

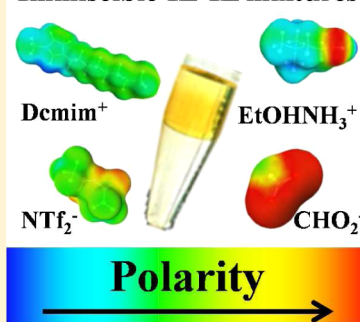
Ionic Liquid Mixtures—An Analysis of Their Mutual Miscibility

Salama Omar,[†] Jesus Lemus,[†] Elia Ruiz,[†] Víctor R. Ferro,[†] Juan Ortega,[‡] and Jose Palomar*,[†][†]Sección de Ingeniería Química (Departamento de Química Física Aplicada), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain[‡]Laboratorio de Termodinámica y Fisicoquímica de Fluidos, Parque Científico-Tecnológico, Universidad de Las Palmas de Gran Canaria, Canary Islands, Spain

S Supporting Information

ABSTRACT: The use of ionic liquid mixtures (IL–IL mixtures) is being investigated for fine solvent properties tuning of the IL-based systems. The scarce available studies, however, evidence a wide variety of mixing behaviors (from almost ideal to strongly nonideal), depending on both the structure of the IL components and the property considered. In fact, the adequate selection of the cations and anions involved in IL–IL mixtures may ensure the absence or presence of two immiscible liquid phases. In this work, a systematic computational study of the mixing behavior of IL–IL systems is developed by means of COSMO-RS methodology. Liquid–liquid equilibrium (LLE) and excess enthalpy (H^E) data of more than 200 binary IL–IL mixtures (including imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, and phosphonium-based ILs) are calculated at different temperatures, comparing to literature data when available. The role of the interactions between unlike cations and anions on the mutual miscibility/immiscibility of IL–IL mixtures was analyzed. On the basis of proposed guidelines, a new class of immiscible IL–IL mixtures was reported, which only is formed by imidazolium-based compounds.

Immiscible IL–IL mixtures



■ INTRODUCTION

Ionic liquids (ILs) are being investigated in a wide diversity of fields involving chemistry, biochemistry, electrochemistry, engineering, material science, and many other areas.¹ They are being evaluated as potential alternative solvents in practical applications due to their favorable properties: low volatility, high solvent capacity, high chemical and thermal stability, wide liquid windows, among others. As a remarkable characteristic, IL properties can be tailored by the selection of adequate cation and anion (among a large variety of ions) to obtain a solvent with specific requirements. In most cases, the design of the IL to be used as separation or reaction media is based on thermodynamics criteria. However, the selection of a cation–anion combination which simultaneously improves various design parameters (as partition coefficient and selectivity in aromatic/aliphatic separation by liquid–liquid extraction with ILs)² is not always an affordable goal. Another main constraint for the practical applications of some ILs is the unfavorable transport properties, due to their high viscosity and surface tension.

Recently, some mixtures between ILs (IL–IL) have been proposed as a possible method to improve target properties of the ILs while expanding their favorable characteristics.^{3,4} Thus, some of those IL mixtures have been used with promising results in liquid–liquid extraction,^{5–8} gas solubilities,^{9–12} dye-sensitized solar cells,^{13,14} batteries,¹⁵ solvent reaction media^{16,17} and as a gas chromatography stationary phase.¹⁸ In addition, IL–IL mixtures have been characterized in some extent, including the measurement of thermodynamic, transport, and other physicochemical properties (excess volume and en-

thalpy,^{19–22} density,^{23,24} viscosity,^{20–25} conductivity,^{21,26,27} diffusivity,^{28,29} surface tension,³⁰ and refractive index²²), spectroscopic measurements (FTIR,³¹ Raman,³² NMR,^{29,33} and UV–visible³³), solvent effects,^{23,34} and melting behaviors.^{15,21,26,29,35} For most physicochemical properties, IL–IL mixtures present an approximating predictable or “simple” mixing behavior, that is, a quasi-linear trend of property as a function of concentration between the two pure ILs.^{15,19–23,25–27,29,30} In these cases, low values of excess properties were generally found, pointing to a nearly ideal mixing behavior in IL–IL systems. However, Navia et al.²⁰ showed that IL–IL mixtures containing imidazolium-based IL compounds present moderately different excess enthalpy (H^E) features depending on the cation and anion used, ranging from endothermic ($\sim +300$ J/mol) to exothermic (~ -300 J/mol) mixing phenomena. Other authors also evidenced nonideal mixing behaviors based on the excess volume obtained.²¹ On the other hand, there have been some instances of synergetic effects by mixing two different ILs, with improved solvent properties above those of the individual components.^{9,11,26} Finally, anomalous conductivity, thermal, and melting behaviors have been reported for binary IL–IL mixtures containing, at least, two very different ionic constituents.^{15,21,23,26,29,35}

The above cited studies have been carried out with totally miscible IL–IL systems at the working temperature, obtained by mixing ILs with common cation, common anion, and two

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cations with similar structure. However, Arce et al.³⁶ reported in 2006 the discovery of mutually immiscible ILs. Certain combinations of two ILs with remarkable differences in their constituent ions give rise to immiscible IL–IL systems, splitting into two liquid phases at certain compositions and temperatures.³⁷ For example, it was found that the long chain phosphonium-based IL $[P_{66614}][NTf_2]$ (see IL constituent nomenclature in Table 1) forms an immiscible IL–IL mixture with $[Emim][NTf_2]$ at room temperature. In contrast, the

