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Aqueous biphasic systems composed of ionic liquids and acetate-based salts: phase diagrams, densities and viscosities

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Abstract

Ionic-liquid-based aqueous biphasic systems (IL-based ABS) have been largely investigated as promising extraction and purification routes. In this context, the determination of their phase diagrams and the physical properties of the coexisting phases are of high relevance when envisaging their large-scale applications. Low viscosities improve the mass transfer and reduce energy consumptions, while the knowledge on their densities is important for the equipment design. In this work, novel phase diagrams for aqueous solutions of imidazolium-based ILs combined with acetate-based salts, namely KCH_3CO_2 or NaCH_3CO_2 , are reported and discussed. The ability of the acetate-based salts to induce the phase separation not only depends on the ions hydration energy, but also on the concentration of “free” ions in solution. The tie-lines, tie-line lengths and critical points are also addressed. Experimental measurements of density and viscosity of the coexisting phases, for the different systems and at several compositions and temperatures, are additionally presented. The Othmer–Tobias and Bancroft equations are also applied to ascertain on the tie-lines coherence. It is here shown that low-viscous IL-based ABS, with a high difference in the densities of the coexisting phases, can be formed with organic and biodegradable salts thus offering enhanced features over conventional polymer-based systems.

Introduction

Aqueous biphasic systems (ABS) have been investigated for the replacement of volatile and hazardous organic compounds in liquid-liquid extraction processes.^{1–4} Typical ABS consist in two aqueous-rich phases containing polymer/polymer, polymer/salt or salt/salt combinations.⁵ In the last decade, ionic-liquid-(IL)-based ABS appeared as a novel alternative to polymer-rich systems due to their enhanced performance in extraction and purification approaches.^{5, 6} In fact, the use of ILs as phase-forming components of ABS permits the tuning of the polarities and affinities of the coexisting phases and improved extractions and selectivities can be foreseen.⁵

Reliable thermophysical data of pure ILs and their mixtures are of paramount relevance for supporting their industrial applications.^{7–10} These data are required in the development of models for process design, energy efficiency, and control of chemical processes.⁷

Anticipating the use of IL-based ABS at a large scale, in addition to the knowledge of their

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phase diagrams and compositions of the coexisting phases, the density and viscosity are also pertinent properties. Low viscosities of the coexisting phases enhance the mass transfer and reduce the energy consumption, while densities are important for the equipment design. Although a large number of publications reporting the phase diagrams of IL-based ABS can be found,⁵ few of them report the thermophysical properties of their coexisting phases.^{11–14}

In literature, most works addressing IL-based ABS have considered high-charge density inorganic salts due to their strong salting-out character.⁵ Nevertheless, the high concentrations of these salts required to form two-phase systems may have some adverse effects upon the (bio)molecules being purified and also lead to environmental concerns. Organic salts, known for their lower toxicity and favorable biodegradability, can also form ABS when combined with ILs in aqueous solutions. Despite these advantages, few works on IL-based ABS formed by organic salts are available.^{15–22} The ability of citrate-, tartrate- and acetate-based salts to induce ABS with ILs has been reported.^{15–22} However, acetate-based salts were only tested with [BF₄]-based ILs,^{18–20} which are non-stable in water even at room temperature,²³ and with [CF₃SO₃]-based compounds.²⁰

In this work, a set of imidazolium-based ILs with ability to induce ABS formation when in presence of sodium or potassium acetate salts, namely 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄mim][CF₃SO₃]), 1-butyl-3-methylimidazolium thiocyanate ([C₄mim][SCN]), and 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][N(CN)₂]), were selected. The ternary phase diagrams at 298 K, as well as the respective tie-lines (TLs) and tie-line lengths (TLLs), were determined. As it will be shown, the ability of the acetate-based salts to induce the phase separation not only depends on their respective hydration energy, but also on the concentration of “free” ions in solution. In addition, the TLs were also validated using the Othmer-Tobias and Bancroft equations.^{24, 25} Finally, the physical properties of the coexisting phases, namely density and viscosity, were characterized to gather a broader picture on the applicability of these systems.

Experimental Section

Materials

Potassium acetate, KCH₃CO₂, 99 wt % of purity from Sigma-Aldrich, and sodium acetate, NaCH₃CO₂, 99 wt % of purity from VWR, were used as received. Several imidazolium-based ILs, namely 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄mim][CF₃SO₃]), 1-butyl-3-methylimidazolium thiocyanate ([C₄mim][SCN]), and 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][N(CN)₂]), acquired from Iolitec and with a purity level > 98 wt %, were investigated. The cation and anion chemical structures of the studied ILs are displayed in Figure 1. It should be highlighted that other ILs were investigated to form ABS with KCH₃CO₂ and NaCH₃CO₂, namely 1-butyl-3-methylimidazolium bromide ([C₄mim]Br), 1-butyl-3-methylimidazolium methylsulfate ([C₄mim][CH₃SO₄]), 1-butyl-3-methylimidazolium ethylsulfate ([C₄mim][C₂H₅SO₄]), 1-butyl-3-methylimidazolium tosylate ([C₄mim][TOS]), 1-butyl-3-methylimidazolium octylsulfate ([C₄mim][C₈H₁₇SO₄]), 1-hexyl-3-methylimidazolium chloride ([C₆mim]Cl), 1-methyl-3-octylimidazolium chloride ([C₈mim]Cl), 1-butyl-1-methylpiperidinium chloride

