Published in final edited form as:

Phys Chem Chem Phys. 2016 September 28; 18(36): 25741–25750. doi:10.1039/c6cp05372f.

Solid–liquid equilibria of binary mixtures of fluorinated ionic liquidst

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Abstract

Within ionic liquids, fluorinated ionic liquids (FILs) present unique physico-chemical properties and potential applications in several fields. However, the melting point of these neoteric compounds is usually higher due to the presence of fluorine atoms. This drawback may be resolved by, for instance, mixing different FILs to create eutectic mixtures. In this work, binary mixtures of fluoro-containing and fluorinated ionic liquids were considered with the aim of decreasing their melting temperatures as well as understanding and characterizing these mixtures and their phase transitions. Five FILs were selected, allowing the investigation of four binary mixtures, each of them with a common ion. Their solid–liquid and solid–solid equilibria were studied by differential scanning calorimetry and the non-ideality of the mixtures was investigated. Overall, a variety of solid–liquid equilibria with systems exhibiting eutectic behavior, polymorphs with solid–solid phase transitions, and the formation of intermediate compounds and solid solutions were surprisingly found. In addition to these intriguing behaviours, novel FILs with lower melting temperatures were obtained by the formation of binary systems, thus enlarging the application range of FILs at lower temperatures.

Introduction

Ionic liquids (ILs) are salts that melt below a postulated temperature of 100 °C.¹ Distinct cation–anion pair associations allow the preparation of task specific ILs leading to their definition of “designer solvents”. In addition to their tune-ability as pure fluids, this feature can be further expanded using mixtures of ILs.^{2,3} Moreover, the use of mixtures of ILs leads to the formation of eutectic mixtures,⁴ by lowering the melting temperature of these mixtures as compared to the neat compounds, thus allowing us to obtain a wider range of solvents that could be liquid at temperatures close to or below room temperature.

There are some barely known ionic liquid families such as the fluorinated ionic liquids (FILs). Herein, FILs are defined as ILs with fluorine tags equal to or longer than four carbon atoms (distinct from mere fluoro-containing ILs based on bis(trifluoromethylsulfonyl)imide, trifluoromethanesulfonate, hexafluorophosphate or tetrafluoroborate anions). Research on FILs has been reported in few works and has mainly focused on their synthesis and characterization,^{5–8} and their application as catalysts,^{9,10} lubricants,¹¹ electrolytes for electricity storage and solar or fuel cells,¹² as well as in materials.¹³ The use of FILs enables us to take unique advantages of both IL and FIL compounds: (i) highly fluorinated compounds, with outstanding chemical and biological inertness; and (ii) ionic liquids, with tuneable solvent quality, vanishing vapour pressure and greater potential. Furthermore, ILs with fluorine alkyl chains can form three nanosegregated domains (polar, nonpolar hydrogenated and nonpolar fluorinated).¹⁴ It has been shown that the presence of these distinct domains increases their surfactant behaviour, increasing their solubilisation power.¹⁵ FILs are also very appealing in relevant applications of fluorinated compounds which have an enhanced tendency to self-assemble in various media into stable, highly organized fluorinated colloids. These media are commonly used as refrigerants, surfactants, polymers, and as components of pharmaceuticals, fire retardants, lubricants, and insecticides.⁶ Moreover, fluorinated compounds are used in biomedical applications such as in liquid ventilation and artificial blood substitute formulations, as well as in drug delivery systems.¹⁶ These applications are a direct result of the unique properties of fluorinated fluids, like high solubility ability for gases and low surface tension, and their exceptional chemical and biological inertness.^{16,17}

The molecular structure of FILs is dominated by the strong C–F bond, causing the formation of a rigid structure and decreasing its polarity.¹⁸ This fact has an impact on their viscosity, melting point, density, surface tension, conductivity, solubility, liquidus range, thermal stability and hydrophobicity.¹⁹ Nevertheless, recent studies have demonstrated that their liquidus range decreases with the increasing incorporation of fluorine atoms, *e.g.* for ionic liquids based on perfluoroalkylsulfonate, perfluoroalkanoate or bis(perfluoroalkylsulfonyl)imide anions (see Table 1). Therefore, and to take advantage of the potential of FILs, the goal of this work is to find binary mixtures of FILs to increment their range of applications by decreasing their melting points by the formation of eutectic mixtures.

