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REVIEW

Solutions of ionic liquids with diverse aliphatic and aromatic solutes – Phase behavior and potentials for applications: A review article

Zoran P. Visak [a,*], Marta S. Calado [a], Jelena M. Vuksanovic [b], Gorica R. Ivanis [b], Adriana S.H. Branco [a], Nikola D. Grozdanic [b], Mirjana Lj. Kijevcanin [b], Slobodan P. Serbanovic [b]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
[b] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

Abstract This article principally reviews our research related to liquid–liquid and solid–liquid phase behavior of imidazolium- and phosphonium-based ionic liquids, mainly having bistriflamide ($[NTf_2]^-$) or triflate ($[OTf]^-$) anions, with several aliphatic and aromatic solutes (target molecules). The latter include: (i) diols and triols: 1,2-propanediol, 1,3-propanediol and glycerol; (ii) polymer poly(ethylene glycol) (PEG): average molecular mass 200, 400 and 2050 – PEG200 (liquid), PEG400 (liquid) and PEG2050 (solid), respectively; (iii) polar aromatic compounds: nicotine, aniline, phenolic acids (vanillic, ferulic and caffeic acid,), thymol and caffeine and (iv) non-polar aromatic compounds (benzene, toluene, *p*-xylene). In these studies, the effects of the cation and anion, cation alkyl chain and PEG chain lengths on the observed phase behaviors were scrutinized. Thus, one of the major observations is that the anion – bistriflamide/triflate – selection usually had strong, sometimes really remarkable effects on the solvent abilities of the studied ionic liquids. Namely, in the case of the hydrogen-bonding solutes, the ionic liquids with the triflate anion generally exhibited substantially higher solubility than those having the bistriflamide anion. Nevertheless, with the aromatic compounds the situation was the opposite – in most of the cases it was the bistriflamide anion that favoured solubility. Moreover, our other studies confirmed the ability of PEG to dissolve both polar and non-polar aromatic compounds. Therefore, two general possibilities of application of alternative, environmentally acceptable, solvents of tuneable solvent properties appeared. One is

* Corresponding author. Tel.: + 351 21 841 9229; fax: + 351 21 846 4455.
E-mail addresses: zoran.visak@ist.utl.pt, zoranvisak@gmail.com (Z.P. Visak).

List of acronyms

[NTf$_2$]$^-$	bistriflamide anion
[OTf]$^-$	triflate anion
PEG	poly(ethylene glycol)
UCST	Upper-Critical-Solution-Temperature
[dca]$^-$	dicyanamide anion
[BF$_4$]$^-$	tetrafluoroborate anion
[PF$_6$]$^-$	hexafluorophosphate anion
[C$_2$mim][NTf$_2$]	1-ethyl-3-methylimidazolium bistriflamide
[C$_4$mim][NTf$_2$]	1-butyl-3-methylimidazolium bistriflamide

[C$_2$mim][OTf]	1-ethyl-3-methylimidazolium triflate
[C$_4$mim][OTf]	1-butyl-3-methylimidazolium triflate
[EtSO$_4$]$^-$	ethyl sulfate anion
[C$_2$mim][EtSO$_4$]	1-ethyl-3-methylimidazolium ethyl sulfate
[C$_n$mim][NTf$_2$]	1-alkyl-3-methylimidazolium bistriflamide
[C$_n$mim][OTf]	1-alkyl-3-methylimidazolium triflate

to use homogeneous mixtures of two ionic liquids having [NTf$_2$]$^-$ and [OTf]$^-$ anions as mixed solvents. The other, however, envisages the application of homogeneous and heterogeneous (PEG + ionic liquid) solutions as tuneable solvents for aromatic solutes.

Such mixed solvents have potential applications in separation of the aforesaid target molecules from their aqueous solutions or in extraction from original matrices. From the fundamental point of view the phase equilibrium studies reviewed herein and the diversity of the pure compounds – ionic liquids and target molecules – represent a good base for the discussion of interactions between the molecules that exist in the studied solutions.

Contents

1. Introduction

There are several reasons to comprehend ionic liquids as exceptional and useful class of ionic compounds: (i) extensive liquid range favorable for solvent applications; (ii) indefinite number of combinations of constitutive cations and anions which, by themselves, may have quite varied structures and complexity (Plechkova and Seddon, 2008); (iii) practical non-volatility in a wide range of temperatures (Rogers and Seddon, 2003; Paulechka et al., 2003; Rebelo et al., 2005), providing environmental sustainability – low atmospheric pollution; thus, ionic liquids are promising substitutes for the existing volatile and generally toxic organic solvents; (iv) ionic nature (polarity) and fine hydrogen bond basicity and acidity (Crowhurst et al.,

2003; Ab Rani et al., 2011), resulting in good ability to form hydrogen bonds (Cammarata et al., 2001; Domanska and Marciniak, 2004; Domanska and Casas, 2007; Domanska et al., 2012; Crosthwaite et al., 2004, 2005, 2006); (v) diversity and versatility in solvent power – being ionic (polar) but, at the same time, possessing non-polar domains (aliphatic chains), primarily in the cations (Rebelo et al., 2007), ionic liquids can dissolve both polar and non-polar compounds (Visak, 2012; Calado et al., 2013a; Łachwa et al., 2006a; Domanska and Casas, 2007; Crosthwaite et al., 2004); (vi) general possibility to design and tune their solvent properties (Freemantle, 1998) either by anion selection (Trindade et al., 2010) or by change of the chain-length of the aliphatic non-polar domains (Rebelo et al., 2007); even more, this opportunity enabled the

concept of so-called "task-specific" ionic liquids – those for which the structures of their cations and/or anions are tailored for particular applications (Davis, 2004).

This review is mainly related to our phase equilibria (Calado et al., 2013a,b,c; Trindade et al., 2010) and volumetric studies (Vuksanovic et al., 2013) covering the solutions of imidazolium and phosphonium ionic liquids, mainly having bistriflamide ([NTf$_2$]$^-$) or triflate ([OTf]$^-$) anions, with several aliphatic and aromatic solutes: (i) diols and triols: 1,2-propanediol, 1,3-propanediol and glycerol (Trindade et al., 2010); (ii) non-polar aromatic compounds (benzene, toluene, p-xylene) (Calado et al., 2013a); (iii) polymer poly(ethylene glycol) (PEG): average molecular mass 200, 400 and 2050 – PEG200 (liquid), PEG400 (liquid) and PEG2050 (solid), respectively (Calado et al., 2013b; Vuksanovic et al., 2013) and (iv) polar aromatic compounds: toxic nicotine and aniline (Calado et al., 2013a) but as well high-value compounds – phenolic acids (vanillic, ferulic and caffeic acid), thymol and caffeine (Calado et al., 2013c). These target molecules have different hydrogen bond acidities and basicities as well as dipole moments. The latter vary from values which are very high (phenolic acids and PEG) or moderately high (nicotine and aniline) to those very low or practically zero (arenes). Also, melting points differ, so that some of the solutes are solid at ambient temperatures (high-value compounds) while others are liquids. Table 1 gives the list of the ionic liquids and solutes considered herein, at the same time showing the physicochemical properties of these compounds.