([C₄mipip]Cl), 1-butyl-1-methylpyrrolidinium chloride ([C₄mpyr]Cl), 1-butyl-3-methylpyridinium chloride ([C₄mpy]Cl), tetrabutylphosphonium chloride ([P₄₄₄₄]Cl), tetrabutylammonium chloride ([N₄₄₄₄]Cl), tributylmethylphosphonium tosylate ([P₄₄₄₁][TOS]), tributylmethylphosphonium ethylsulfate ([P₄₄₄₁][C₂H₅SO₄]) and tributylethylphosphonium diethylphosphate ([P₄₄₄₂][(C₂H₅)₂PO₂]). Nevertheless, these ILs were not able to undergo liquid-liquid demixing with the acetate-based salts investigated. Before use, ILs samples were purified and dried for a minimum of 24 h at constant agitation, at a moderate temperature (≈ 353 K), and under vacuum. After this step, the purity of each IL was further confirmed using ¹H, ¹³C and ¹⁹F (whenever applicable) NMR spectroscopy. The water employed was ultra-pure water, double distilled, and treated with a Milli-Q plus 185 water purification device.

Phase diagrams, tie-lines, tie-line lengths and critical points

The binodal curve of each ternary phase diagram was determined through the cloud point titration method at (298 ± 1) K and at atmospheric pressure. The experimental procedure adopted was validated by us in a previous work.²⁶ In brief, aqueous solutions of the acetate salts (≈ 25 wt %) and aqueous solutions of ILs with variable concentrations (from 60 to 80 wt %) were prepared gravimetrically ($\pm 10^{-4}$ g) and used for the determination of the saturation curves. Drop-wise addition of the aqueous salt solution to each IL aqueous solution was carried out until the detection of a cloudy solution (biphasic region), followed by the drop-wise addition of ultra-pure water until the detection of a limpid solution (monophasic regime). In some situations, the addition of the IL solution to the salt-rich medium was also carried out to complete the phase diagrams. These additions were carried out under constant agitation. Each mixture composition was determined by the weight quantification of all components added within $\pm 10^{-4}$ g.

The TLs of the system [C₄mim][CF₃SO₃] + NaCH₃CO₂ were determined analytically (by quantifying the IL by UV spectroscopy, the water gravimetrically by evaporation down to a constant weight and the salt by weight difference), while the TLs of the systems [C₄mim][SCN] + NaCH₃CO₂, [C₄mim][CF₃SO₃] + KCH₃CO₂, [C₄mim][SCN] + KCH₃CO₂ and [C₄mim][N(CN)₂] + KCH₃CO₂ were determined by a gravimetric method originally described by Merchuk et al.²⁷ The method described by Merchuk et al.,²⁷ commonly applied to describe the binodal data of ABS, is not able to correctly describe TLs highly concentrated in IL and salt.²⁸ Some problems were found in the application of this method to the aqueous system formed by [C₄mim][CF₃SO₃] and NaCH₃CO₂, where no consistency of the TLs' data was found, maybe due to the highly hydrophobicity of this IL which implies an IL-rich phase with a low water content. The selected mixture, at the biphasic regime, was prepared by weighting the appropriate amounts of salt + IL + water, vigorously stirred, and further submitted to centrifugation for 30 min and at controlled temperature, (298 ± 1) K. After centrifugation, each phase was carefully separated and weighted. For the first situation, the quantification of each compound in each phase was determined as described before. For the gravimetric method approach, each individual TL was determined by the application of the lever-arm rule to the relationship between the weight of the top and bottom phases and the overall system composition. The experimental binodal curves were fitted using Equation 1,²⁷

$$100w_{IL} = A \exp[(B \times 100w_{salt}^{0.5}) - (C \times 100w_{salt}^3)] \quad (1)$$

where $100w_{IL}$ and $100w_{salt}$ are the IL and salt weight fraction percentages, respectively, and A , B and C are fitted parameters obtained by least-squares regression.

