.67	0.6354	380.92	0.7021	321.05
0.7576	375.58	0.5735	413.04	0.6398	335.91
0.6649	404.36	0.5040	430.01	0.5634	352.82
0.6344	416.49	0.4447	437.92	0.5422	360.58
0.5965	430.47	0.4010	441.30	0.4756	374.01
0.5106	451.79	0.3414	439.19	0.3762	388.63
0.4704	455.60	0.2732	427.97	0.2706	382.93
0.4156	458.82	0.2011	409.03	0.2171	371.90
0.3310	454.58	0.1600	382.82	0.1565	340.49
0.2505	436.63	0.1315	361.27	0.0978	316.69
0.1513	407.46	0.1046	342.83	0.0731	295.27
0.0241	366.87	0.0499	303.19		

anion and eleven mono- and polyhydroxy alcohols exhibit complete miscibility in the examined temperature range. Such miscibility might be explained by the fact that dicyanamide ionic liquids are hydrophilic and are strong proton acceptors. The solvent polarity, thus defined, cannot be described quantitatively by single physical solvent parameters, such as dielectric constants, dipole moments, etc. The lack of comprehensive theoretical expressions for the calculation or prediction of solvent effects on chemical reactivity, and the inadequacy of defining solvent polarity in terms of simple physical solvent characteristics, have led to the introduction of so-called empirical parameters of solvent polarity.[33] One of the method describing the polarity of ionic liquids is the use of Kamlet—Taft parameters.[34−37] There are three Kamlet—Taft parameters characterizing the polarity of compounds: the hydrogen bond acidity (α), the hydrogen bond basicity (β), and the polarizability effect (π^*). Compared to conventional solvents ionic liquids have π^* generally higher and variation of their values depends on both the anion and cation.[38] The value of α is dictated largely by the nature of cation and in case of imidazolium ILs is determined by the acidity of the C-2 proton in the imidazolium ring. Contrary to α, the hydrogen bond basicity of the solvent is described by β parameter. The values for the ionic liquids are rather moderate and dominated by the nature of the anion that is illustrated in Table 3. The literature reports show that the β parameter approximates the Coulombic contribution to the hydrogen bonds formed between ILs and the solute.[38]

The aforementioned proton-accepting ability of dicyanamide anion is illustrated by hydrogen bond basicity (β). The hydrogen bond basicity for $[C_4\text{mim}][DCA]$ equals to 0.708[39] and is one of the highest among all the tested ionic liquids. The presence of a strong proton donor (alcohol) and a proton acceptor, such as dicyanamide anion, guides to the formation of a strong intermolecular net that favors the mutual miscibility of dicyanamide ionic liquids with polyhydroxy and aliphatic alcohols. On the contrary, hydrophobic bis(trifluoromethylsulfonyl)amide based ionic liquids exhibit very low tendency to form hydrogen bonds. The hydrogen bond basicity of this group of ionic liquids is placed in the lower region of values for β parameter and for example the values of β for $[C_4\text{mim}][NTf_2]$ are in the range of 0.24 to 0.25.[39,40,45,46] That is why $[NTf_2]$ ionic liquids demonstrate the tendency to form a two phase solutions in systems with strong proton donors, such as alcohols (Figure 2).[12] These two types of ionic liquids show very distinct solvent abilities toward studied mono- and polyhydroxy alcohols. Thus, the purpose of this work was to study the influence of ionic liquid and alcohol's properties on their mutual solubility.

Influence of the Imidazolium Cation of Bis(Trifluoromethylsulfonyl)Amide Ionic Liquid on the Solubility of Polyhydroxy Alcohols. The investigation into influence of the alkyl chain length of the cation of imidazolium ionic liquid was performed based on ionic liquids with bis(trifluoromethylsulfonyl)amide anion as a model compound. Phase envelopes for systems containing butane-1,2-diol and four different bis(trifluoromethylsulfonyl)amide ILs are presented in Figure 2.