The literature related to ionic liquid mixtures is focused on their interactions,^{21–23} physical properties (such as densities,^{24,25} viscosities,^{24,26,27} excess volumes,^{24–28} surface tensions,^{2,29,30} diffusion coefficients³¹ and conductivities^{24,26}) mutual miscibility^{32,33} and phase behaviour,^{20,32,34–36} among others. Several mixtures of simple ILs do not show a clear freezing point and never form a crystalline phase⁴ which leads to the difficult task of determining their complete phase diagrams.^{20,31,37} Recently, another work² showed the existence of a system that exhibits a continuous solid solution which was the first IL alloy reported in the literature.² However, most systems display solid–liquid phase equilibria with common eutectic-type phase diagrams.^{2,34,38–45} This kind of phase diagram means that a eutectic physical reaction occurs as an isothermal equilibrium between a liquid phase and two (or more) different solid phases. This phenomenon is typically observed during the cooling of a mixture of salts. The advantage of using mixtures of ILs is that the melting

point may be widely decreased and it is possible to enlarge the liquid phase temperature range down to near room temperature in some cases. The right choice of the cation–anion pair in these mixtures allows the adjustment of the melting profile of the mixture by manipulating the chemical structure of the ion-pairs and their interactions, by modifying the lattice energy of the solid state.^{46,47}

In this work, we studied binary mixtures, each of them with a common ion, based on FILs and fluoro-containing ILs in order to enlarge the liquidus range of these fluids and to enrich the understanding and characterization of mixtures of ionic liquids. The examination of solid–liquid equilibria (SLE) of mixtures of FILs and that of FILs plus fluoro-containing ILs provide important information to understand fundamental aspects underlying their interactions at a molecular level. We have studied the solid–liquid phase behaviour of four binary mixtures (see Fig. 1) containing FILs with melting points higher than 361 K, namely [C₄C₁pyr][N(C₄F₉SO₂)₂][C₄F₉SO₃], [C₂C₁pyr][N(C₄F₉SO₂)₂][CF₃SO₃], [C₄C₁pyr][C₂C₁pyr][N(C₄F₉SO₂)₂] and [C₄C₁pyr][N₁₁₁₂(OH)][C₄F₉SO₃]. Table 2 depicts the melting temperatures and enthalpies of the pure compounds studied in this work. The phase diagrams for the different mixtures were obtained by differential scanning calorimetry (DSC) and were complemented using X-ray diffraction and polarized optical microscopy. The data were used to access the non-ideality of the mixtures allowing a better understanding of the interactions occurring in ILs.

Materials

Binary mixtures were prepared using the following FILs and fluoro-containing ILs: 1-butyl-1-methylpyrrolidinium nonafluorobutanesulfonate, >98% mass fraction purity, [C₄C₁pyr][C₄F₉SO₃]; 1-butyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide, >98% mass fraction purity, [C₄C₁pyr][N(C₄F₉SO₂)₂]; 1-ethyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide, >97% mass fraction purity, [C₂C₁pyr][N(C₄F₉SO₂)₂]; (2-hydroxyethyl)trimethylammonium nonafluorobutanesulfonate, >97% mass fraction purity, [N₁₁₁₂(OH)][C₄F₉SO₃]; and 1-ethyl-1-methylpyrrolidinium trifluoromethanesulfonate, 99% mass fraction purity, [C₂C₁pyr][CF₃SO₃]. All FILs and fluoro-containing ILs were acquired from IoLiTec (Heilbronn, Germany) and dried under high vacuum (10^{−5} Pa) at moderate temperature (≈323 K) and constant stirring for at least one week. This step is crucial to remove impurities and water. The water content of these salts was analysed using a Karl Fischer (Metrohm Ion analysis, 831 KF Coulometer). The water content was less than 100 ppm for all of them. No further purification was carried out and their purity was checked by ¹H, ¹³C and ¹⁹F NMR.