For the determination of the TLs through the gravimetric approach, the following system of four equations (Equations 2 to 5) was used to estimate the composition of each phase

(namely, $100w_{IL}^{IL}$, $100w_{salt}^{IL}$, $100w_{IL}^{salt}$ and $100w_{salt}^{salt}$):²⁷

$$100w_{IL}^{IL} = A \exp \left[(B \times 100w_{salt}^{IL 0.5}) - (C \times 100w_{salt}^{IL 3}) \right] \quad (2)$$

$$100w_{IL}^{salt} = A \exp \left[(B \times 100w_{salt}^{salt 0.5}) - (C \times 100w_{salt}^{salt 3}) \right] \quad (3)$$

$$100w_{IL}^{IL} = \frac{100w_{IL}^M}{\alpha} - \frac{1-\alpha}{\alpha} \times 100w_{IL}^{salt} \quad (4)$$

$$100w_{salt}^{IL} = \frac{100w_{salt}^M}{\alpha} - \frac{1-\alpha}{\alpha} \times 100w_{salt}^{salt} \quad (5)$$

where the superscripts “IL” and “salt” designate the IL-rich and salt-rich aqueous phases, respectively, and “M” is the initial mixture composition. The parameter α is the ratio between the weight of the IL-rich phase and the total weight of the mixture. The solution of this system provides the concentration (wt %) of the salt and IL in the top and bottom phases. For the calculation of the tie-line lengths (TLLs), Equation 6 was used,

$$TLL = \sqrt{(100w_{salt}^{IL} - 100w_{salt}^{salt})^2 + (100w_{IL}^{IL} - 100w_{IL}^{salt})^2} \quad (6)$$

The consistency of the measured TLs was further checked using the Othmer–Tobias²⁴

$$\left(\frac{1 - 100w_{IL}^{IL}}{100w_{IL}^{IL}} \right) = k_1 \left(\frac{1 - 100w_{salt}^{salt}}{100w_{salt}^{salt}} \right)^n \quad (7)$$

and Bancroft²⁵ equations,

$$\left(\frac{100w_{H_2O}^{salt}}{100w_{salt}^{salt}}\right) = k_2 \left(\frac{100w_{H_2O}^{IL}}{100w_{IL}^{IL}}\right)^r \quad (8)$$

where k_1 , n , k_2 and r are fitting parameters. A linear dependency of $\log \left(\frac{1 - 100w_{IL}^{IL}}{100w_{IL}^{IL}} \right)$ against $\log \left(\frac{1 - 100w_{salt}^{salt}}{100w_{salt}^{salt}} \right)$ and $\log \left(\frac{100w_{H_2O}^{salt}}{100w_{salt}^{salt}} \right)$ against $\log \left(\frac{100w_{H_2O}^{IL}}{100w_{IL}^{IL}} \right)$ indicates the consistency of the results.

The critical point of each ABS was also determined by extrapolating the TLs' slopes of individual systems followed by the fitting using Equation 9,

$$100w_{IL} = f \times 100w_{salt} + g \quad (9)$$

where f and g are the fitting parameters.

Ions speciation

The speciation of the salt ions in aqueous solution and the respective concentration were estimated using VisualMINTEQ29 (version 3.0), a thermodynamic speciation model, based on the MinteqA2 software with the Minteq database. Previously we confirmed the capability of VisualMINTEQ to describe the metal salt ions speciation and its impact upon the formation of IL-based ABS.²⁰ In these thermodynamic calculations, the concentration of salt in each ternary mixture was used as the input.

Density and viscosity

Density and viscosity measurements for both the IL-rich and organic-salt-rich phases were performed at atmospheric pressure and at the temperature range between (298.15 and 328.15) K, with an uncertainty of ± 0.02 K, using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The dynamic viscosities have a relative uncertainty of 0.35 % while the absolute uncertainty for the density is $5 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$. Prior to the measurements, the equipment was calibrated using standard solutions, as well as with pure ILs or their mixtures.^{7, 30}

Results

Phase diagrams, tie-lines, tie-line lengths and critical points

Ternary phase diagrams were determined for each IL + KCH_3CO_2 + H_2O (Figure 2) and IL + NaCH_3CO_2 + H_2O (Figure 3) system, at 298 K and at atmospheric pressure. To form ABS, *i.e.*, two aqueous rich-phases, composed of ILs and salts, only hydrophilic or water-miscible ILs should be chosen. Among all the studied ILs, only $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$, $[\text{C}_4\text{mim}][\text{SCN}]$ and $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ were able to promote the ABS formation with acetate-based

salts. These ILs comprise imidazolium-based cations with a butyl chain, that turns the IL more hydrophobic and easier to undergo through phase-separation, and anions with a low hydrogen-bond basicity or a weak ability to accept protons from water.³¹ For most systems, the top phase corresponds to the IL-rich phase while the bottom phase represents the salt-rich phase. An exception was observed for the ABS containing $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$. The phase inversion is directly related with the high density of the fluorinated anion.³²