Thus, the results presented herein clearly depict the aforementioned features of ionic liquids, particularly their diversity and versatility as solvents. At the same time, they envisage potential applications of ionic liquids or their solutions, both homogeneous and heterogeneous, as alternative solvents.

Besides the applicative implications the fundamental importance of the solutions reviewed herein exists as well. Comprehensive diversity of their phase behaviors – presented in the related phase diagrams – along with a variety in physicochemical properties of the solvents and solutes offers good grounds for the discussion of molecular interactions that stand behind the phenomena.

2. Phase Behavior of solutions of imidazolium ionic liquids with typical hydrogen bonding and aromatic compounds: solutions of imidazolium ionic liquids as potential tuneable solvents

One of the most important observations that emerge from the studies reviewed herein is that the selection between [NTf$_2$]$^-$ and [OTf]$^-$ anion had very strong and sometimes even extraordinary effects on the phase behavior due to the distinctions that exist between these two anions. These are exposed either (i) as a superiority of the [OTf]$^-$ over the [NTf$_2$]$^-$ anion to form strong attractive interactions – particularly hydrogen bonds or (ii) in higher solubility of aromatic compounds in the ionic liquids with the [NTf$_2$]$^-$ anion compared to those with the [OTf]$^-$ anion.

2.1. Solubility of ionic liquids with aliphatic primary and secondary alcohols

At this point, it is interesting to briefly review the phase behavior of the solutions of ionic liquids with aliphatic primary and secondary alcohols. In these solutions, the constituents comprise of both polar and non-polar moieties (aliphatic chains) and their competition is a main feature of the Upper-Critical-Solution-Temperature (UCST) liquid-liquid phase behavior (Crosthwaite et al., 2004, 2005, 2006). The cited studies show that the UCST can indeed be tuned by the length of the aliphatic chains – both in ionic liquid cations and alcohols. Namely the solubility decreases as the aliphatic chain in ionic liquid cation shortens but increases if the same occurs with the aliphatic chain in alcohol, regardless of being primary or secondary. However, it was found that secondary alcohols generally exhibit higher solubility with imidazolium ionic liquids than the primary ones (Crosthwaite et al., 2004; Domanska and Marciniak, 2004).

As it was noticed in the previous review (Visak, 2012) the effect of the alcohol chain length exits as well in solid–liquid-equilibria (SLE) of the solutions of ionic liquids with alcohol, often accompanied with the liquid–liquid immiscibility (Domanska and Marciniak, 2004; Domanska and Casas, 2007; Domanska, 2010; Domanska et al., 2011).

With respect to the anion-alcohol affinity, the trend determined, namely dicyanamide [dca]$^-$ > triflate [OTf]$^-$ > bistriflamide [NTf$_2$]$^-$ > tetrafluoroborate [BF$_4$]$^-$ > hexafluorophosphate [PF$_6$]$^-$ (Crosthwaite et al., 2004) follows that of an anion-water hydrogen bond strength (Cammarata et al., 2001) and, generally of the hydrogen bond basicities (the exception to this rule is the advantage of the [NTf$_2$]$^-$ over the [BF$_4$]$^-$ anion). The conclusion is that the anion selection has a dramatic impact on ionic liquid-anion solubility.

2.2. Different solvent properties of imidazolium ionic liquids with [NTf$_2$]$^-$ and [OTf]$^-$ anions toward typical hydrogen bonding compounds

Imidazolium ionic liquids with triflate and bistriflamide anions show distinct phase behavior with typical hydrogen bonding compounds such as water and alcohols: (i) [C$_n$mim][OTf] has excellent aqueous solubility – in particular, Room Temperature Ionic Liquids (RTILs) [C$_n$mim][OTf] (n = 2–6) are even completely soluble in water (Calado et al., 2013a; Trindade et al., 2010); on the other hand RTILs with the same cation but having [NTf$_2$]$^-$ anion are hydrophobic and, thus, exhibit very limited aqueous solubility (Crosthwaite et al., 2004; Freire et al., 2008); (ii) in the case of aliphatic alcohols, as their chain increases, [C$_4$mim][OTf] starts to be partially miscible only with dodecanol; however, for [C$_4$mim][NTf$_2$], this phenomenon occurs already with n-butanol (Crosthwaite et al., 2004); (iii) some polymers which are strong hydrogen bonding compounds such as poly(methacrylic acid), poly(vinyl alcohol) and poly(2-hydroxyethyl methacrylate) are practically not soluble in the ionic liquid [C$_2$mim][NTf$_2$] (Ueki and Watanabe, 2006).

Fourier transform infrared (FT-IR) spectroscopy performed on aqueous solutions of imidazolium-based ionic liquids with several anions (Cammarata et al., 2001) determined the spectral shifts due to the anion-water hydrogen bonds and the (negative) enthalpies related to these interactions. The latter were about 50% higher by absolute values in the case of the [OTf]$^-$ anion, compared to [NTf$_2$]$^-$ indicating that the first anion builds much stronger hydrogen bonds with water.

Table 1 Physicochemical properties – dipole moment (μ), hydrogen bond acidity (α)[a], hydrogen bond basicity (β)[a] and melting point (Tm) of the compounds considered in the current review.