Experimental

Preparation of ionic liquid mixtures

To obtain the solid–liquid phase diagrams, binary mixtures were prepared inside a glove box under an Argon atmosphere, using an analytical balance, Kern AIS220-4N, with an uncertainty of ±1 × 10^{−4} g. The samples were prepared weighting a total of 0.50 g of mixtures over the whole composition range. In order to achieve full homogenization, stirring was applied at 20 K above the melting temperature of the pure IL with the highest melting

temperature, for 30 min, to ensure complete homogenization. The systems were then allowed to cool down to room temperature.

Solid–liquid phase diagrams

All solid–liquid transitions of the pure compounds and their mixtures were determined using a differential scanning calorimeter (DSC), Hitachi DSC7000X, working at atmospheric pressure. The DSC was previously calibrated with a primary calibration standard, indium, with weight fraction purities higher than 99%, and at a heating rate of 2 K min^{−1}.

Samples of about 10 mg were tightly sealed in aluminium crucibles. All compounds were subjected to three repeated cycles of cooling and heating at 2 K min^{−1} from $T = 293.15$ K to a temperature higher than the melting point (different temperatures were considered in order to leave a range of ≈ 20 –30 K between the last transition and the end of the cycle). In general, the first cycle showed slight differences in comparison with the second and the third. This is due to both the solid–solid transition temperatures and enthalpies and due to the thermal history of the sample, and thus, proper homogenization of the samples in the crucible. The properties reported herein correspond to the last two heating runs.

In order to avoid the condensation of water at the lowest temperatures inside the oven a constant nitrogen flow of 50 cm³ min^{−1} was supplied to the DSC cell. Transition temperatures were taken as the peak top values. The uncertainty of the transition temperatures and the enthalpies are taken to be ± 2 K and ± 1 kJ mol^{−1}, respectively. The melting properties of the pure compounds reported in Table 2 were obtained from similar experimental procedures.

X-ray diffraction measurements

For [C₄C₁pyr][C₂C₁pyr][N(C₄F₉SO₂)₂] and [C₄C₁pyr][N₁₁₁₂(OH)][C₄F₉SO₃] mixtures, powder X-ray diffraction analysis was performed using an Empyrean powder diffractometer (PANalytical, Almelo, Netherlands) at room temperature, with a nickel filter, Cu-K α radiation ($\lambda = 1.54180$ Å), Bragg–Brentano para-focusing optics configuration, and step-scanned in 0.04° (2 θ) at each 30 s. A standard reference material, lanthanum hexaboride powder, was used for the calibration of diffraction line positions and line shapes and determined through powder diffractometry. Pure [N₁₁₁₂(OH)][C₄F₉SO₃] was analysed at 298.15 K, 343.15 K and 408.15 K as well as the binary mixture x [C₄C₁pyr][C₄F₉SO₃] + (1 − x)[N₁₁₁₂(OH)][C₄F₉SO₃] with a mole fraction of $x = 0.24$ at 298.15 K, 368.15 K and 378.15 K.

Temperature controlled optical microscopy

Micrographs of some mixtures of the system [C₄C₁pyr][N₁₁₁₂(OH)][C₄F₉SO₃] were obtained using an Olympus BX51 light polarized microscope (Olympus Co., Tokyo, Japan) coupled with a LTS120 temperature controller (Linkam Scientific Instruments Ltd, Tadworth, UK) with a precision of 0.05 K. Approximately 1 mg of sample was placed in a conclave glass slide, covered with a lamella and sealed with thermal glue in order to improve the thermal transfer of the heating process and to avoid the adsorption of water.