In Figures 2 and 3, the biphasic regime is located above the solubility curve. The area of this region is proportional to the ability of each IL to undergo liquid-liquid demixing with salt solutions. The aptitude of each IL to form two phases in presence of ~ 10 wt % of KCH_3CO_2 is as follows: $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] > [\text{C}_4\text{mim}][\text{SCN}] > [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$. This rank to promote phase separation is similar to previous results for ABS composed of ILs and NaSO_4 ,³³ citrate-based²² and phosphate-based²⁶ salts. Previous works^{34–36} have shown that water mainly interacts with ILs through its anion, in which it plays a major role as a hydrogen-bond acceptor. Furthermore, the ability of the IL anions to form ABS closely follows the decrease on their hydrogen-bond accepting strength or electron pair donation ability.²⁶ The same trend of ILs to promote ABS was observed for ~ 10 wt % of NaCH_3CO_2 ; however, it is interesting to highlight that this salt is not able to form ABS with $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$, despite its higher hydration energy ($G_{\text{hyd}}(\text{Na}^+) = -365 \text{ kJ}\cdot\text{mol}^{-1}$ and $G_{\text{hyd}}(\text{K}^+) = -295 \text{ kJ}\cdot\text{mol}^{-1}$).^{21, 37}

The formation of ABS with ILs and salts is normally characterized by the occurrence of a competition between the IL and salt ions to be solvated by water. The competition is won by the salt ions due to their higher hydration energy when compared to IL ions. Consequently, there is a migration of water from the IL-solvated region towards the salt-rich phase and thus forming two liquid phases. The strength of the salt ions to be solvated by water can be characterized either by the Gibbs free energy (G_{hyd}) or the molar entropy of hydration (S_{hyd}). The lower G_{hyd} and S_{hyd} of the acetate ion when compared with other high-charge density anions, for instance PO_4^{3-} ,^{26, 38} confirms its weaker salting-out ability (according to the Hofmeister series^{21, 39}) and, consequently, a lower aptitude to create ABS with ILs.

As the studied salts share the same anion, the capability of the salts to promote ABS depends on their cation counterpart, Na^+ and K^+ . Figure 4 depicts the effect of the salt on the formation of two-phase systems. NaCH_3CO_2 is more able to form ABS, *i.e.*, lower amounts of salt are required for the liquid-liquid demixing. This trend is in agreement with the G_{hyd} and S_{hyd} of the respective salt cations: Na^+ ($G_{\text{hyd}} = -365 \text{ kJ}\cdot\text{mol}^{-1}$, $S_{\text{hyd}} = -111 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and K^+ ($G_{\text{hyd}} = -295 \text{ kJ}\cdot\text{mol}^{-1}$, $S_{\text{hyd}} = -74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).^{21, 37} Thus, if KCH_3CO_2 can form ABS with $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$, one might also expect that NaCH_3CO_2 , with higher G_{hyd} and S_{hyd} , should also form ABS. Nevertheless, the unexpected inability of NaCH_3CO_2 to promote phase separation with aqueous solutions of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ is an indication that the formation of ABS is not only governed by the Gibbs free energy of hydration (or molar entropy of hydration). In fact, the concentration of “free” ions in aqueous solution plays a major role as discussed below.

Several works^{37, 40–42} have addressed the presence of ion pairs of organic (or inorganic) salts in aqueous solution. For instance, using Raman Spectroscopy, Fournier and co-workers⁴² have confirmed ion pairing of NaCH_3CO_2 in aqueous media. In a previous work,²⁰ we have shown that the ion pairing of polyvalent salt ions has a significant impact towards their ability to promote phase separation in ABS. Therefore, we turned here our attention to estimate the ions speciation that might occur in aqueous solutions of NaCH_3CO_2 and KCH_3CO_2 aiming at understanding the inability of the sodium-based salt to form ABS with $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$. Details on the ions speciation, at 298 K, along with their concentration are given in the Supporting Information. It is shown that, for the concentration range where the salt is able to form ABS, the dissolution of NaCH_3CO_2 in aqueous media not only produces Na^+ and CH_3CO_2^- , but also NaCH_3CO_2 . In addition, the concentration of the NaCH_3CO_2 ion pair increases with increasing the concentration of salt. Although a similar trend is observed for the dissolution of KCH_3CO_2 , in which it produces the KCH_3CO_2 ion pair, when comparing the ion speciation profiles of both salts it is interesting to note that for the same concentration, the sodium-based salt presents a higher abundance of the pair NaCH_3CO_2 . This ion pairing reduces therefore the concentration of “free” and further hydrated Na^+ and CH_3CO_2^- , that coupled with the weaker ability of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ to form ABS, support the inexistence of a two-phase system for the $\text{NaCH}_3\text{CO}_2/[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ combination.

The parameters obtained by the regression of the experimental binodal curves using Equation 1 are presented in Table 1. In general, good correlation coefficients were obtained for all systems, indicating that these fittings can be used to predict data in a given region of the phase diagram where no experimental results are offered. The detailed experimental weight fraction data for each phase diagram are reported in the Supporting Information.