Table 1. List of Cations and Anions Studied in This Work

cation name	cation abbreviation
1,3-dimethylimidazolium	$[Mim]^+$
1-ethyl-3-methylimidazolium	$[Emim]^+$
1-propyl-3-methylimidazolium	$[Prmim]^+$
1-butyl-3-methylimidazolium	$[Bmim]^+$
1-pentyl-3-methylimidazolium	$[Pnmim]^+$
1-hexyl-3-methylimidazolium	$[Hxmim]^+$
1-heptyl-3-methylimidazolium	$[Hpimim]^+$
1-octyl-3-methylimidazolium	$[Omim]^+$
1-nonyl-3-methylimidazolium	$[Nmim]^+$
1-decyl-3-methylimidazolium	$[Dcmim]^+$
1-ethylpyridinium	$[Epy]^+$
1-butylpyridinium	$[Bpy]^+$
1-butyl-3-methylpyridinium	$[1,3Bmpy]^+$
1-butyl-4-methylpyridinium	$[1,4Bmpy]^+$
1-octyl-3-methylpyridinium	$[1,3Ompy]^+$
1-methyl-1-methylpyrrolidinium	$[Mmpyr]^+$
1-ethyl-1-methylpyrrolidinium	$[Empyr]^+$
1-propyl-1-propylpyrrolidinium	$[Prmpyr]^+$
1-butyl-1-propylpyrrolidinium	$[Bmpyr]^+$
1-pentyl-1-propylpyrrolidinium	$[Pnmpyr]^+$
1-hexyl-1-propylpyrrolidinium	$[Hxmpyr]^+$
1-(2-hydroxyethyl)-3-methylimidazolium	$[EtOHmim]^+$
2-hydroxy-ethylammonium	$[EtOHNH_3]^+$
dimethylammonium	$[Me_2NH_2]^+$
methylammonium	$[MeNH_3]^+$
butyl(trioctyl)ammonium	$[N_{8884}]^+$
tetrabutylphosphonium	$[P_{4444}]^+$
triethyl(tetradecyl)phosphonium	$[P_{66614}]^+$
anion name	anion abbreviation
bis(trifluoromethylsulfonyl)imide	$[NTf_2]^-$
hexafluorophosphate	$[PF_6]^-$
tetrafluoroborate	$[BF_4]^-$
dicyanamide	$[DCN]^-$
tetrachloroferrate	$[FeCl_4]^-$
trifluoromethanesulfonate	$[CF_3SO_3]^-$
trifluoroacetate	$[CF_3CO_2]^-$
acetate	$[CH_3CO_2]^-$
nitrate	$[NO_3]^-$
formate	$[CHO_2]^-$
bromide	$[Br]^-$
chloride	$[Cl]^-$
hydrogensulfate	$[HSO_4]^-$
methanesulfonate	$[MeSO_3]^-$
methylsulfate	$[MeSO_4]^-$
ethylsulfate	$[EtSO_4]^-$
propylsulfate	$[PrSO_4]^-$
butylsulfate	$[BuSO_4]^-$
hexylsulfate	$[HxSO_4]^-$
octylsulfate	$[OcSO_4]^-$

structurally similar $[P_{66614}][NTf_2] + [Bmim][NTf_2]$ and $[P_{66614}][Cl] + [Emim][Cl]$ binary IL–IL mixtures present only one liquid phase under these conditions. These features may expand the opportunities for the practical applications of IL–IL mixtures, for instance, for separating aromatic and aliphatic hydrocarbons by solvent extraction.³⁸ Other examples of immiscible IL–IL systems have been reported, again formed by ILs presenting remarkable different structural characteristics.^{21,36,37} MacFarlane et al. reported that the IL–IL mixture $[P_{66614}][NTf_2] + [Prmpyr][NTf_2]$ presents an immiscible window in the $[Prmpyr][NTf_2]$ -rich region, exhibiting unusual physical properties (volume, viscosity, conductivity) in its miscible mixtures with composition near the demixing line.²¹

In sum, the available information of binary IL–IL systems indicates, first, that simple mixing is not ubiquitous and, second, the properties of the IL–IL system may be significantly influenced by the selection of the ions, presenting from simple/ideal to complex/nonideal mixing behaviors with component concentrations, which depends on both the IL structures and the property considered. However, reported experimental data are still limited for a systematic analysis of the IL–IL mixing behavior as a function of the type of ions. In this context, *a priori* computational methods capable of predicting thermodynamic data of IL-based systems may be of utility. The quantum-chemical approach COSMO-RS has demonstrated to present a general suitability to describe thermodynamic properties in systems containing ILs,³⁹ including gas–liquid (GLE),^{10,40–44} vapor–liquid (VLE),^{45–49} liquid–liquid (LLE),^{50–57} and solid–liquid (SLE)^{58–60} equilibrium data. COSMO-RS has recently been applied with success to calculate the temperature–composition diagram of the binary IL–IL mixture and the LLE diagram at 298 K of a quaternary system including two different IL components.^{8,39} On the other hand, the suitability of COSMO-RS to predict the excess enthalpy (H^E) for several binary mixtures of ILs and organic solvents has also been reported.^{61,62} In addition, H^E is related to the net formation or destruction of interactions in the mixing process; therefore, H^E has been demonstrated as a valuable thermodynamic property to analyze the mixture behavior of ILs with organic compounds. Relationships between H^E values and GLE,^{40,41,44} VLE,⁶² LLE,^{53,61} and SLE⁵⁸ data have been systematically established. It was generally found that components with more exothermic mixing processes present more favorable behavior when acting as solute and separating agent in separation process. An additional advantage of the COSMO-RS method is that it estimates the contribution of the intermolecular interactions between the components to the excess enthalpy of the mixture, allowing a better understanding of the mixing behavior from a molecular point of view.