Compound	μ/D	Literature	α	β	Literature	Tm/K	Literature
[C$_2$mim][NTf$_2$]	c	–	0.705	0.233	Chiappe and Pieraccini (2006)	264.15	Bonhôte et al. (1996)
[C$_4$mim][NTf$_2$]	c	–	0.617	0.243	Crowhurst et al. (2003)	269.15	Bonhôte et al. (1996)
[C$_4$mim][OTf][b]	c	–	0.625	0.464	Crowhurst et al. (2003)	289.15	Bonhôte et al. (1996)
[P$_{6,6,6,14}$][NTf$_2$]	c	–	0.37	0.27	Coleman et al. (2009)	N/A	–
[C$_2$mim][EtSO$_4$]	c	–	N/A	0.710	Palgunadi et al. (2011)	208.15[d]	Holbrey et al. (2002)
1,2-PD	2.20	Reid et al. (1987)	0.83	0.78	Fonrodona et al. (1996)	213	Sigma–Aldrich Material Data Sheet
1,3-PD	2.50	Reid et al. (1987)	0.80	0.77	Fonrodona et al. (1996)	246	Sigma–Aldrich Material Data Sheet
Glycerol	2.16	Rizk and Elanwar (1968)	0.88–1.06	0.66	Jessop et al. (2012)	254.9	Pagliaro and Rossi (2008)
PEG200	3.06–3.94	Rudan-Tasic and Klofutar (2005)	0.46	0.63	Kim et al. (2002)	218–233	Sigma–Aldrich Material Data Sheet
PEG400	3.70–4.96	Rudan-Tasic and Klofutar (2005)	0.31	0.65	Kim et al. (2002)	277–281	Sigma–Aldrich Material Data Sheet
PEG2050	6.53–8.51[e]	Rudan-Tasic and Klofutar (2005)	N/A	N/A	–	330.14	Ivanis et al. (2012)
Nicotine	1.81	Ochoa and Harrington (2004)	N/A	0.69	Abraham et al. (1990)	194	Sigma–Aldrich Material Data Sheet
Aniline	1.15	Zakrzewska et al. (2005)	N/A	0.38	Abraham et al. (1990)	267	Sigma–Aldrich Material Data Sheet
Thymol	1.54	Le Févre et al. (1935)	f	f	–	322.0	Manic et al. (2012)
Ferulic acid	5.4–6.2	Thomas et al. (2012)	f	f	–	444.9	Manic et al. (2012)
Vanillic acid	4.07	Clavijo et al. (2008)	f	f	–	480.7	Manic et al. (2012)
Caffeic acid	3.626	Leopoldini et al. (2006)	f	f	–	464.1	Manic et al. (2012)
Caffeine	3.70	Weiler-Feilchenfeld and Neiman (1970)	N/A, assumed low	1.35	Tian and Row (2008)	505.4	Manic et al. (2012)
Benzene	0.0–0.18	Altschuller (1953)	0.0	0.1	Hofmann et al. (2008)	278	Sigma–Aldrich Material Data Sheet
Toluene	0.34–0.38	Altschuller (1953)	0.0	0.11	Hofmann et al. (2008)	180	Sigma–Aldrich Material Data Sheet
o-Xylene	0.53–0.62	Altschuller (1953)	0.0	0.16	Jessop et al. (2012)	247–250	Sigma–Aldrich Material Data Sheet
p-Xylene	0.0–0.13	Altschuller (1953)	0.0	0.12	Lagalante et al. (1996)	285–286	Sigma–Aldrich Material Data Sheet

[a] Hydrogen bond acidity (α) and hydrogen bond basicity (β) are mainly cation and anion controlled, respectively (Ab Rani et al., 2011).

[b] The values of α and β for [C$_2$mim][OTf], not available in literature, can be reasonably estimated on the basis of α and β for [C$_4$mim][OTf].

[c] Ionic (charged) compounds – polarity is estimated through polarity scales (hydrogen bond acidity α, hydrogen bond basicity β and polarizability π^*) (Ab Rani et al., 2011).

[d] Glass transition temperature.

[e] These values are determined for PEG1500 – since dipole moment rises with the average molecular mass, for PEG2050 it will only be higher.

[f] Parameters α and β are not available in literature, but phenolic acids have multiple hydrogen bonding sites (Ota et al., 2011; Belkov et al., 2012) while thymol has one (proton donor) site according to the International Union of Basic and Clinical Pharmacology Database.
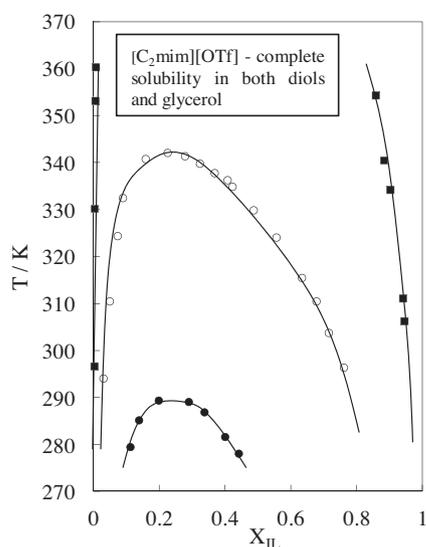
Figure 1 Temperature-composition liquid–liquid equilibria (LLE) phase diagrams at 0.1 MPa for the solutions of [C$_2$mim][NTf$_2$] with: (a) 1,2-propanediol (filled circles), (b) 1,3-propandiol (hollow circles), (c) glycerol (filled squares). Lines represent only guides to eye. Two-phase regions are placed inside the respective envelopes. X_{IL} presents the mole fractions of ionic liquid in the solution.

Hydrogen bond basicity, which is mainly anion controlled (Ab Rani et al., 2011) of the [OTf]$^-$ anion is almost two times higher than that of [NTf$_2$]$^-$ (Crowhurst et al., 2003; Ab Rani et al., 2011).

2.2.1. Specific properties of the [NTf$_2$]$^-$ anion and their consequences on its interaction abilities

Two specific properties of the [NTf$_2$]$^-$ anion that obstruct its interaction abilities, including hydrogen bonding (proton acceptance with neighboring donors) should particularly be addressed: delocalization of the negative charge and steric hindrance (due to the anion's bulkiness) (Golding et al., 1998; MacFarlane et al., 1999; Deetlefs et al., 2006).

The first feature considers that the specific interactions between the neighboring sulfur and nitrogen atoms in the anion delocalize the negative charge mainly along the anion's S–N–S moiety, while only a small portion of the charge remains delocalized on the sulfonyl oxygen atoms (Cruickshank, 1961). In this way, the oxygen atoms and terminal – CF$_3$ groups shield the negative charge and obstruct Coulomb interactions with the coupled cation (MacFarlane et al., 1999). However, the ability of the sulfonate oxygens to accept

protons has to be decreased as well (Deetlefs et al., 2006), being reflected in much lower hydrogen bond basicity of the anion (see above). The delocalization phenomenon is supported by the bond lengths in the crystal structure of [NTf$_2$]$^-$ anion reported in the literature (Golding et al., 1998).