The experimental TLs, along with their respective length (TLL), are reported in Table 2. Their representation can be found in the Supporting Information. In addition, the critical point of each system was also determined using Equation 9 based on a geometrical approach schematized on Figure 5 for the system composed of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2] + \text{KCH}_3\text{CO}_2 + \text{H}_2\text{O}$. The critical points of all the investigated systems are depicted in Figures 2 and 3. For the potassium-based ABS, the content of IL at the critical point is similar amongst all the systems investigated, while a larger difference is noticeable in the salt amount. On the other hand, for the stronger salting-out salt, NaCH_3CO_2 , the critical point is more dependent on the type and amount of IL and salt.

The consistency of the TLs was further checked using the Othmer–Tobias²⁴ and Bancroft²⁵ equations (Equations 7 and 8) and the respective fitting parameters and correlation coefficient (R^2) are shown in Table 3 – cf. the Supporting Information with the graphical representation. The TL data are reliable since the obtained regression coefficients are close to 1, indicate therefore a good degree of consistency of the experimental data.

Density and viscosity

The characterization of the top and bottom phases in different ternary systems, at different compositions and temperatures, are important for the design and scale up of extraction processes. Hence, the density and viscosity in the temperature range between 298.15 K and

328.15 K were determined for one or two ternary compositions of each ABS studied. The following mixture compositions were investigated: 12 wt % of KCH_3CO_2 + 24 wt % of $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ + 64 wt % of H_2O (TL1); 31 wt % of KCH_3CO_2 + 40 wt % of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ + 29 wt % of H_2O (TL1); 33 wt % of KCH_3CO_2 + 40 wt % of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ + 27 wt % of H_2O (TL2); 14 wt % of KCH_3CO_2 + 40 wt % $[\text{C}_4\text{mim}][\text{SCN}]$ + 46 wt % of H_2O (TL1); 20 wt % of KCH_3CO_2 + 40 wt % $[\text{C}_4\text{mim}][\text{SCN}]$ + 40 wt % of H_2O (TL2); 15 wt % of NaCH_3CO_2 + 30 wt % $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ + 64 wt % of H_2O (TL1); 15 wt % of NaCH_3CO_2 + 34 wt % of $[\text{C}_4\text{mim}][\text{SCN}]$ + 51 wt % of H_2O (TL1); 19 wt % of NaCH_3CO_2 + 33 wt % of $[\text{C}_4\text{mim}][\text{SCN}]$ + 29 wt % of H_2O (TL2) – cf. Table 2 with the respective TLs data. Figures 6 to 9 show the density and viscosity data, as a function of temperature, for the mixtures investigated. The complete experimental data are available in the Supporting Information.

Viscosity is mainly dependent on intra- and intermolecular interactions. Since aqueous solutions of ILs and salts are being analyzed, H-bonding and Coulombic interactions are amongst the most important. An increase in temperature substantially decreases the intensity of H-bonding interactions and, therefore, the viscosity decreases with an increase in temperature, as shown in Figures 6 and 7.

Figure 6 displays the IL anion effect on the viscosity of the IL-rich and salt-rich phases for ABS composed of KCH_3CO_2 and NaCH_3CO_2 . At 298.15 K and at the TL1' compositions (Table 2), the viscosity of the IL-rich phase of the KCH_3CO_2 -based ABS decreases in the following order: $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (12.08 mPa·s) > $[\text{C}_4\text{mim}][\text{SCN}]$ (7.33 mPa·s) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (5.99 mPa·s). The opposite trend was observed with NaCH_3CO_2 where the viscosity decreases in the rank: $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (11.12 mPa·s) > $[\text{C}_4\text{mim}][\text{SCN}]$ (7.91 mPa·s). For the salt-rich phase of ABS composed of KCH_3CO_2 the trend observed was: $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (8.23 mPa·s) > $[\text{C}_4\text{mim}][\text{SCN}]$ (2.95 mPa·s) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (1.96 mPa·s); for NaCH_3CO_2 -based ABS the series is as follows: $[\text{C}_4\text{mim}][\text{SCN}]$ (5.21 mPa·s) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (3.03 mPa·s). In general, the trend on the viscosity values of both phases seems to be closely related with their compositions. For IL-rich phases, the viscosity decreases with a decrease in the IL content and concomitant increase in the water amount – data given in Table 2. For KCH_3CO_2 -based ABS at 298 K, the viscosity decreases in the order: $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (76.41 wt % of IL, 15.79 wt % of H_2O) > $[\text{C}_4\text{mim}][\text{SCN}]$ (64.76 wt % of IL, 32.78 wt % of H_2O) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (57.41 wt % of IL, 38.85 wt % of H_2O); and for NaCH_3CO_2 -based ABS at 298 K: $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (82.22 wt % of IL, 15.54 wt % of H_2O) > $[\text{C}_4\text{mim}][\text{SCN}]$ (60.68 wt % of IL, 35.35 wt % of H_2O). In a similar way, the viscosity of the salt-rich phase decreases with the increase on the water content and simultaneous decrease on the salt content according to the rank: $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (50.65 wt % of salt, 40.64 wt % of water) > $[\text{C}_4\text{mim}][\text{SCN}]$ (31.07 wt % of salt, 66.10 wt % of water) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (13.23 wt % of salt, 68.46 wt % of water) for KCH_3CO_2 -based ABS; and $[\text{C}_4\text{mim}][\text{SCN}]$ (27.11 wt % of salt, 69.03 wt % of water) > $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ (21.20 wt % of salt, 73.48 wt % of water) for NaCH_3CO_2 -based ABS.