Modelling and ideal behaviour assessments

The modelling of the solid–liquid equilibrium to describe the phase diagrams can be carried out using the following equation:⁴⁸

$$\ln \frac{x_i \gamma_i^L}{z_i \gamma_i^S} = \frac{\Delta_{\text{fus}} H}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) + \sum_{\text{Tr}=1}^n \left[\frac{\Delta_{\text{Tr}} H}{R} \left(\frac{1}{T_{\text{Tr}}} - \frac{1}{T} \right) \right] + \frac{\Delta_{\text{fus}} C_p}{R} \left(\frac{T_{\text{fus}}}{T} - \ln \frac{T_{\text{fus}}}{T} - 1 \right) \quad (1)$$

where x_i and z_i are the mole fractions of the component i in the liquid and solid phases, respectively; γ_i^L and γ_i^S are the activity coefficients of the component i in the liquid and solid phases, respectively; T is the melting temperature (K) of the mixture; R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T_{fus} and $\Delta_{\text{fus}} H$ are the melting temperature (K) and the enthalpy (J mol^{-1}) of component i ; T_{Tr} and $\Delta_{\text{Tr}} H$ are the thermal transitions temperatures (K) and enthalpies (J mol^{-1}) of the n solid–solid transitions of the component i ; and $\Delta_{\text{fus}} C_p$ is the heat capacity change on fusion ($\text{J mol}^{-1} \text{ K}^{-1}$) of component i at the melting temperature, T_{fus} .

As the absolute values of the $\Delta_{\text{fus}} C_p$ are small as compared with $\Delta_{\text{fus}} H$,^{49,50} the term related to the heat capacity can normally be ignored as discussed elsewhere.^{51,52} Moreover, if the compound presents no polymorphic forms, the term related to them is not applied. Thus, the following equation can be used to describe the solid–liquid equilibrium of the investigated mixtures:

$$\ln \frac{x_i \gamma_i^L}{z_i \gamma_i^S} = \frac{\Delta_{\text{fus}} H}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) \quad (2)$$

Additionally, if one considers a simple eutectic behaviour, where the pure compounds are immiscible in the solid phase, the term associated with the non-ideality of the component i in the solid phase is taken as $z_i \gamma_i^S = 1.0$. Thus, the following equation can be used:

$$\ln x_i \gamma_i^L = \frac{\Delta_{\text{fus}} H}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) \quad (3)$$

Results and discussion

In this work, four binary mixtures using five different ILs—namely 1-butyl-1-methylpyrrolidinium nonafluorobutanesulfonate, $[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3]$, 1-butyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide, $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$, 1-ethyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide, $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$, (2-hydroxyethyl)trimethylammonium nonafluorobutanesulfonate, $[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$, and 1-ethyl-1-methylpyrrolidinium trifluoromethanesulfonate, $[\text{C}_2\text{C}_1\text{pyr}][\text{CF}_3\text{SO}_3]$ —were

studied in order to understand the solid–liquid equilibria or phase behaviour of these systems. Detailed experimental data are shown in Tables S1–S4 of the ESI.†

The SLE phase diagrams of each binary mixture were built from DSC data. The binary mixtures investigated show three different types of SLE behaviour. As discussed below, two of the systems—namely $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{CF}_3\text{SO}_3]$ —exhibit a eutectic type phase behaviour. The eutectic points are below 373 K but none of these mixtures presented a eutectic point below room temperature. The other two binary systems show interesting phase behaviour, including the formation of an intermediate compound for the binary mixture of $[\text{C}_4\text{C}_1\text{pyr}][\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$ with solid–solid phase transitions as well as the formation of a continuous solid solution for the system $[\text{C}_4\text{C}_1\text{pyr}][\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$.

Eutectic type phase diagrams

The phase diagrams for the binary mixtures $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{CF}_3\text{SO}_3]$ are displayed in Fig. 2. These mixtures present eutectic profiles with partial miscibility close to the pure compounds, as confirmed by the Tamman plots (Fig. S1 and S2 in the ESI†). The eutectic point occurs around 305 K for $x_{[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]} = 0.48$ for the system $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$ and close to 357 K for $x_{[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]} = 0.38$ for the system $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{CF}_3\text{SO}_3]$. These compositions were further confirmed by the analysis of the Tamman plots, being in close agreement.

In order to evaluate the non-ideality of the systems studied, the activity coefficients of the liquid phase were calculated for both binary systems. The results obtained are depicted in Fig. 3. The activity coefficients were calculated using two approaches: (i) using eqn (2), *i.e.* considering that the solid phase is considered partially soluble; and (ii) using eqn (3), *i.e.* considering that the solid phase is immiscible and thus the liquid phase activity coefficients can be calculated from the experimental data. The activity coefficients were calculated by the correlation of the experimental data with the Margules 3-suffix equation (parameters are presented in the caption to Fig. 2).