Steric hindrance is seen (Golding et al., 1998; Holbrey et al., 2004) mainly as a consequence of (i) S–N–S angle (125°) slightly larger than that in the trigonal pyramidal molecular structure (∼107°) and ii) bulkiness of the – SO$_2$CF$_3$ groups in the anion which shield the negative charge. This hindrance sustains the aforesaid charge delocalization and helps in reducing interaction ability of the [NTf$_2$]$^-$ anion. However, the irregular shape and large size of the [NTf$_2$]$^-$ anion which result in its inefficient packing can be as well seen as contributors to steric difficulties which impede interactions (Forsyth et al., 2002).

2.2.2. Solubility with diols and glycerol

The aforementioned challenging findings which do implicate interaction superiority of the [OTf]$^-$ anion over the [NTf$_2$]$^-$ – particularly in hydrogen bond formation – turned our attention to the solutions of the ionic liquids cited above with other typical hydrogen bonding compounds: 1,2-propanediol, 1,3-propanediol, glycerol (phase equilibria and spectroscopic studies (Trindade et al., 2010)) and poly(ethylene glycol) (volumetric and viscosity studies (Vuksanovic et al., 2013)).

In the first study, it was found that the ionic liquid 1-ethyl-3-methylimidazolium triflate [C$_2$mim][OTf] was completely soluble with all the aforementioned polyalcohols. On the other hand, 1-ethyl-3-methylimidazolium bistriflamide [C$_2$mim][NTf$_2$] behaved dramatically different – it has always shown partial miscibility, which was even very extended in the case of 1,3-propanediol and glycerol (see Fig. 1). This behavior is in agreement with that with water and aliphatic mono-alcohols described above.

FTIR spectroscopic studies performed within the same work provided the stretching frequencies of the hydroxyl groups of each diol in the solution and in pure alcohols. Afterward, the shifts with respect to the frequencies of the pure alcohols were calculated. These shifts, associated with the hydrogen bonds between alcohol hydroxyl groups (proton donors) and ionic liquid anions (proton acceptors), were significantly reduced in the solutions with [C$_2$mim][NTf$_2$] when compared to those with [C$_2$mim][OTf] – (see Table 2), thus clearly indicating weaker hydrogen bonds in the case of the solutions with [C$_2$mim][NTf$_2$].

Finally, our recent study (Vuksanovic et al., 2013) has shown negative excess molar volumes of the solutions of ionic liquid [C$_2$mim][OTf] with liquid poly(ethylene glycol), PEG200, (average molecular mass 200). However, for the solutions of this liquid polymer with ionic liquid [C$_2$mim][NTf$_2$]

Table 2 Shifts of the stretching frequencies of the hydroxyl group in 1,2-propanediol, 1,3-propanediol and glycerol in the presence of imidazolium ionic liquids with [OTf]$^-$ and [NTf$_2$]$^-$ anions.

Component	Pure alcohol	Alcohol + [C$_2$mim][OTf]		Alcohol + [C$_2$mim][NTf$_2$]	
	Stretching frequency ν/cm^{-1}	Stretching frequency ν/cm^{-1}	Shift	Stretching frequency ν/cm^{-1}	Shift
1,2-Propanediol	3635	3384	251	3469	166
1,3-Propanediol	3634	3423	211	3489	145
Glycerol	3634	3432	202	3530	104
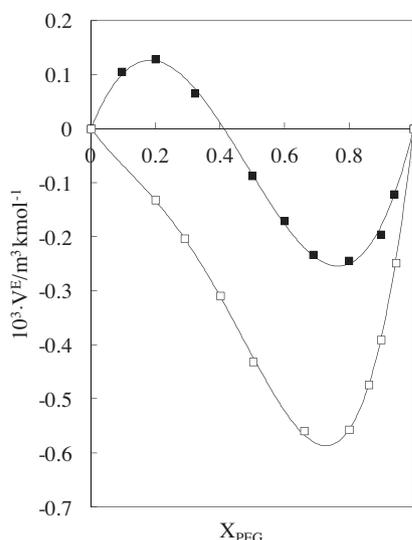
Figure 2 Comparison of the excess molar volumes at 308.15 K and 0.1 MPa: filled squares – (PEG200 (1) + [C$_2$mim][NTf$_2$] (2)) solutions, hollow squares – (PEG200 (1) + [C$_2$mim][OTf] (2)) solutions. X_{PEG} stands for the mole fractions of liquid PEG in the solution.

excess molar volumes change sign from positive to negative as the content of PEG200 increases, with the absolute values far lower than in the case of the first solution (see Fig. 2). This behavior and even more the excess molar volumes at infinite dilution (see Fig. 3) – which exclude solvent–solvent interactions – indicate much stronger attractive interactions (hydrogen bonds and ion–dipole interactions) in the case of [C$_2$mim][OTf]. The effect can be reasonably attributed to the anion, since the cation is kept the same. Thus, it coincides with the discussion related to hydrogen bond abilities of the studied anions (see above).
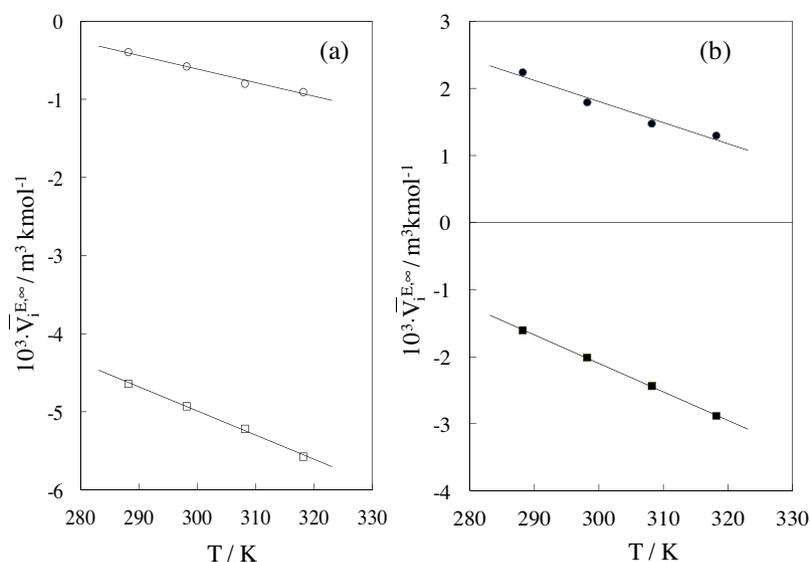
Therefore, all these significant distinctions open the possibility to use the mixtures of [C$_2$mim][NTf$_2$] and [C$_2$mim][OTf] ionic liquids as mixed solvents which hydrophobic/hydrophilic nature and, consequently, hydrogen bonding capabilities are tuneable by composition. Namely, more [C$_2$mim][OTf] increases the hydrophilic nature of the mixed solvent and improves the formation of hydrogen bonds, while the addition of [C$_2$mim][NTf$_2$] does the opposite. In principle, this adjustment provides a possibility to find the best performance of such a solvent, thus providing an optimum efficiency of separation process – the best partition coefficients of a target molecule and separation factors.