Different ABS compositions were also investigated, and from the results displayed in Figure 7, the viscosities differences among the coexisting phases generally increase with the

increase of the TLL (from TL1 to TL2) due to the larger differences in the mixture compositions (*cf.* Table 2).

Comparing the viscosity values obtained for $\text{KCH}_3\text{CO}_2 + [\text{C}_4\text{mim}][\text{SCN}]$ and $\text{NaCH}_3\text{CO}_2 + [\text{C}_4\text{mim}][\text{SCN}]$ ABS (Figure 6 and 7), it seems that the type of salt used in the ABS formulation does not influence the viscosity of the IL-rich phases - probably due to their low concentration in these phases (less than 4 wt %). On the other hand, salt-rich phases are composed of *ca.* 30 wt % of each salt, and there are significant differences in the viscosities values of these phases that are further dependent on the salt used in the preparation of a given ABS.

One of the critical problems related with conventional ABS composed of polymers is the high viscosity of the polymeric-rich phase which hinders the mass transfer and adds significant energetic inputs into the process.⁴³ It was already demonstrated that phosphonium- K_3PO_4 -based ABS display lower viscosities than polymer-based ABS.¹² In addition, a recent work comprising ABS composed of imidazolium-based ILs and K_3PO_4 reported that imidazolium-based ABS lead to coexisting phases of lower viscosity than their phosphonium counterparts.¹¹ In general, while the viscosities of the IL-rich phases here studied are 1.5 to 3 times higher than the salt-rich ones these are of much lower viscosity than those of typical polymer-based ABS.⁴⁴

Density data for all the studied systems are presented in Figures 8 and 9. In general, the density decreases with the increase of temperature. For most systems, and for both salts, the density of the salt-rich phase is higher than the density of the IL-rich phase. An exception was observed with the $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ -based ABS – the IL-rich phase presents a higher density than the salt-rich phase (Figure 8). This is a consequence of the low concentration of inorganic salt at the IL-rich phase and of the high density of the fluorinated IL.

For the ABS formed by KCH_3CO_2 , the density values of the IL-rich phases at 298.15 K and at the TL1' compositions, are $1.0707 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_4\text{mim}][\text{SCN}]$, $1.0822 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ and $1.2058 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$. For ABS composed of $[\text{C}_4\text{mim}][\text{SCN}] + \text{NaCH}_3\text{CO}_2$ and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] + \text{NaCH}_3\text{CO}_2$ the densities of the IL-rich phases are $1.0667 \text{ g}\cdot\text{cm}^{-3}$ and $1.2509 \text{ g}\cdot\text{cm}^{-3}$, respectively. These tendencies are in close agreement with other systems previously reported.^{11, 13} Moreover, when compared with other salts, such as K_3PO_4 , the densities of the IL-rich phases are quite similar; for instance, at 298.15 K, the densities range between $1.2169 \text{ g}\cdot\text{cm}^{-3}$ ($[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$) and $1.0366 \text{ g}\cdot\text{cm}^{-3}$ ($[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$).¹¹

For salt-rich phases the density values at 298.15 K for both the studied salts are very similar: $1.1746 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_4\text{mim}][\text{SCN}] + \text{KCH}_3\text{CO}_2$ (TL1) and $1.1594 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_4\text{mim}][\text{SCN}] + \text{NaCH}_3\text{CO}_2$ (TL1). These results indicate that the change of the cation of the salt does not induce considerable variations in the densities of the coexisting phases. Nevertheless, the differences between the IL-rich and salt-rich phases cannot be neglected (Figure 8). As observed for viscosity, the density differences between the phases increase with the TLL (from TL1 to TL2 - Figure 9 and Table 2). For the IL-rich phase the density values are very close for the two TLLs tested (they are overlapped). On the other hand, for

the salt-rich phase, an increase in the TLL leads to an increase in the density values as presented in Figure 9. In fact, for TL2, the amount of salt at the salt-rich phase is higher - shown in Table 2.

Comparing with typical polymer-salt ABS,⁴⁵ the differences in the densities of the coexisting phases are higher for IL-based ABS. This is a very relevant result since higher density differences allow an easier and faster separation of the coexisting phases in ABS.