In this work, a comprehensive thermodynamic analysis of mixing behavior of IL–IL systems was performed by using the quantum-chemical COSMO-RS method. For this purpose, the suitability of COSMO-RS to predict the presence or absence of two immiscible liquid phases in IL–IL mixtures was first evaluated, through comparison with the experimental evidence (38 totally miscible and 9 partially immiscible IL–IL systems) reported in the bibliography. Two molecular models were checked to simulate the IL fluid: ion-pair structure, $[CA]$, and independent ions, $[C + A]$. In addition, the capability of COSMO-RS to describe the excess enthalpy behavior of IL–IL mixtures was checked by comparison with the available experimental data. Then, the effects of the ionic constituents on the LLE behavior of IL–IL mixtures were systematically

Table 2. Miscibility and Excess Enthalpies (H^E) at Equimolar Composition Calculated by COSMO-RS, Using the [CA] Model, at 298 K for Binary IL–IL Mixtures Reported in the Bibliography

	binary mixture IL–IL	ref	miscibility	H^E (J/mol)
1	[1,3Bmpy][BF ₄] + [1,3Bmpy][DCN]	31	total	−1115
2	[Pnmim][NTf ₂] + [Pnmim][Br]	32		−1057
3	[Emim][CF ₃ CO ₂] + [Emim][CH ₃ CO ₂]	10		−894
4	[Bmim][EtSO ₄] + [Emim][NTf ₂]	11		−664
5	[Emim][BF ₄] + [Emim][DCN]	23		−654
6	[Emim][EtSO ₄] + [Emim][NTf ₂]	11		−545
7	[Prmpyr][NTf ₂] + [Prmpyr][DCN]	28		−253
8	[Bmim][BF ₆] + [Bmim][BF ₄]	20		−245
9	[Emim][BF ₄] + [Emim][PF ₆]	8		−236
10	[Emim][EtSO ₄] + [Emim][MeSO ₃]	8		−229
11	[Bpy]BF ₄] + [1,4Bmpy][BF ₄]	6		−155
12	[Bmim][BF ₄] + [Bmim][MeSO ₄]	20		−95
13	[Pnmim][PF ₆] + [Pnmim][CF ₃ CO ₂]	32		−49
14	[P ₄₄₄₄][NTf ₂] + [Bmim][NTf ₂]	17		−26
15	[Emim][EtSO ₄] + [Emim][MeSO ₄]	8		−2
16	[Prmpyr][NTf ₂] + [Empyr][NTf ₂]	28		6
17	[Pnmim][NTf ₂] + [Bmim][NTf ₂]	30		10
18	[Prmpyr][NTf ₂] + [Bmpyr][NTf ₂]	28		11
19	[Epy][EtSO ₄] + [Epy][MeSO ₄]	8		15
20	[Hxmim][NTf ₂] + [Bmim][NTf ₂]	30		32
21	[Bpyr][NTf ₂] + [Epyr][NTf ₂]	28		45
22	[N ₈₈₈₄][NTf ₂] + [N ₈₈₈₄][NO ₃]	5		49
23	[Emim][NTf ₂] + [Bmim][NTf ₂]	37		52
24	[Bmpyr][NTf ₂] + [Mmpyr][NTf ₂]	28		54
25	[Hxmim][BF ₄] + [Bmim][BF ₄]	20		56
26	[1,3Bmpy][BF ₄] + [1,3Ompy][BF ₄]	31		87
27	[Prmpyr][NTf ₂] + [Hxmpyr][NTf ₂]	28		9
28	[Pnmpyr][NTf ₂] + [Emim][NTf ₂]	28		106
29	[Omim][NTf ₂] + [Bmim][NTf ₂]	30		126
30	[Mmim][NTf ₂] + [Bmim][NTf ₂]	30		136
31	[Pnmpyr][NTf ₂] + [Mmpyr][NTf ₂]	28		145
32	[Emim][NTf ₂] + [Hxmim][NTf ₂]	36		172
33	[Bpy][BF ₄] + [Bpy][NTf ₂]	22		173
34	[Bmim][BF ₄] + [Omim][BF ₄]	8		196
35	[Dcmim][NTf ₂] + [Bmim][NTf ₂]	30		242
36	[Pnmpyr][NTf ₂] + [Emim][NTf ₂]	28		267
37	[Hxmim][BF ₄] + [Emim][BF ₄]	20		290
38	[Bpy][BF ₄] + [1,4Bmpy][NTf ₂]	6		362
39	[Pnmim][Cl] + [P ₆₆₆₁₄][Cl]	36	partial	549
40	[Bmim][Cl] + [P ₆₆₆₁₄][Cl]	36		657
41	[Prmim][Cl] + [P ₆₆₆₁₄][Cl]	36		694
42	[Emim][Cl] + [P ₆₆₆₁₄][Cl]	36		725
43	[Mmim][Cl] + [P ₆₆₆₁₄][Cl]	36		694
44	[Emim][NTf ₂] + [P ₆₆₆₁₄][NTf ₂]	36		2157
45	[Prmpyr][NTf ₂] + [P ₆₆₆₁₄][NTf ₂]	21		2427
46	[Epy][NTf ₂] + [P ₆₆₆₁₄][NTf ₂]	37		3161
47	[Emim][MeSO ₃] + [P ₆₆₆₁₄][NTf ₂]	36		3837