The results obtained show that when the partial miscibility is not considered, the activity coefficients calculated (Fig. 3, symbols) present small positive deviations, *i.e.* unfavourable interactions are occurring in both binary mixtures ($[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{CF}_3\text{SO}_3]$). However, when the partial miscibility of the solid phase is accounted for (Fig. 3, continuous line) and the activity coefficients are calculated by using the Margules 3-suffix equation, different behaviours are obtained. For the system $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$, a negative deviation to the ideal behaviour is observed. This is in agreement with the formation of solid solutions, for which the compounds must present favourable interactions. For the system $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{CF}_3\text{SO}_3]$, however, two different behaviours were observed. At the left hand side of the diagram, where few or no solid solutions were observed (Fig. 2b), the activity coefficient calculated using both approaches was the same, showing its real tendency to be in an immiscible condition at the solid phase. Also, the activity coefficient for $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ calculated using the Margules equation showed a high positive deviation, which also agrees

with the immiscibility assumption. At the right hand side of the diagram, the deviation calculated using the Margules equation is lower than the experimental ones. Also, the positive deviation for $[\text{C}_2\text{C}_1\text{pyr}][\text{CF}_3\text{SO}_3]$ is lower than that for the other compound in the left hand side of the diagram. Both observations agree with the formation of solid solutions, in which the decrease of the positive deviations reveals favourable interactions in this region of the phase diagram.

The density and dynamic viscosity of mixtures close to the eutectic point for the binary system $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2][\text{C}_4\text{F}_9\text{SO}_3]$ were determined in order to better characterize this mixture. The experimental results are reported in the ESI.†

$[\text{C}_4\text{C}_1\text{pyr}][\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$: a binary system with solid solution

The SLE diagram for the binary mixture $[\text{C}_4\text{C}_1\text{pyr}][\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ is presented in Fig. 4, revealing their complete miscibility in the solid phase. This means that the melting point of $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ decreases with the addition of $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ and that of $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$, unlike observed in eutectic systems, is increased by the addition of $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$. This behaviour, although very unusual for solid phases of organic compounds, has been previously observed in other mixtures of ionic liquids.² This profile, *i.e.* continuous solid solution behaviour, is observed in systems where the ions are replaced by others that are similar in size and that do not change the crystal behaviour of the compounds, as is the case of this binary system where the $[\text{C}_2\text{C}_1\text{pyr}]^+$ cation is replaced by the $[\text{C}_4\text{C}_1\text{pyr}]^+$ cation. The thermograms obtained by DSC for this binary mixture are illustrated in Fig. S5 of the ESI.†

The structure of the solid phase was confirmed by X-ray diffraction measurements, shown in Fig. 5. When a solid solution is present, the two compounds crystallize in the same crystalline cell and the solid phase is a monophasic system. Fig. 5 shows very similar diffractograms for the two compounds, suggesting a similar crystal structure. In this system, the $[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ is incorporated into the $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$ crystalline structure as a guest due to the high similarity of their molecular structures.

$[\text{C}_4\text{C}_1\text{pyr}][\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$: a binary system with solid–solid phase transitions and intermediate compound formation

The most complex phase diagram obtained in this work is for the mixture of $[\text{C}_4\text{C}_1\text{pyr}][\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$. The respective phase diagram is depicted in Fig. 6. The full line shows our interpretation of phase transitions in this system. Given its complexity no attempt to model this system was done. The complex nature of this binary system is directly related to the nature of the studied ionic liquids, with $[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$ presenting several polymorphic forms as reported in Table 2 and represented in Fig. 6. Moreover, the formation of an intermediate compound was observed at the composition of $x_{[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3]} = 0.33$. The compound was denominated A_2B as it results from the combination of two ion pairs of $[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$ and one ion pair of $[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3]$. A small region with partial solubility (region $\alpha_{\text{s.s.}}$) of polymorph α of the $[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$ ionic liquid (α_{A}) and the intermediated compound A_2B is postulated as described in the phase diagram. Furthermore, phase transitions between polymorphs β and γ of the $[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$