The obtained results reveal that the solubility of butane-1,2-diol increases when the length of the alkyl chain in the imidazolium cation increases from $[C_4\text{mim}]$ < $[C_8\text{mim}]$ < $[C_{10}\text{mim}]$. Unexpected is the highest solubility of butane-1,2-diol in $[C_2\text{mim}][NTf_2]$ because it does not follow the presented tendency. The significant difference between the shortest, ethyl-, and longer alkyl chain length of imidazolium ionic liquids is

visibly tilted toward low mole fractions of the ionic liquid. The LLE phase envelopes of systems that exhibit mutual solubility are characterized by asymmetry versus equimolar composition. It is due to a much higher molar volumes of ionic liquids in comparison to alcohols. It is a typical behavior of systems with ionic liquids, which was reported for other systems with polyhydroxy alcohols.[8,12]

Impact of the Anion of Ionic Liquid on the Mutual Miscibility with Polyhydroxy Alcohols. The investigated systems containing imidazolium based ionic liquids with dicyanamide

Table 2. Critical Parameter for Scaling Equation[a]

	x_c		T_c/K		A		δ	
system	value	σ	value	σ	value	σ	value	σ
$[C_2mim][NTf_2]$+ butane-1,2-diol	0.2455	0.0016	303.62	0.23	2.976	1.215	0.808	0.105
$[C_4mim][NTf_2]$+butane-1,2-diol	0.4131	0.0016	458.72	0.60	0.664	0.043	0.461	0.026
$[C_8mim][NTf_2]$+butane-1,2-diol	0.3933	0.0011	441.31	0.47	0.773	0.052	0.531	0.027
$[C_{10}mim][NTf_2]$+butane-1,2-diol	0.3517	0.0040	389.88	1.71	0.916	0.187	0.617	0.086
$[C_2mim][NTf_2]$+butane-1,3-diol	0.2633	0.0046	326.86	0.37	1.916	0.858	0.622	0.112
$[C_2mim][NTf_2]$+butane-1,4-diol	0.3423	0.0273	345.86	0.062	1.411	0.377	0.370	0.073

[a] x_c, Critical composition; T_c, critical temperature; A, critical amplitudes; δ, critical exponent; σ, root-mean-square deviation.

Table 3. Literature Kamlet–Taft Parameters of the Investigated Ionic Liquids[a]

	π^*		α		β	
ionic liquid	value	ref	value	ref	value	ref
$[C_4mim][DCA]$	1.129	39	0.464	39	0.708	39
$[C_8mim][DCA]$	nd	nd	nd	nd	nd	nd
$[C_2mim][NTf_2]$	0.98	39	0.705	39	0.233	39
	0.90	43	0.76	44	0.28	44
	0.998	44	0.627	45	0.225	45
$[C_4mim][NTf_2]$	0.971	39	0.635	39	0.248	39
	0.984	45	0.617	46	0.243	46
	0.98	46	0.61	47	0.24	47
	0.97	41	0.69	41	0.25	41
$[C_8mim][NTf_2]$	0.97	47	0.597	47	0.28	47
$[C_{10}mim][NTf_2]$	nd	nd	nd	nd	nd	nd

[a] nd, No data in literature.

Figure 4. Linear relation between the upper critical solution temperature and the number of carbon of butane-1,z-diol skeleton bonded with the second hydroxyl group.

difficult to explain. Nevertheless, the literature reports are in good coincidence with the result found in this investigation. The data published for ethane-1,2-diol[8] and propane-1,2-diol[12] confirm the highest solubility in $[C_2mim][NTf_2]$. Additionally, for the monohydroxy alcohols the trend is similar to that indicated here. Generally, the solubility of aliphatic alcohols increases when the side alkyl chain length of the cation of ILs increases due to an increase of the van der Waals interactions between the alkyl chain of alcohol and a side chain of cation.[2,3,10,41,42] It can be assumed that butane-1,2-diol contrary to ethane-1,2-diol is more similar to normal alcohols and follows trend observed for n-alcohols.[8] It can be assumed that it is true because butane-1,2-diol possesses relatively long alkyl chain that opens room for van der Waals interactions but at the same time is characterized by highly polar spot of two hydroxyl groups that act as a strong proton donor. The van der Waals interaction between a hydrophobic part of alcohol and aliphatic domain of the cation of ionic liquid starts to dominate and is even more effective for longer side chains of ionic liquids, thus, increases the mutual solubility of ionic liquids and butane-1,2-diol.