Conclusions

ILs are currently seen as potential phase-forming promoters of ABS to be used in liquid-liquid separation processes. Aiming at developing more benign systems, we report here novel ternary phase diagrams, TLs, TLLs and critical points for ABS composed of imidazolium-based ILs and two biodegradable organic salts (potassium and sodium acetate). It was found that the phase-separation ability of the investigated ILs follows the order: $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] > [\text{C}_4\text{mim}][\text{SCN}] > [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$. Sodium acetate revealed to be a stronger salting-out agent or with a higher capacity to form ABS. Furthermore, the coherence of the TL data were ascertained using the Othmer-Tobias and Bancroft equations. The densities and viscosities of the coexisting phases at given mixtures of all IL-based ABS were also determined. The system formed by KCH_3CO_2 and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ presents the lower viscosity values, while the system constituted by $\text{KCH}_3\text{CO}_2 + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ is the most viscous. Nevertheless, the viscosities of the coexisting phase of the investigated IL-based ABS were found to be substantially lower than those observed in typical polymer-based systems, representing thus a major contribution for the development of industrial processes based on ILs. At last, it was observed that the differences in the densities of the coexisting phases are higher for IL-based ABS than for polymer-based systems, allowing therefore an easier and faster separation of the coexisting phases.

Supporting Information

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Chemical structure of the ILs studied: (i) $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$, (ii) $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$, (iii) $[\text{C}_4\text{mim}][\text{SCN}]$.

Figure 2.
Ternary phase diagrams for ABS composed of IL + KCH₃CO₂ + H₂O: [C₄mim][CF₃SO₃] (●); [C₄mim][SCN] (■); [C₄mim][N(CN)₂] (◆); critical point (▲); adjusted binodal using Equation 1 (—).

Figure 3.
Ternary phase diagrams for ABS composed of IL + $NaCH_3CO_2$ + H_2O : $[C_4mim][CF_3SO_3]$ (●); $[C_4mim][SCN]$ (■); critical point (▲); adjusted binodal using Equation 1 (—).

Figure 4. Evaluation of salt effect on the formation of $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ - (●) and $[\text{C}_4\text{mim}][\text{SCN}]$ -based ABS (■): KCH_3CO_2 (full symbols) and NaCH_3CO_2 (open symbols).

Figure 5.
Phase diagram for the ternary system composed of $[C_4mim][N(CN)_2] + KCH_3CO_2 + H_2O$:
binodal curve data (◆); adjusted binodal data through Equation 1 (—); TL data (▲); TLs
relation (■); critical point (●).

Figure 6.

Experimental viscosity as a function of temperature for IL-rich (full symbols) and salt-rich (open symbols) phases of ternary mixtures identified in Table 2 as TL1: [C₄mim][CF₃SO₃] + KCH₃CO₂ (—); [C₄mim][CF₃SO₃] + NaCH₃CO₂ (●); [C₄mim][SCN] + KCH₃CO₂ (■); [C₄mim][SCN] + NaCH₃CO₂ (▲); [C₄mim][N(CN)₂] + KCH₃CO₂ (◆).

Figure 7.

Experimental viscosity as a function of temperature for ternary mixtures identified in Table 2 as TL1 (full symbols) and TL2 (open symbols): $[\text{C}_4\text{mim}][\text{SCN}] + \text{KCH}_3\text{CO}_2$ (■); $[\text{C}_4\text{mim}][\text{SCN}] + \text{NaCH}_3\text{CO}_2$ (▲); $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2] + \text{KCH}_3\text{CO}_2$ (◆). A: IL-rich phase; B: salt-rich phase.

Figure 8.

Experimental density as a function of temperature for IL-rich (full symbols) and salt-rich (open symbols) phases of ternary mixtures identified in Table 2 as TL1: $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] + \text{KCH}_3\text{CO}_2$ (—) $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] + \text{NaCH}_3\text{CO}_2$ (●); $[\text{C}_4\text{mim}][\text{SCN}] + \text{KCH}_3\text{CO}_2$ (■); $[\text{C}_4\text{mim}][\text{SCN}] + \text{NaCH}_3\text{CO}_2$ (▲); $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2] + \text{KCH}_3\text{CO}_2$ (◆).

Figure 9. Experimental density as a function of temperature for ternary mixtures identified in Table 2 as TL1 (full symbols) and TL2 (open symbols): [C₄mim][SCN] + KCH₃CO₂ (■); [C₄mim][N(CN)₂] + KCH₃CO₂ (◆). A: IL-rich phase; B: salt-rich phase.

Table 1

Correlation parameters used to describe the experimental binodal data by Equation 1 and respective standard deviations (σ) and correlation coefficients (R^2).