As it was pointed-out (Trindade et al., 2010), one of the possible applications of such a mixed solvent could be in the separation of the 1,3-propandiol from glycerol and/or its aqueous solutions. This is an important issue in the microbial production of this diol, since the fermentation broth is aqueous (Xiu and Zeng, 2008). Thus, Fig. 4 shows that a mixture of 60 mol% [C$_2$mim][NTf$_2$] and 40 mol% [C$_2$mim][OTf] is an excellent solvent for 1,3-propanediol, while it does not dissolve much glycerol at the same time. Also, the figure indicates that there is an interval of compositions in which it would be possible to separate the diol from both water and glycerol, at ambient or near-ambient temperatures.

2.3. Solubility of the aromatic compounds in imidazolium ionic liquids having ($[NTf_2]^-$) and ($[OTf]^-$) anions

Several studies (Łachwa et al., 2006a,b; Blesic et al., 2009; Holbrey et al., 2003; Deetlefs et al., 2005) confirmed that imidazolium ionic liquids form specific cation and anion interactions with the aromatic arene ring which result in a cage-like structure. The latter can be explained using the case of ionic liquids with [NTf$_2$]$^-$ anion and benzene (Łachwa et al., 2006a,b): (i) the anion-aromatic ring interactions are planar and occur mainly between the benzene hydrogen atoms and oxygen atoms in the anion sulfonyl groups while (ii) ionic liquid cations are situated above and below the aromatic rings

Figure 3 Excess molar volumes at infinite dilution, $\bar{V}_i^{E,\infty}$ ($i = 1,2$) and 0.1 MPa for the solutions of PEG200 (1) with (a) [C$_2$mim][OTf] (2): hollow circles – $\bar{V}_1^{E,\infty}$; hollow squares – $\bar{V}_2^{E,\infty}$; (b) [C$_2$mim][NTf$_2$] (2): filled circles – $\bar{V}_1^{E,\infty}$; filled squares – $\bar{V}_2^{E,\infty}$.
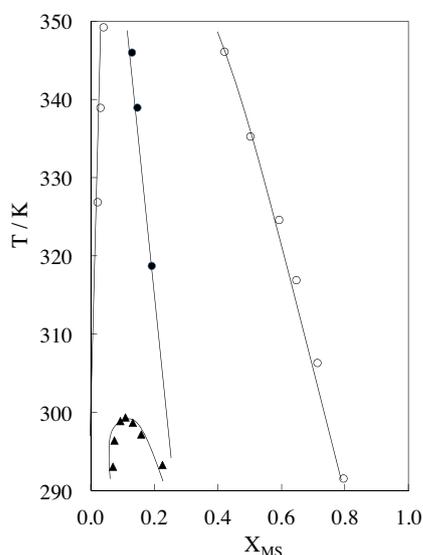
Figure 4 Temperature-composition liquid–liquid equilibria (LLE) phase diagram at 0.1 MPa showing the possibility to use a mixture of 60 mol% $[C_2mim][NTf_2]$ and 40 mol% $[C_2mim][OTf]$ as a mixed solvent (MS) for the sustainable separation of 1,3-propanediol from aqueous solutions with glycerol. The symbols refer to the solutions of MS with: filled triangles – 1,3-propanediol, filled circles – water, hollow circles – glycerol. Lines are given only as a guide to eye. X_{MS} is the mole fraction of the mixed solvent (MS) in the solution. The experimental points on the water-rich side were experimentally inaccessible since the miscibility limit is below the accuracy of the experiments. Two-phase regions are placed inside the respective envelopes.

Figure 5 Temperature-composition liquid–liquid equilibria (LLE) phase diagrams at 0.1 MPa for the solutions: hollow circles – $([C_2mim][NTf_2]$ + benzene), hollow squares – $([C_2mim][NTf_2]$ + toluene), hollow triangles – $([C_2mim][NTf_2]$ + p-xylene), filled circles – $([C_2mim][OTf]$ + benzene), filled triangles – $([C_2mim][OTf]$ + toluene), filled squares – $([C_2mim][OTf]$ + p-xylene). The arrows indicate the direction of 1-phase to 2-phase transition (and vice versa). The points on the arene-rich sides of the diagrams were experimentally inaccessible due to extremely low solubility of the ionic liquids in arenes. X_{IL} presents the mole fractions of ionic liquid in the solutions.

and their interactions are mostly π–π interactions between the two aromatic rings or interactions between acidic hydrogen in the imidazolium cation and π electrons in the aromatic ring. This structure significantly supports the solubility of virtually non-polar aromatic compounds such as arenes (Łachwa et al., 2006a) but as well of the polar aromatics, for instance nicotine and aniline (Calado et al., 2013a; Visak et al., 2007) in ionic liquids. It was also found (Łachwa et al., 2006a,b) that the extension of the cation alkyl chains – non-polar domains – supports the formation of the cage-like structure and provides higher solubility of arenes. This phenomenon is in agreement with the non-polar or weakly polar character of arenes.

One of the interesting features of the phase behavior of the solutions of imidazolium ionic liquid with aromatic compounds is that the $[NTf_2]^-$ anion, coupled with the same cation, significantly improves the solubility of the aromatic compounds when compared to the $[OTf]^-$ anion (Calado et al., 2013a; Blesic et al., 2009; Ferreira et al., 2011) – Fig. 5 clearly depicts this phenomenon.

The aforementioned distinction stands as well in the case of the solutions of ionic liquids with polar aromatic compounds such as nicotine and aniline. Ionic liquids 1-ethyl-3-methylimidazolium bistriflamide $[C_2mim][NTf_2]$ and 1-butyl-3-methylimidazolium $[C_4mim][NTf_2]$ were found to be completely soluble with these aromatics (Calado et al., 2013a; Visak et al., 2007) while, on the contrary, ionic liquids $[C_2mim][OTf]$ and $[C_4mim][OTf]$ show very limited solubility (Calado et al., 2013a) – see Fig. 6.

Figure 6 Temperature-composition liquid–liquid equilibria (LLE) phase diagrams at 0.1 MPa for the solutions of $[C_2mim][OTf]$ with: filled squares – nicotine, hollow squares – aniline. Two-phase regions are placed inside the respective envelopes. X_{IL} represents the mole fractions of ionic liquids in the solutions.