Dependence of Mutual Solubility of Polyhydroxy Alcohols and Bis(Trifluoromethylsulfonyl)Amide Ionic Liquid on the Position of Hydroxyl Group in Alcohol. The results presented for bis(trifluoromethylsulfonyl)amide ionic liquid with butanediol isomers demonstrate that the solvent with vicinal hydroxyl groups is a better solvent than its isomers. The miscibility gap increases as the distance between hydroxyl group
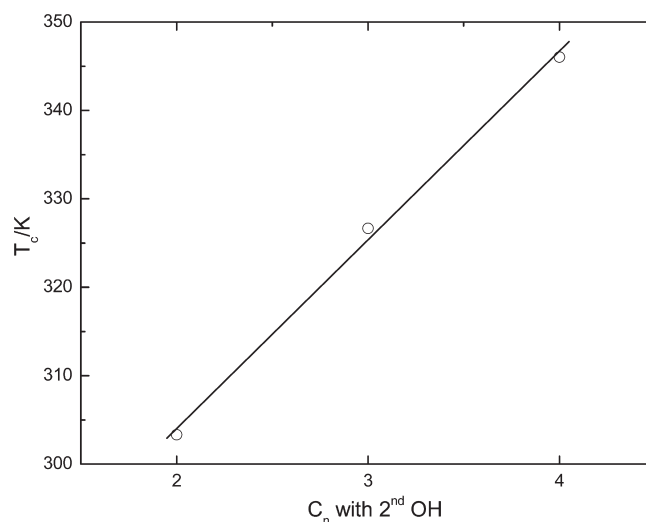
augments and is the highest for butane-1,4-diol as Figure 3 depicts. The upper critical solution temperature for three of the studied isomers of butane-1,z-diol is following the aforementioned tendency which is presented in Figure 4. The miscibility gap increases due to the rearrangement (migration of second hydroxyl group from C-2 to C-4) in the butanediol skeleton that reduces the hydrophobic effect thus increases the van der Waals interaction forces between the alcohol and the IL. In consequences it leads to decrease of the mutual solubility of the components of these binary mixtures.

An interesting behavior has been noticed for system containing $[C_2mim][NTf_2]$ and butane-2,3-diol. The mentioned binary system exhibits complete miscibility in the range of temperature being of interest of this work. Data obtained for this system confirms our previous conclusions about the effect of the hydrophobic domain of alkyl chain of an alcohol. The hydroxyl groups located in the middle of butanediol skeleton reduced the effect of butyl chain and the van der Waals forces between butane-2,3-diol and $[C_2mim][NTf_2]$ became highly ineffective.

■ CONCLUSIONS

The liquid–liquid phase equilibria of twenty binary systems involving ILs ($[C_4mim][DCA]$, $[C_8mim][DCA]$, $[C_2mim]$

$[NTf_2]$, $[C_4mim][NTf_2]$, $[C_8mim][NTf_2]$, $[C_{10}mim][NTf_2]$), glycols (propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, butane-2,3-diol, ethylene glycol, diethylene glycol, dipropylene glycol), glycerol, and *n*-alcohol (butan-1-ol) have been reported. The systems containing hydrophilic dicyanamide ionic liquid exhibit complete miscibility with the studied polyhydroxy alcohols. The solutions containing bis(trifluoromethylsulfonyl)amide ionic liquids demonstrate limited solubility with the studied butane-1,2-diol and its structural isomers. The shape of the curve is characteristic for the systems with the upper critical solution temperature. The presented results show that both the structure of ionic liquid and alcohol affects the phase behavior. It was found that miscibility of $[C_nmim][NTf_2]$ with butane-1,2-diol depends on the choice of cation. The observed results demonstrate that the solubility is generally in good agreement with the data reported for monohydroxy alcohols except the case with $[C_2mim][NTf_2]$ that is still coincident with the results for polyhydroxy alcohols. The arrangement of hydroxyl groups in the alcohol structure affects the miscibility, as well. The solubility is the highest for butanediol that has vicinal hydroxyl groups and the solubility diminishes as the distance between the hydroxyl groups rises. Rearrangement of the hydroxyl group to butane-2,3-diol levels effect of hydrophobic domain of alkyl chain of alcohol that leads to complete miscibility with hydrophobic $[C_2mim][NTf_2]$.

The obtained LLE data are important from the practical point of view because can serve as a background for a designing of the various chemical reactions with diols, that is, telomerization and can be useful for the development of the extraction and separation studies of polyhydroxy alcohols from, for example, postfermentation broth.

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