ionic liquid are represented by the horizontal line ($\gamma_A \leftrightarrow \beta_A$ at the isothermal line of 400 K). On the other hand, this phase diagram shows the eutectoid reaction upon cooling of polymorph β (one solid) $\rightarrow \alpha_{s.s.} + A_2B$ (two solid phases). In this region of the phase diagram, a clear solid–solid phase transition can be observed which was confirmed by polarized optical microscopy. The optical micrographs presented in Fig. 6 were obtained at the points corresponding to the grey lines shown in the phase diagram and clearly support the interpretation proposed. The optical micrographs at $C_{0.15}$ show only a solid phase at all temperatures, while $C_{0.24}$ at the highest temperature shows a mixture of polymorph solid β along with a liquid phase. Finally, a possible eutectic reaction upon cooling of one liquid $\rightarrow A_2B + B$ (two solid phases) is observed at $x_{[C_4C_1pyr][C_4F_9SO_3]} \cong 0.95$.

The X-ray diffractograms represented in Fig. 7 demonstrate the formation of an intermediate compound at around $x_{[C_4C_1pyr][C_4F_9SO_3]} = 0.33$. Once again, X-ray diffraction measurements have helped to understand the mechanism of crystallization of these mixtures and support the idea of the presence of an intermediate compound A_2B .

An X-ray study in which the temperature was varied was also carried out and the results are plotted in Fig. 8. The crystalline structure of the pure $[N_{1112}(OH)][C_4F_9SO_3]$ changes with temperature. This fact supports the polymorphs reported in Table 2 and Fig. 6. In the diffractogram for the mixture $x_{[C_4C_1pyr][C_4F_9SO_3]} = 0.24$ (see Fig. 8), some peaks decrease their intensity along with an increase in temperature confirming the phase transitions shown in the phase diagram (see Fig. 6).

Conclusions

In this work, the solid–liquid phase behaviour of four binary mixtures composed of fluorinated and fluoro-containing ionic liquids was investigated. The four studied binary systems have shown diverse types of solid–liquid equilibria. The mixtures $[C_4C_1pyr][N(C_4F_9SO_2)_2][C_4F_9SO_3]$ and $[C_2C_1pyr][N(C_4F_9SO_2)_2][CF_3SO_3]$ have shown a quasi-ideal eutectic behaviour. However, a eutectic point was not found for the mixture constituted of $[C_4C_1pyr][C_2C_1pyr][N(C_4F_9SO_2)_2]$, and where a solid solution was identified instead. On the other hand, an intermediate compound at about $x = 0.33$ of $[C_4C_1pyr][C_4F_9SO_3]$ was found for the mixture $[C_4C_1pyr][N_{1112}(OH)][C_4F_9SO_3]$. Moreover, the last binary system presents solid–solid transitions with a eutectoid point at around $x = 0.15$ of $[C_4C_1pyr][C_4F_9SO_3]$. X-ray diffraction analysis for the binary systems with non-ideal behaviour confirmed the complete miscibility for the binary system $[C_4C_1pyr][C_2C_1pyr][N(C_4F_9SO_2)_2]$ and the molecular structures of the intermediate compound in the binary system $[C_4C_1pyr][N_{1112}(OH)][C_4F_9SO_3]$. In addition to these intriguing behaviours, novel fluorinated ionic liquids with lower melting temperatures were found by mixing high-melting temperature FILs, thus enlarging the range of ILs that can be used at lower temperatures for target applications.

Supplementary Material

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Acknowledgements

The authors wish to acknowledge FCT/MCTES (Portugal) for the financial support through FCT Investigator 2014 of Ana B. Pereiro and through projects PTDC/QUE-EPR/5841/2014 and UID/Multi/04551/2013. This work was developed in the scope of the project CICECO-Aveiro Institute of Materials POCI-01-0145-FEDER-007679, UID/CTM/50011/2013, financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. Mara G. Freire acknowledges the European Research Council (ERC) for the Starting Grant ERC-2013-StG-337753. Guilherme J. Maximo thanks FAPESP (2014/03992-7).