studied by COSMO-RS calculations. Binary (2 IL components, 3 ionic constituents: [A][X] + [A][Y] or [A][X] + [B][X]) and reciprocal binary (2 IL components, 4 ionic constituents: [A][X] + [B][Y]) IL–IL mixtures were considered in the computational analysis, screening more than 200 mixtures including 20 anions and 28 cations from imidazolium, pyridinium, pyrrolidinium, phosphonium, and ammonium families (see Table 1). The COSMO-RS computational method allows obtaining theoretically the excess enthalpy of miscible but also mutually immiscible IL–IL mixtures, even

when this later value cannot be measured experimentally. In this work, H^E values of equimolar IL–IL mixtures were successfully related to LLE data, allowing the analysis of the different mixing behavior of IL–IL systems in terms of the interactions between their ionic constituents. Excess entropy (S^E) and activity coefficient of components for IL–IL binary mixtures were also calculated to complete the analysis. COSMO-RS screening was finally used as a guide to design IL–IL mixtures with presence or absence of two immiscible phases. As a result, new cases of mutually immiscible IL–IL

systems are reported, being for the first time found reciprocal IL–IL binary mixtures with both components belonging to the imidazolium family.

■ COMPUTATIONAL AND EXPERIMENTAL DETAILS

COSMO-RS calculations were carried out following a multistep procedure. First, the software Gaussian 03⁶³ was used for the quantum-chemical calculation to generate the COSMO files for each compound studied. For this purpose, the molecular geometry for every compound was optimized at the B3LYP/6-31++G** computational level in the ideal gas phase. Vibrational frequency calculations were performed to confirm the presence of an energy minimum. Ion pairs [CA] and independent ions [C + A] were used as molecular models to simulate IL compounds in COSMO-RS calculations. Once the molecular models were optimized, Gaussian 03 was used to compute the COSMO files. The ideal screening charges on the molecular surface for each species were calculated by the continuum solvation COSMO model using the BVP86/TZVP/DGA1 level of theory. Subsequently, the COSMO files were used as an input in the COSMOthermX⁶⁴ code to calculate the thermodynamic properties, as LLE data, activity coefficient of mixture components, and excess enthalpy and entropy of IL binary mixtures. In the COSMO-RS model, the excess enthalpy (H^E) of a binary mixture is obtained by the algebraic sum of three contributions associated with electrostatic-misfit (MF), van der Waals (vdW), and hydrogen bond (HB) intermolecular interactions. According to our chosen quantum method, we used the corresponding parametrization (BP_TZVP_C30_1201) that is required for the calculation of physicochemical data and that contains the intrinsic parameters of COSMOtherm.

The ILs used for preparing IL–IL mixtures were supplied by Io-Li-Tec (Ionic Liquid Technologies), in the highest purity available (purity >97–98%). All of the ILs were used without further purification.

¹H NMR experiments of IL–IL mixtures were recorded on a Varian Unity 500 spectrometer, using a solution of each IL phase (upper and lower phases) on deuterated acetone or water in a concentration over 10 mmol·L^{−1}.

■ RESULTS AND DISCUSSION

For the purpose of evaluating the COSMO-RS suitability to predict the mutual miscibility of two IL compounds, a wide sample of 47 IL–IL systems with remarkably different mixing behaviors was collected after thoroughly revising the literature (Table 2). Most of the studied ILs (38 IL–IL mixtures) were found to be completely soluble with each other at nearly room temperature, involving 38 binary ([A][X] + [A][Y] or [A][X] + [B][X]) and only 2 reciprocal binary ([A][X] + [B][Y]) IL–IL mixtures, with a significant variety of imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, and phosphonium-based ILs. For these cases, the LLE calculations by COSMO-RS (using ion-pair structures, [CA] model, or independent ions, [C + A] model, to simulate IL components) correctly predict the total miscibility of the two ILs in the 38 binary mixtures at 298 K. On the other hand, the nine binary system examples of mutually immiscible ILs reported in the bibliography (Table 2) are well-described by the COSMO-RS method when using the ion-pair molecular model, [CA], presenting LLE points at 298 K. On the contrary, the model of independent ions, [C + A], does not allow correctly predicting the IL immiscibility in these

nine IL–IL systems. Thus, Table S1 in the Supporting Information shows that the COSMO-RS method with the [C + A] model incorrectly predicts total miscibility for all of the [P₆₆₆₁₄][Cl]–[Xmim][Cl] binary mixtures, whereas two immiscible phases are obtained when using the [CA] model. Figure S1 of the Supporting Information collects the histogram of polarized charge for [Emim][Cl] corresponding to the [C + A] and [CA] models. [C + A] describes this IL as a more polar compound, whereas the [CA] model, since it includes the mutual cation–anion interactions to some extent, represents the IL as a less polarized structure. On the basis of the above results, current computational analysis was carried out only using the ion-pair [CA] model for COSMO-RS calculations. Figure 1 depicts the temperature–composition diagram