Non-polar aromatic compounds (arenes) are significant water pollutants due to their elevated toxicity (Shim et al.,

2004). The same stands for nicotine which is an emerging aqueous pollutant in discarded waters from tobacco industry (Sponza, 2002), ground waters (Stuart et al., 2012; Jurado et al., 2012) and urban waste waters (Benotti and Brownawell, 2007; Muñoz et al., 2008). The discussed distinctions of the imidazolium ionic liquids with bistriflamide and triflate anions toward water and aromatic compounds bring the possibility to use hydrophobic ionic liquids $[C_nmim][NTf_2]$ or their mixtures with hydrophilic $[C_nmim][OTf]$, ($[C_nmim][NTf_2] + [C_nmim][OTf]$), in separation of aromatic compounds – both polar and non-polar – from their aqueous and non-aqueous solutions. Tunable solvent power of these mixed solvents, feasible by adjusting their composition (see above), once again opens further opportunities for the improvement of separation process efficiency.

3. "Green Meets Green": solutions of poly(ethylene glycol) and ionic liquids and their potentials as homogeneous/or heterogeneous mixed solvents

Detailed toxicity studies (Heldebrant et al., 2006) revealed poly(ethylene glycol) (PEG) as an environmentally acceptable and non-toxic, practically eatable polymer. Also, liquid PEG is virtually non-volatile and also represents an appropriate alternative for classical (toxic) solvents in catalysis (Heldebrant et al., 2006) and organic synthesis (Liang et al., 2009) since it is highly polar (Rudan-Tasic and Klofutar, 2005), good proton donor and even better acceptor due to the repeating oxygen atoms in its ethylene oxide monomer units (Kim et al., 2002). However, this polymer can sometimes change its polar conformation (ordered, helical structure) to non-polar (random coil-like structure), following the solution's polarity (Chen et al., 2002). Thus, PEG becomes a good solvent for virtually non-polar aromatic compounds such as arenes
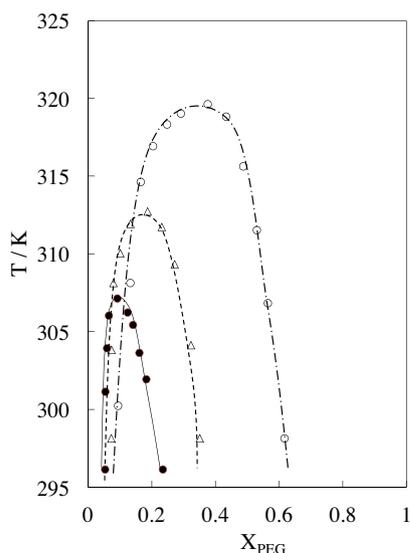
Figure 7 Temperature-composition liquid–liquid equilibria (LLE) phase diagrams at 0.1 MPa for the solutions: hollow triangles – (PEG200 + toluene), filled circles – (PEG400 + o-xylene), hollow circles – (PEG400 + p-xylene). Two-phase regions are placed inside the respective envelopes. X_{PEG} represents the mole fractions of ionic liquids in the solutions.
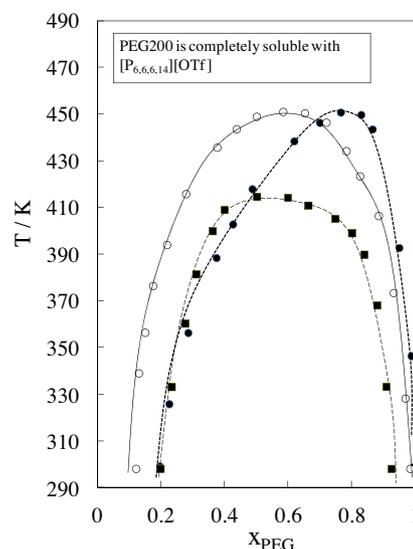
Figure 8 The comparison of the liquid–liquid phase behavior at 0.1 MPa of the (PEG200 + $[P_{6,6,6,14}][NTf_2]$) (filled circles), (PEG400 + $[P_{6,6,6,14}][NTf_2]$) (hollow circles), and (PEG400 + $[P_{6,6,6,14}][OTf]$) (filled squares) solutions. Two-phase regions are placed inside the respective envelops. The lines are given only as guides to eye. X_{PEG} represents mole fractions of PEG in the solutions.

(Sabadini, 1993; Ivanis et al., 2012): benzene is completely miscible in liquid PEG200, PEG400 and PEG600, toluene in PEG400. Also, toluene shows limited but yet very good solubility in PEG200 and the same can be stated for o- and p-xylene in PEG400 (Ivanis et al., 2012) (see the phase diagrams in Fig. 7).

Due to the favorable features of PEG and ionic liquids (see the Introduction) we have studied the solubility and phase behavior in the solutions of these compounds of complex solvent powers (Calado et al., 2013c). Ionic liquids studied were imidazolium-($[C_nmim]^-$) and phosphonium-($[P_{6,6,6,14}]^-$) based having bistriflamide $[NTf_2]^-$, triflate $[OTf]^-$ and ethyl-sulfate $[EtSO_4]^-$ anions while the studied poly(ethylene glycols) (PEGs) were PEG200, PEG 400 (both liquid) and PEG2050 (solid).

From the fundamental aspect, interesting impacts of cation and anion were observed.

Imidazolium cation provided substantially better liquid–liquid and solid–liquid solubility than phosphonium, principally due to its higher hydrogen bond acidity (see Table 1) which allows stronger hydrogen bonds with PEG as a proton acceptor at its oxygen atoms in the chain. Thus, imidazolium ionic liquids studied have shown complete miscibility with liquid PEG200 and PEG400 while those phosphonium – except the fully soluble system (PEG200 + $[P_{6,6,6,14}][OTf]$) -exhibited a very limited solubility (see Fig. 8).