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Fig. 1.

Matrix of the binary systems, each of them with a common ion, composed of fluorinated ionic liquids and fluoro-containing ionic liquids studied in this work.

Fig. 2.

Solid–liquid phase diagram (temperature *versus* mole fraction) for: (a) the mixture $x[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2] + (1-x)[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3]$; and (b) the mixture $x[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2] + (1-x)[\text{C}_2\text{C}_1\text{pyr}][\text{CF}_3\text{SO}_3]$. Solid–liquid transition (○) and eutectic thermal transitions (●) obtained by DSC. Modelling results using eqn (2) and Margules 3-suffixes for activity coefficient calculations (A) $A_{ij} = [-1.5; 0.5] \text{ kJ mol}^{-1}$, $B_{ij} = [6.0; -0.5] \text{ kJ mol}^{-1}$; (B) $A_{ij} = [3.0; -1.8] \text{ kJ mol}^{-1}$, $B_{ij} = [12.0; -4.0] \text{ kJ mol}^{-1}$. A_{ij} = liquid phase parameters, B_{ij} = solid phase parameters. The dashed lines are only a guide to the eye.

Fig. 3.

Activity coefficient for the mixtures: (a) $x[C_4C_1pyr][N(C_4F_9SO_2)_2] + (1-x)[C_4C_1pyr][C_4F_9SO_3]$; and (b) $x[C_2C_1pyr][N(C_4F_9SO_2)_2] + (1-x)[C_2C_1pyr][CF_3SO_3]$ versus mole fraction. Symbols are for activity coefficients calculated using experimental data and using eqn (3). Continuous lines are for activity coefficients calculated by the Margules 3-suffix model, considering eqn (2). Open circles and gray lines are for compound 1. Crosses and black lines are for compound 2.

Fig. 4. Solid-liquid phase diagram of the mixture $x[C_4C_1pyr][N(C_4F_9SO_2)_2] + (1-x)[C_2C_1pyr][N(C_4F_9SO_2)_2]$, temperature *versus* mole fraction of $[C_4C_1pyr][N(C_4F_9SO_2)_2]$. Solid-liquid transition obtained by DSC (○). Modelling results (solid line) using eqn (2) and Margules 3-suffixes: $A_{ij} = [-0.600; -0.200]$ kJ mol⁻¹ and $B_{ij} = [0.600; -0.500]$ kJ mol⁻¹. A_{ij} = liquid phase parameters and B_{ij} = solid phase parameters.

Fig. 5. X-ray diffractograms for the binary system $x[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2] + (1-x)[\text{C}_2\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$. The numbers on the right hand side represent the mole fraction of $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$.

Fig. 6. Solid-liquid phase diagram of the mixture $x[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3] + (1-x)[\text{N}_{1112}(\text{OH})][\text{C}_4\text{F}_9\text{SO}_3]$, temperature *versus* mole fraction of $[\text{C}_4\text{C}_1\text{pyr}][\text{C}_4\text{F}_9\text{SO}_3]$. Solid-liquid transition (○), eutectic and eutectic thermal transitions (●), and solid-solid transitions (+) and (×), obtained by DSC. The solid line and dashed lines (area with higher uncertainty) represent the interpretation of the diagram. $A_{0.15}$, $B_{0.15}$ and $C_{0.15}$ are polarized optical microscopy images of the solid-solid transitions depicted in the diagram for a mole fraction

of 0.15. $A_{0.24}$, $B_{0.24}$ and $C_{0.24}$ are polarized optical microscopy images of the solid–solid transitions depicted in the diagram for a mole fraction of 0.24.

Fig. 7.
X-ray diffractograms for the binary system $x[C_4C_1pyr][C_4F_9SO_3] + (1 - x)[N_{1112(OH)}][C_4F_9SO_3]$. The numbers on the right hand side represent the mole fraction of $[C_4C_1pyr][C_4F_9SO_3]$.