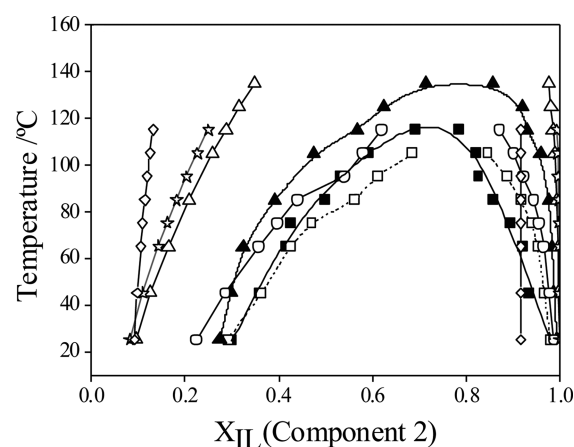


Figure 1. Temperature–composition diagram of the binary mixtures formed by the IL component 1, [P₆₆₆₁₄][NTf₂], and the IL component 2: [Emim][NTf₂] (squares); [Epy][NTf₂] (triangles); [Prmpyr][NTf₂] (circles); [Bmim][BF₄] (stars); and [Emim][MeSO₃] (rhombus). Filled and open symbols correspond, respectively, to experimental^{36,37} and COSMO-RS (using [CA] model) values.

obtained by the COSMO-RS approach for five binary IL–IL mixtures containing the common phosphonium-based IL [P₆₆₆₁₄][NTf₂] (component 1) and a second IL (component 2) belonging to different cation families (imidazolium, [Emim][NTf₂] and [Bmim][BF₄]; pyridinium, [Epy][NTf₂]; pyrrolidinium, [Epyr][NTf₂]). For comparison purposes, Figure 1 also included the experimentally available diagrams for [P₆₆₆₁₄][NTf₂] + [Emim][NTf₂] and [P₆₆₆₁₄][NTf₂] + [Epy][NTf₂] mixtures. As can be seen, the COSMO-RS method provides a reasonable qualitative description of the mixture composition dependence with equilibrium temperature. It is remarkable that the solubility of the IL named compound 2 (imidazolium-, pyridinium-, and pyrrolidinium-based IL) is much larger in the compound 1-rich phase ([P₆₆₆₁₄][NTf₂], which is an IL with marked aliphatic and nonpolar structural features) than vice versa.

Following, the excess enthalpy, H^E , of the binary IL mixtures is analyzed. Figure 2 compares the experimental and COSMO-RS predicted data of excess molar enthalpies as a function of composition at 303 K for four miscible binary IL–IL systems, using the [CA] model to simulate IL solvents: [Hxmim][BF₄] + [Emim][BF₄], [Bmim][BF₄] + [Hxmim][BF₄], [Bmim][BF₄] + [Bmim][MeSO₄], and [Bmim][BF₄] + [Bmim][BF₆]. As can be seen, the COSMO-RS method provides good predictions of the different behaviors of H^E for these experimentally studied IL mixtures. It is found that ILs with

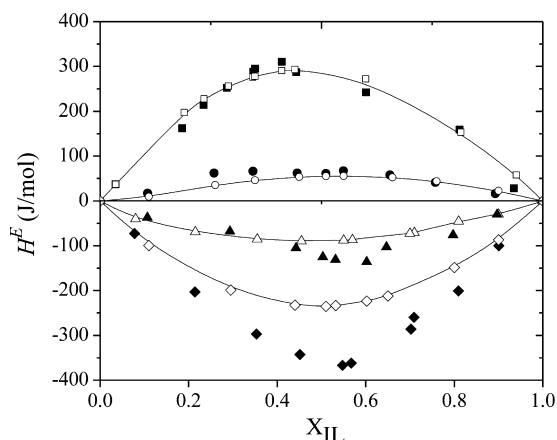


Figure 2. Comparison of experimental²⁰ (filled symbols) and COSMO-RS (open symbols) H^E as a function of the composition at 303.15 K for the binary IL–IL mixtures: $x[\text{Hxmim}][\text{BF}_4] + (1-x)[\text{Emim}][\text{BF}_4]$ (squares); $x[\text{Bmim}][\text{BF}_4] + (1-x)[\text{Hxmim}][\text{BF}_4]$ (circles); $x[\text{Bmim}][\text{BF}_4] + (1-x)[\text{Bmim}][\text{MeSO}_4]$ (rhombus); $x[\text{Bmim}][\text{BF}_4] + (1-x)[\text{Bmim}][\text{PF}_6]$ (triangles).

common anion and different lengths of alkyl chain imidazolium cation present endothermic mixing phenomena. In contrast, IL–IL binary systems with common cation and different anions provided negative H^E values. It indicates a variety of interactions between unlike anions and cations determining different excess properties of the IL–IL binary mixtures. Table 2 reports the H^E values calculated by COSMO-RS at 298 K for the equimolar mixture of the mutually miscible (38) but also for the partially immiscible (9) IL–IL systems. It is noted that for completely soluble ILs the mixing processes are endo/exothermic with estimated H^E values ranging in the interval $-1000 \leftrightarrow 400$ J/mol. However, ILs forming two immiscible phases show marked nonideal endothermic mixing phenomena, with estimations for H^E reaching values close 4000 J/mol for binary $[\text{Emim}][\text{MeSO}_3] + [\text{P}_{66614}][\text{NTf}_2]$. Figure 3 illustrates the contributions of the different intermolecular interactions [electrostatic-misfit (MF), hydrogen-bond (HB), and van der Waals (vdW)] to the total H^E values for equimolar mixtures of the 47 binary IL–IL systems collected in Table 2. All reported immiscible mixtures present the ionic liquid $[\text{P}_{66614}][\text{NTf}_2]$ or $[\text{P}_{66614}][\text{Cl}]$, which include a large phosphonium cation with main aliphatic character. COSMO-RS analysis indicates that $[\text{P}_{66614}][\text{NTf}_2]$ and $[\text{P}_{66614}][\text{Cl}]$ compounds promote strong