However, the anion effect was found to be far more complex; in the solutions of liquid PEG200 and PEG400 with the phosphonium ionic liquids the $[OTf]^-$ anion significantly improved the solubility with liquid PEG when compared to the $[NTf_2]^-$ (see also Fig. 8), which agrees with the discussion above. However, in the solutions of the imidazolium ionic liquids and solid PEG2050 the solubility followed the order of the
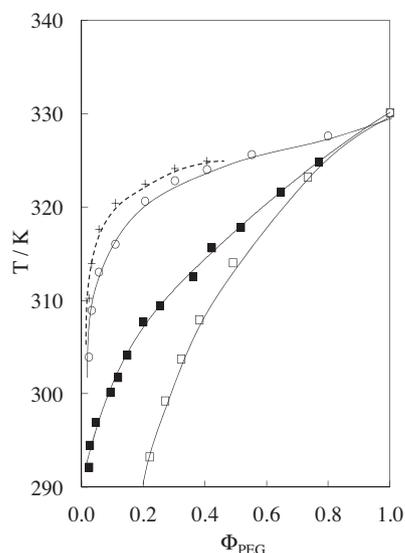
Figure 9 (a) Temperature–composition phase diagrams at 0.1 MPa for the solutions of PEG2050 with: [C$_2$mim][NTf$_2$] (hollow squares), solid–liquid equilibria; [C$_2$mim][OTf] (filled squares), solid–liquid equilibria; [C$_2$mim][EtSO4] (hollow circles), solid–liquid equilibria; [C$_2$mim][EtSO$_4$] (crosses), liquid–liquid equilibria. All the lines are given only as guides to eye. Φ_{PEG} represents segment fractions of PEG in the solutions, calculated using the equation $rX_1/(rX_1 + X_2)$. In this equation r, X_1 and X_2 represent the ratio of average molecular masses of the components (Calado et al., 2013b), mole fraction of PEG2050 and mole fraction of ionic liquid, respectively. Two-phase regions are placed inside the respective envelopes. (a) reprinted from Fluid Phase Equilibria, Vol. 344, Copyright (2013), pages 6–12: Authors: Calado, M.S., Ivanis, G.R., Vuksanovic, J.M., Kijevcanin, M. Lj., Serbanovic, S.P., Visak, Z.P. Title of article: "Green Meets Green" – Sustainable Solutions of Imidazolium and Phosphonium Ionic Liquids with Poly(ethylene glycol): Solubility and Phase Behaviour", pages 6–12, with the permission from Elsevier.

anions [NTf$_2$]$^-$ > [OTf] > [EtSO$_4$] (see Fig. 9) which does not correspond to their hydrogen bond basicities (see Table 1). Thus, this anion effect has to be seen as an outcome of the interplay between cation–anion, PEG-PEG and PEG-anion interactions. The first two types of interaction, which support phase separation, sometimes prevail over the last one that sustains solubility. There are at least three reasons for this occurrence. Firstly, the increase in the anion facility to form hydrogen bonds does not always improve the solubility with PEG in the solutions with PEG2050 – in fact it may provide stronger cation–anion interactions. Secondly, spectroscopic evidences indicate that cation–anion interactions are stronger in [C$_n$mim][OTf] ionic liquids than in [C$_n$mim][NTf$_2$] (Fernandes et al., 2011; Bini et al., 2007) and high hydrogen bond basicity of 1-ethyl-3-methylimidazolium [C$_2$mim][EtSO$_4$] (practically of its anion) (Table 1) suggests that it can be reasonably assumed that these interactions are even stronger in the case of this ionic liquid. Finally, strong inter- and intramolecular hydrogen bonds (PEG–PEG) exist in longer-chain solid polymer PEG2050 (Philippova et al., 1985).

Diverse solvent properties of PEGs and ionic liquids toward both non-polar and polar aromatic compounds and

the related phase behavior – see Figs. 7–9 – enable applications of (PEG + ionic liquid) solutions as potential mixed (combined) and tunable solvents. In this respect, the opportunities one can envisage are to combine highly hydrophilic (water-soluble) PEG with i) hydrophobic bistriflamide ionic liquids or ii) hydrophilic ionic liquids with longer cation alkyl chain. These solvents can exist either as homogeneous solutions or as liquid biphasic systems – the latter application was already discussed by Rodríguez et al. (2009). The solvent power of these mixed solvents is primarily adjusted by the composition of a homogeneous solution or the initial heterogeneous solution that forms a liquid biphasic system. As in the case of homogeneous solutions of ionic liquids (see above) these applications may include non-aqueous and aqueous solutions of arenes, and aqueous solutions of nicotine.

Our solubility and phase equilibrium studies (Calado et al., 2013c) can be seen as an important first step or a guide for the aforementioned applications. First, it revealed which of the studied (PEG200/or PEG400 + ionic liquid) solutions exhibited complete liquid–liquid miscibility – hence they can be potentially used as homogeneous mixed solvents. Or, in the case of the solutions with solid PEG2050 or partially miscible systems with the liquid PEGs, the temperature-composition phase diagrams, at pressure of 0.1 MPa, were determined thus actually mapping temperature and composition borders of their applications as homogeneous solvents or liquid biphasic systems.

4. Ionic liquids as potential solvents for high-value compounds

High-value compounds: thymol, ferulic acid, caffeic acid, vanillic acid and caffeine represent compounds with important positive health effects – anti-cancer, anti-sickling and anthelmintic as well as potential helpful neurological impacts (Manic et al., 2012). Consequently, there is an ever growing necessity to search for alternative solvents which would allow sustainable extraction of these compounds from their natural matrices. On the other hand, these five compounds are highly polar and have excellent abilities to form hydrogen bonds. Namely, caffeine and phenolic acids have several hydrogen bonding sites (Ota et al., 2011; Belkov et al., 2012; Tian and Row, 2008) while thymol has one proton donor site as reported by the International Union of Basic and Clinical Pharmacology Database.

Therefore, ionic liquids and liquid PEG as polar, environmentally friendly and hydrogen bonding compounds are appealing alternative solvents for the cited high-value compounds as we have shown in our recent work (Calado et al., 2013c). This study included ionic liquids 1-butyl-3-methylimidazolium bistriflamide [C$_4$mim][NTf$_2$] and 1-butyl-3-methylimidazolium triflate [C$_4$mim][OTf], principally having in mind the aforesaid distinct impacts of the bistriflamide and triflate anions on solubility/phase behavior of solutions of ionic liquids with hydrogen bonding substances.