IL	salt	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$	R^2
[C ₄ mim][CF ₃ SO ₃]		209.0 ± 1.8	-0.67 ± 0.03	0.01 ± 0.19	0.998
[C ₄ mim][SCN]	KCH ₃ CO ₂	84.9 ± 3.7	-0.17 ± 0.02	18.14 ± 0.95	0.992
[C ₄ mim][N(CN) ₂]		205.8 ± 13.9	-0.57 ± 0.02	1.00 ± 0.43	0.996
[C ₄ mim][CF ₃ SO ₃]	NaCH ₃ CO ₂	265.1 ± 9.7	-0.89 ± 0.02	0.01 ± 3.20	0.995
[C ₄ mim][SCN]		98.9 ± 1.8	-0.24 ± 0.01	9.94 ± 0.70	0.999

Table 2

Weight fraction compositions (100 *w*) for TLs and respective TLLs of IL + KCH₃CO₂ + H₂O and IL + NaCH₃CO₂ + H₂O ABS, at the top (T) and bottom (B) phases and at the initial biphasic composition of the mixture (M) at 298 K and at atmospheric pressure (0.1 MPa). Viscosity and density properties were measured for the identified TLs (ID).^a

IL	salt	Weight fraction composition / wt %										TLL	ID
		100w ^T _{IL}	100w ^T _{salt}	100w ^T _{water}	100w ^M _{IL}	100w ^M _{salt}	100w ^M _{water}	100w ^B _{IL}	100w ^B _{salt}	100w ^B _{water}			
[C ₄ mim][CF ₃ SO ₃]		18.31	13.23	68.46	24.22	11.83	63.95	57.41	3.74	38.85	47.76	TL1	
		11.83	18.47	69.70	25.95	15.07	58.98	80.16	2.06	17.78	70.27	---	
		10.67	19.80	69.53	29.88	15.11	55.01	84.15	1.85	14.00	75.63	---	
[C ₄ mim][SCN]	KCH ₃ CO ₂	64.76	2.46	32.78	40.18	13.81	46.01	2.83	31.07	66.10	68.22	TL1	
		81.31	0.06	18.63	40.13	19.84	40.03	0.23	38.99	60.78	89.93	TL2	
		82.76	0.02	17.22	39.94	22.23	37.83	0.04	42.93	57.03	93.18	---	
[C ₄ mim][N(CN) ₂]		63.57	12.23	24.20	39.84	26.91	33.25	18.51	40.11	41.38	52.99	---	
		71.70	9.25	19.05	39.97	28.94	31.09	12.55	45.94	41.51	69.60	---	
		75.10	8.18	16.72	41.18	28.88	29.94	11.78	46.81	41.41	74.18	---	
[C ₄ mim][CF ₃ SO ₃]		76.41	7.80	15.79	39.86	30.93	29.21	8.71	50.65	40.64	80.12	TL1	
		84.27	5.77	9.96	39.88	32.96	27.16	7.06	53.06	39.88	90.53	TL2	
[C ₄ mim][CF ₃ SO ₃]		6.61	17.69	75.70	29.82	11.70	58.48	73.56	2.20	24.24	68.72	---	
		5.40	19.94	74.66	29.99	14.06	55.95	79.56	2.04	18.40	76.23	---	
		5.32	21.20	73.48	30.08	15.54	54.38	82.22	2.24	15.54	79.22	TL1	
[C ₄ mim][SCN]	NaCH ₃ CO ₂	60.68	3.97	35.35	33.60	15.12	51.23	3.86	27.11	69.03	61.34	TL1	
		82.93	0.53	16.54	33.02	18.86	48.12	1.59	30.41	68.00	86.65	TL2	
		88.65	0.20	11.15	33.58	20.69	45.73	0.80	32.58	66.62	93.36	---	

^aThe standard uncertainty for the weight fraction $u(100\ w)$ is 0.01, the standard uncertainty for the temperature $u(T)$ is 1 K, and the standard uncertainty for pressure $u(P)$ is 10 kPa.

Table 3

Values of the fitting parameters of Equations 7 and 8 for the systems composed of IL+ salt + H₂O at 298 K, and respective standard deviations (σ) and correlation coefficients (R^2).

IL	salt	Othmer-Tobias24 (Equation 7)			Bancroft25 (Equation 8)		
		$n \pm \sigma$	$k_1 \pm \sigma$	R^2	$r \pm \sigma$	$k_2 \pm \sigma$	R^2
[C ₄ mim][CF ₃ SO ₃]	KCH ₃ CO ₂	2.846 ± 0.051	0.004 ± 0.036	1.000	0.275 ± 0.004	5.734 ± 0.003	1.000
[C ₄ mim][SCN]		1.970 ± 0.445	0.109 ± 0.107	0.951	0.477 ± 0.117	2.962 ± 0.066	0.943
[C ₄ mim][N(CN) ₂]		1.945 ± 0.344	0.273 ± 0.030	0.914	0.271 ± 0.049	1.307 ± 0.021	0.910
[C ₄ mim][CF ₃ SO ₃]	NaCH ₃ CO ₂	2.264 ± 0.011	0.011 ± 0.007	1.000	0.379 ± 0.001	6.518 ± 0.001	1.000
[C ₄ mim][SCN]		6.285 ± 0.645	0.001 ± 0.240	0.990	0.138 ± 0.017	2.751 ± 0.011	0.985