repulsive electrostatic interactions in the fluid with ILs containing the same anion but more polar cationic species, as imidazolium or pyridinium aromatic rings, which is well-known to contain hydrogen acidic groups. In addition, the disruption of cation–cation dispersion interactions from neat $[\text{P}_{66614}][\text{NTf}_2]$ to IL–IL fluid also contributes to the endothermicity of the mixture. In addition, Figure 3 presents the excess Gibbs energy (G^E) calculated by COSMO-RS, using the [CA] molecular model, at 298 K. The values of H^E and G^E provided by COSMO-RS indicated that the nonspontaneous mixing process for mutually immiscible IL–IL mixtures is mainly determined by endothermic enthalpic contribution. The calculated activity coefficients of both IL components in these immiscible IL–IL systems, with values higher than 1 (see Table S2 in the Supporting Information), also anticipate a nonideal mixing behavior, with strong positive deviation from Raoult's law. On the other hand, Figure 3 and Table S2 (Supporting Information) revealed that completely miscible ILs with the same common cation and different anions may lead to significant exothermic mixing phenomena, with activity coefficient values <1 , mainly related to the net creation of favorable van der Waals interactions between the anionic constituents in the IL–IL mixture in some cases (as $[\text{1,3Bmpy}][\text{BF}_4] + [\text{1,3Bmpy}][\text{DCN}]$ mixture). Attractive cation–anion electrostatic and hydrogen bonding interactions may be also promoted by mixing in these miscible IL–IL systems with common/similar cation or anion.

The computational study of mutual miscibility/immiscibility of ILs is now extended to a much wider sample of IL–IL systems, including both binary ($[\text{A}][\text{X}] + [\text{B}][\text{X}]$) and reciprocal binary ($[\text{A}][\text{X}] + [\text{B}][\text{Y}]$) mixtures. LLE equilibrium calculations by COSMO-RS were performed for 170 binary mixtures constituted by the common IL $[\text{P}_{66614}][\text{NTf}_2]$ and a second IL component, which is defined by combination of 10 imidazolium-based cations and 17 anions. Of course, some of the ILs included in this analysis present melting point >298 K (even larger than 373 K); therefore, in these cases, LLE data from COSMO-RS calculation may only indicate the tendency of the IL–IL system to form immiscible phases. Figure 4A presents the screening map of the predicted molar fraction, $X_{[\text{P}_{66614}][\text{NTf}_2]}$, for the phosphonium-based IL of reference, $[\text{P}_{66614}][\text{NTf}_2]$, in the imidazolium-based IL-rich phase. A significant number of highly immiscible and, also, completely soluble IL–IL mixtures are found. In general, $[\text{P}_{66614}][\text{NTf}_2]$ presents a higher solubility in imidazolium-based ILs with

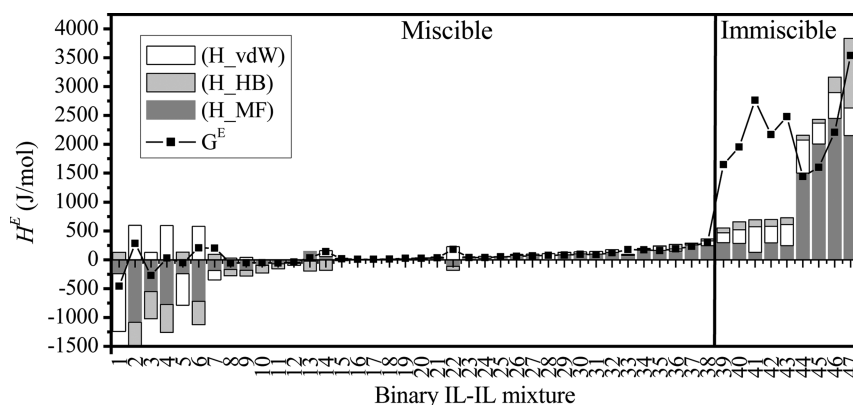


Figure 3. Description of the excess enthalpy and excess Gibbs energy of the equimolar IL–IL binary mixtures (reported in the bibliography) in terms of the intermolecular interaction contributions [$H^E(\text{MF})$, $H^E(\text{vdW})$, and $H^E(\text{HB})$] computed by COSMO-RS, using the [CA] model, at $T = 298$ K.

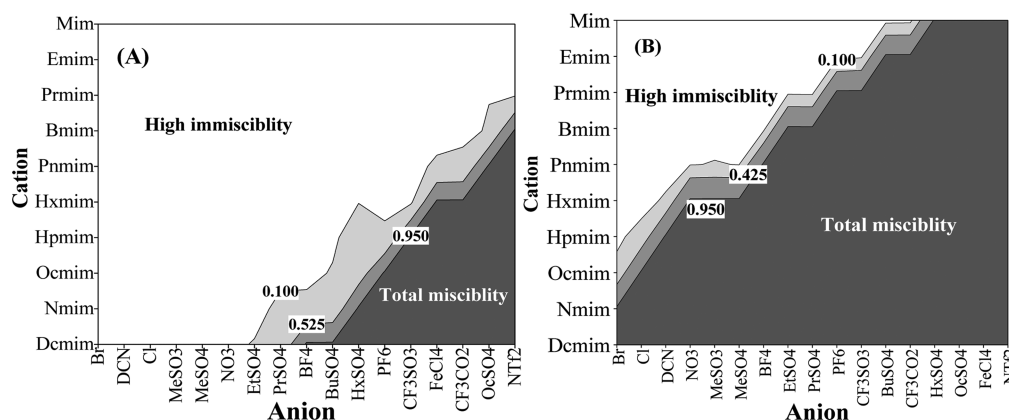


Figure 4. Screening of predicted LLE composition ($X_{[P66614][X]}$) of (A) $[P66614][NTf_2]$ and (B) $[P66614][Cl]$ in imidazolium-based IL-rich phase for 170 binary IL–IL mixtures calculated by COSMO-RS, using the [CA] model, at $T = 298$ K.