Fig. 10(a–e) shows the performance of ionic liquids [C$_4$mim][NTf$_2$] and [C$_4$mim][OTf] as well as of PEG400 as solvents for the cited high-value compounds. It is very clear that the [OTf]$^-$ anion has again shown its advantage over the [NTf$_2$]$^-$ in solubilizing these hydrogen bonding compounds. The exception is caffeine which is predominantly proton acceptor (see Table 1) and good hydrogen bond basicity of
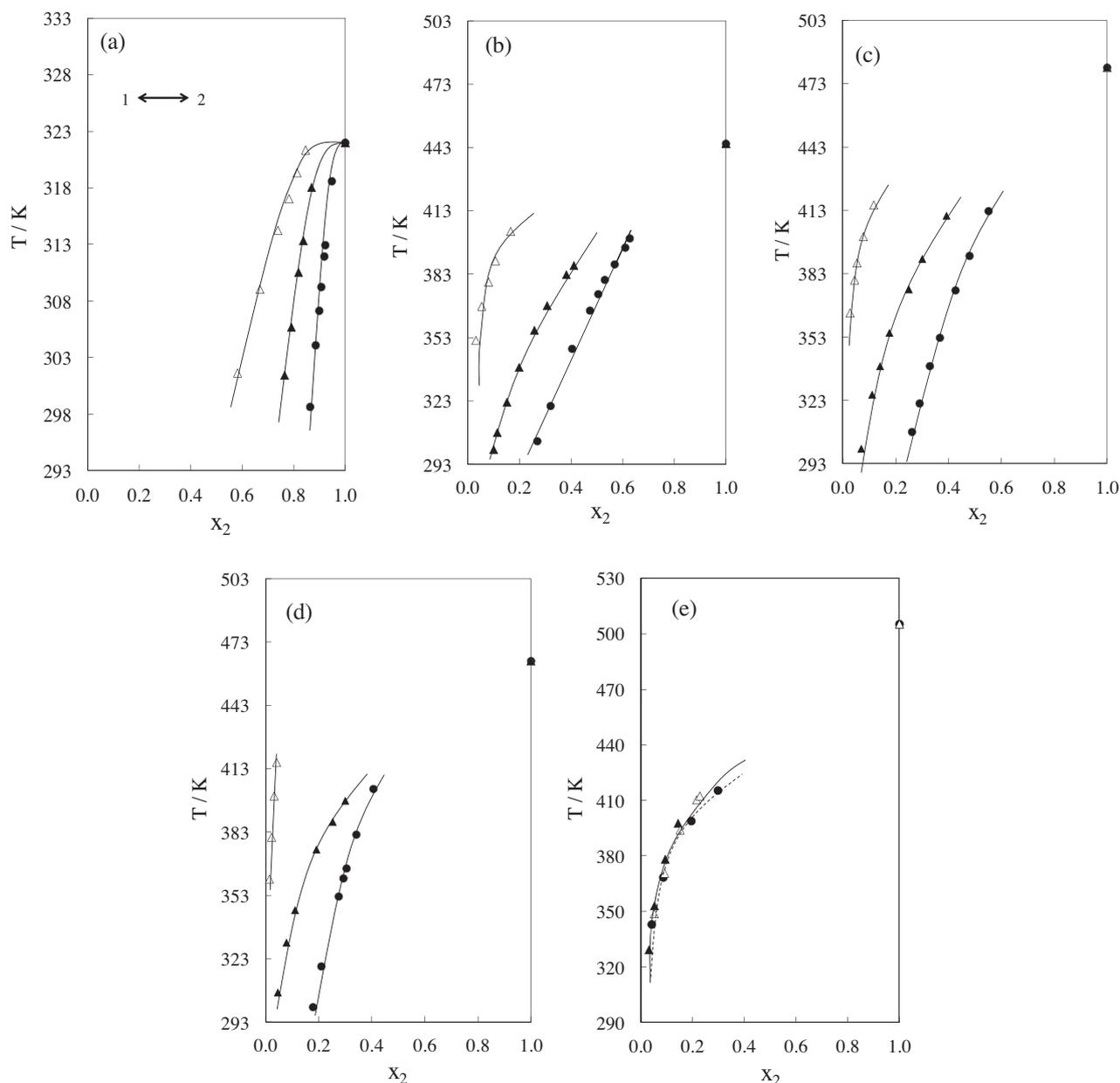
Figure 10 Temperature–composition (solid + liquid) equilibria (SLE) phase diagrams, at 0.1 MPa, for the solutions of [C$_4$mim][OTf] (filled triangles), [C$_4$mim][NTf$_2$] (hollow triangles) and PEG400 (filled circles) with the following solutes: (a) thymol; (b) ferulic acid; (c) vanillic acid; (d) caffeic acid, and (e) caffeine. X_2 stands for mole fractions of the respective high-value compound in the solution. The lines are merely guide to eye. The direction of 1 phase to 2-phase transition is shown at Fig. 10 (a) and remains the same in all the other cases (b–e).

the [OTf]$^-$ anion virtually had no impact. However, the thermodynamic analysis accomplished in the study has shown that the low solubility of the studied compounds in ionic liquids [C$_4$mim][NTf$_2$] also has strong entropic reasons behind it. On the other hand, PEG400 appeared as an excellent solvent for the four of the five studied compounds – caffeine is once more to be excluded. High polarity of this liquid polymer along with its good proton donor/acceptor abilities certainly contributed to this behavior.

It can be concluded that ionic liquids [C$_4$mim][OTf] and liquid PEG are very good alternative solvents for thymol and three phenolic acids (ferulic, vanillic and caffeic) – thus,

they can be recommended as media for possible extractions of these high-value compounds from their natural matrices. Caffeine, however, mainly due to its high melting point and zero hydrogen bond acidity, exhibited much worse solubility in these solvents.

5. Summary

This short review outlines our solubility and phase behavior studies of the solutions of ionic liquids with a number of important aliphatic and aromatic solutes different by their

physicochemical properties – polarity, hydrogen bond acidities and basicities and melting points. The impact of these properties, of ionic liquid anion selection and of intermolecular interactions on the observed behaviors is scrutinized. In this way, the current review shows the diversity and versatility of ionic liquids as alternative, environmentally acceptable solvents that can potentially be applied in separations of the studied solutes from their (aqueous) solutions or, in the case of high-value compounds, from their natural matrices.

The possibilities to use solutions of ionic liquids or ionic liquids and liquid PEG as mixed solvents – homogeneous solutions or liquid biphasic systems – with tunable solvent properties were particularly emphasized and discussed. In principle, such mixed solvents are obtained by the combination of components that have different solvent abilities toward a target molecule and water (hydrophilic/hydrophobic combination, distinct hydrophilic character and/or hydrogen bond abilities): (i) hydrophilic and hydrophobic imidazolium ionic liquid having a common cation (homogeneous mixed solvents), (ii) hydrophobic ionic liquid and hydrophilic liquid PEG (homogeneous mixed solvent or liquid biphasic system), (iii) hydrophilic ionic liquid and hydrophilic liquid PEG. The tuning is primarily achieved by changing the composition of the homogeneous mixed solvent or of the initial solution that forms a liquid biphasic system. In this way it is much more feasible to obtain the optimum efficiency of separation process – the most favorable partition coefficients of a target molecule and separation factors.

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