Fig. 8. X-ray diffractograms of: (a) pure $[N_{1112}(OH)][C_4F_9SO_3]$ at 408.15 K, 343.15 K and 298.15 K; and (b) the binary mixture $[C_4C_{1pyr}][C_4F_9SO_3] + [N_{1112}(OH)][C_4F_9SO_3]$ at $x_{[C_4C_{1pyr}][C_4F_9SO_3]} = 0.24$ for the temperatures 378.15 K, 368.15 K and 298.15 K.

Table 1Melting temperature, T_{fus} , of fluorinated ionic liquids and fluoro-containing ionic liquids

Name/abbreviation	T_{fus}/K	Reference
1-Ethyl-3-methylimidazolium perfluoromethanesulfonate $[\text{C}_2\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]$	260	7
1-Ethyl-3-methylimidazolium perfluorobutanesulfonate $[\text{C}_2\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$	293	7
1-Ethyl-3-methylimidazolium perfluorooctanesulfonate $[\text{C}_2\text{C}_1\text{im}][\text{C}_8\text{F}_{17}\text{SO}_3]$	368	7
1-Ethyl-3-methylimidazolium perfluoroethanoate $[\text{C}_2\text{C}_1\text{im}][\text{CF}_3\text{CO}_2]$	255	7
1-Ethyl-3-methylimidazolium perfluoropentanoate $[\text{C}_2\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{CO}_2]$	278	7
1-Methyl-3-octylimidazolium perfluoroethanoate $[\text{C}_8\text{C}_1\text{im}][\text{CF}_3\text{CO}_2]$	279	7
1-Methyl-3-octylimidazolium perfluoropentanoate $[\text{C}_8\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{CO}_2]$	297	7
1-Butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{FSO}_2)_2]$	255	20
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{CF}_3\text{SO}_2)_2]$	266	20
1-Butyl-1-methylpyrrolidinium bis(pentafluoroethylsulfonyl)imide $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_2\text{F}_5\text{SO}_2)_2]$	280	20
1-Butyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide $[\text{C}_4\text{C}_1\text{pyr}][\text{N}(\text{C}_4\text{F}_9\text{SO}_2)_2]$	371	8

Table 2

Chemical structures, solid–solid transitions, T_{Tr} , melting points, T_m , enthalpies of fusion, $_{fus}H$ and molecular weight, M_w , of the fluorinated and fluoro-containing ionic liquids studied in this work

Name/abbreviation	Chemical structure
1-Butyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide [C ₄ C ₁ pyr][N(C ₄ F ₉ SO ₂) ₂] $T_m = 374\text{ K}$ $_{fus}H = 6\text{ kJ mol}^{-1}$ $M_w = 722.38\text{ g mol}^{-1}$	Compound A
1-Butyl-1-methylpyrrolidinium nonafluorobutanesulfonate [C ₄ C ₁ pyr][C ₄ F ₉ SO ₃] $T_m = 361\text{ K}$ $_{fus}H = 13\text{ kJ mol}^{-1}$ $M_w = 441.35\text{ g mol}^{-1}$	Compound B
2-(Hydroxyethyl)trimethylammonium nonafluorobutanesulfonate [N ₁₁₁₂ (OH)][C ₄ F ₉ SO ₃] $T_{Tr} = 378\text{ K}$ 406 K $T_m = 449\text{ K}$ $_{fus}H = 3.7\text{ kJ mol}^{-1}$ $M_w = 403.22\text{ g mol}^{-1}$	Compound C
1-Ethyl-1-methylpyrrolidinium bis(nonafluorobutylsulfonyl)imide [C ₂ C ₁ pyr][N(C ₄ F ₉ SO ₂) ₂] $T_m = 431\text{ K}$ $_{fus}H = 7.9\text{ kJ mol}^{-1}$ $M_w = 694.32\text{ g mol}^{-1}$	Compound D
1-Ethyl-1-methylpyrrolidinium trifluoromethanesulfonate [C ₂ C ₁ pyr][CF ₃ SO ₃] $T_m = 384\text{ K}$ $_{fus}H = 6.7\text{ kJ mol}^{-1}$ $M_w = 263.13\text{ g mol}^{-1}$	Compound E