longer alkyl chains linked to the cation ring. In addition, the mutual miscibility between $[P66614][NTf_2]$ and imidazolium-based ILs is enhanced by anions presenting high size with disperse charge, as $[NTf_2]^-$, or significant aliphatic character, as $[OCSO_4]^-$. On the contrary, small cations (as $[Mmim]^+$) and anions (as $[DCN]^-$ or $[Cl]^-$), with located charge, promote the separation of two immiscible phases when mixing with $[P66614][NTf_2]$ solvent. The corresponding solubility, $X_{\text{imidazolium-based IL}}$ of imidazolium-based ILs in the $[P66614][NTf_2]$ -rich phase shows a similar trend (see Figure S2-A in the Supporting Information) but obtaining much higher equilibrium compositions of the aromatic imidazolium-based ILs in the less polar $[P66614][NTf_2]$ phase, as it was also found for IL–IL mixtures of Figure 1. In order to evaluate the effect of changing the anion nature of the phosphonium-based IL, Figure 4B (and Figure S2-B, Supporting Information) shows the COSMO-RS predicted mutual miscibility/immiscibility of IL mixtures of $[P66614][Cl]$ and the 170 imidazolium-based ILs. COSMO-RS screening indicates that $[P66614][Cl]$ presents a higher solubility in the imidazolium-based ILs than $[P66614][NTf_2]$. These results evidenced that the four ionic constituents of the IL–IL binary mixture can be selected to evolve from practically immiscible to completely soluble compounds. Figure 5A shows the COSMO-RS energetic analysis for the series of reciprocal binary IL–IL mixtures corresponding to $[P66614][NTf_2] + [\text{imidazolium-cation}][BF_4]$ in Figure 4A. The H^E values computed by COSMO-RS at 298 K for the equimolar IL–IL mixtures are compared to LLE data trends (in terms of $X_{[P66614][NTf_2]}$ mole fraction). It is obtained that increasing the length of the alkyl chain in the imidazolium cation leads to a systematic decrease of electrostatic repulsions between the components of the mixture, also presenting a progressive increase of $[P66614][NTf_2]$ solubility in the imidazolium-based IL-rich phase. The total miscibility of IL components is reached for the $[P66614][NTf_2] + [Dcmim][BF_4]$ mixture. Figure 5B shows similar relationships between H^E and $X_{[P66614][NTf_2]}$ values for the series $[P66614][NTf_2] + [Bmim][\text{anion}]$ of IL–IL systems in Figure 4A, where the anion nature of the second IL component is modified. COSMO-RS analysis indicates that the IL–IL mixing behavior significantly depends on the anion ability to establish electrostatic and hydrogen-bond interactions with other ionic species in the fluid. Thus, the solubility of $[P66614][NTf_2]$ in the imidazolium-based IL-rich phase can be increased by using an (hydrophobic) anion with strong aliphatic character or disperse charge (the cases of $[OCSO_4]^-$

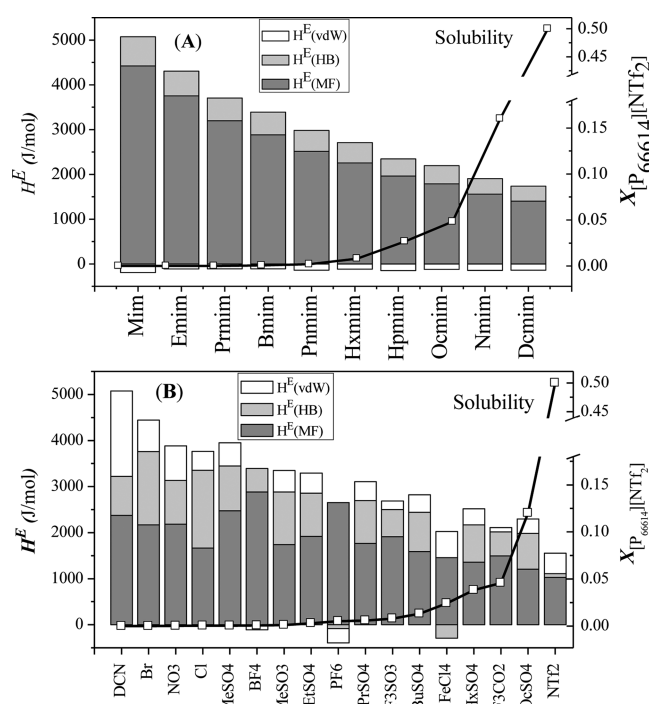


Figure 5. Analysis of the intermolecular interaction contributions to H^E of equimolar IL–IL binary mixtures formed by $[P66614][NTf_2] + [\text{imidazolium-based ILs}]$ with (A) common anion $[BF_4]$ and (B) common cation $[Bmim]$, calculated by COSMO-RS using the [CA] model at 298 K.

or $[NTf_2]^-$, respectively) but easily decreases, forming two immiscible liquid phases for most anions, which present more localized charges and polar (hydrophilic) character.

The COSMO-RS method has allowed over viewing the mutual miscibility of ILs belonging to different cation families (i.e., phosphonium vs imidazolium) but also common cation family (i.e., imidazolium vs imidazolium). The most explored application of IL–IL mixtures is currently modulating their solvent properties by mixing totally miscible imidazolium- and pyridinium-based IL compounds. In order to anticipate this case, COSMO-RS LLE screening, using the [CA] molecular model, was systematically carried out at 298 K for a series of binary ($[A][X] + [B][X]$ or $[A][X] + [A][Y]$) and reciprocal binary ($[A][X] + [B][Y]$) IL–IL mixtures, using the 17 anions and 10 cations reported in Figure 4. The results indicate that

Table 3. New Examples of Reciprocal IL–IL Binary Mixtures Presenting Two Immiscible Phases at 298 K

IL–IL Mixture	IL ₁	IL ₂	phase 1	phase 2
1	[EtOHmim][Cl]	[Dcmim][NTf ₂]	liquid/up	liquid/down
2	[EtOHNH ₃][CHO ₂]	[Dcmim][NTf ₂]	liquid/up	liquid/down
3	[Emim][Cl]	[Dcmim][NTf ₂]	solid/up	liquid/down
4	[EtOHmim][BF ₄]	[Dcmim][NTf ₂]	solid/down	liquid/up
5	[MeNH ₃][NO ₃]	[Dcmim][NTf ₂]	solid/down	liquid/up
6	[Emim][HSO ₄]	[Dcmim][NTf ₂]	liquid/down	liquid/up
7	[Emim][Br]	[Dcmim][NTf ₂]	solid/down	liquid/up
8	[Me ₂ NH ₂][NO ₃]	[Dcmim][NTf ₂]	solid/up	liquid/down
9	[EtOHNH ₃][CHO ₂]	[Omim][PF ₆]	liquid/up	liquid/down

ILs presenting an identical imidazolium cation are totally soluble with each other with independence of anion nature. The same general conclusion is achieved maintaining fixed the anion in the imidazolium-based IL–IL binary mixture and screening for different cations. Therefore, the binary mixtures, [A][X] + [B][X] or [A][X] + [A][Y], of imidazolium-based ILs are generally described as miscible by COSMO-RS. On the contrary, the COSMO-RS method predicts the existence of two immiscible liquid phases in reciprocal binary ([A][X] + [B][Y]) imidazolium-based IL–IL mixtures. They can be obtained by combining four ions with remarkably different structural features. Thus, COSMO-RS anticipates that ILs as [Dcmim][NTf₂] or [Omim][PF₆], constituted by (hydrophobic) cations and anions with nonpolar character and disperse charge, will form immiscible binary mixtures with ILs presenting small imidazolium cation ([Emim]⁺) and small anion ([Cl][−]) with located charge (hydrophilic character). Table 3 and Figure 6 collect nine new pair examples of

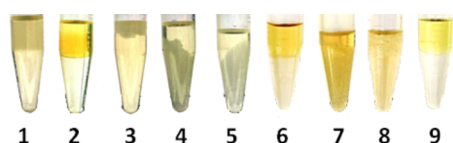


Figure 6. New immiscible reciprocal IL–IL binary mixtures reported in this work. Entry numbers given in Table 3.

mutually immiscible ILs, presenting two liquid–liquid or liquid–solid phases at 298 K. It should be remarked that five of these mixtures (mixtures 1, 3, 4, 6, and 7 of Table 3) are constituted exclusively for imidazolium-based ILs. In addition, it is also possible to apply the same rules to obtain IL–IL mixtures with two immiscible phases formed by ILs from other families (mixtures 2, 5, 8, and 9 in Figure 6). Five IL–IL mixtures in Figure 6 present one IL in solid state at 298 K, suggesting the capability of COSMO-RS to anticipate the immiscibility of IL compounds even when they do not form liquid phases at the studied temperature. ¹H NMR spectroscopy was used to assign the major IL component of both phases (Table 3) in these new immiscible IL–IL reciprocal binary mixtures.

CONCLUSIONS

This study examined the variety of mixing behaviors of binary ([A][X] + [B][X] or [A][X] + [A][Y]) and reciprocal binary ([A][X] + [B][Y]) ionic liquid mixtures by means of liquid–liquid equilibrium and excess enthalpy estimated by COSMO-RS. The results indicate that mutually miscible ILs present ionic constituents with similar structural features, leading to exothermic or well nearly ideal (excess enthalpy/Gibbs energy

near to zero) mixing phenomena. On the contrary, it is possible to obtain partially immiscible IL–IL systems by mixing four ions with remarkable structural differences ([cation aromatic] + [cation aliphatic] + [anion hydrophobic] + [anion hydrophilic]), systems rising large deviation from ideality with strong endothermic mixing phenomena. New cases of mutually immiscible ILs are reported, including examples of reciprocal IL–IL binary mixtures containing only imidazolium-based ILs, opening new challenges for practical applications of IL solvents.

ASSOCIATED CONTENT

Supporting Information

Table S1: LLE composition at 298 K predicted by COSMO-RS with different IL molecular models ([CA] and [C+A]) for the nine immiscible IL–IL mixtures reported in the bibliography. Table S2: Excess entropy and activity coefficients of IL components calculated by COSMO-RS, using the [CA] model, at 298 K for 47 binary IL–IL mixtures reported in the bibliography. Figure S1: σ -Profile of [Emim][NTf₂] obtained using [CA] and [C+A] models in COSMO-RS calculations. Figure S2: Screening of COSMO-RS predicted LLE composition of imidazolium-based IL in (A) [P₆₆₆₁₄]-[NTf₂]- and (B) [P₆₆₆₁₄][Cl]-rich phase for 170 binary equimolar mixtures at $T = 298$ K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pepe.palomar@uam.es.

Notes

The authors declare no competing financial interest.

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