Critical Assessment of the Formation of Ionic-Liquid-Based Aqueous Two-Phase Systems in Acidic Media

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Ⓢ Supporting Information

ABSTRACT: In this work, the ability of Na_2SO_4 and ionic liquids to induce the formation of acidic aqueous two-phase systems (ATPS) is investigated. Ternary phase diagrams, tie lines, and tie-line lengths for several systems were determined and reported at 298 K and atmospheric pressure. It is here shown that among the ionic liquids studied only those containing long alkyl side chains at the ions and/or anions with low hydrogen bond basicity are capable of undergoing liquid–liquid demixing in the presence of Na_2SO_4 aqueous solutions. The results obtained indicate that, besides the salting-out ability of the inorganic salt, the pH of the aqueous solution plays a crucial role toward the formation of ionic-liquid-based ATPS. In acidic media the range of ionic liquids that are able to undergo ATPS formation is substantially reduced when compared to alkaline aqueous salt solutions. The use of inorganic salts and ionic liquids to promote acidic ATPS is envisaged as particularly valuable in the extraction of compounds that exhibit low acid dissociation constants.

Aqueous Two-Phase Systems

[C_4mim]Cl + Na_2SO_4 + H_2O ✗

[C_4mim]Br + Na_2SO_4 + H_2O ✓

INTRODUCTION

The purity, extraction yield, environmental hazards, and costs associated with the recovery of added-value products from raw sources, industrial and/or residual wastes, or biotechnological processes are crucial issues in the implementation of a specific separation/purification process. In this context, in past decades, some efforts have been devoted to the development of aqueous two-phase systems (ATPS)[1] aiming at avoiding the use of organic solvents as extractive phases. ATPS consist of two aqueous-rich phases formed by polymer/polymer, polymer/salt, or salt/salt combinations. The basis of separation of (bio)molecules in ATPS is a direct result of their equilibration and selective distribution between the two distinct aqueous phases.[2]

In recent years, ionic liquids (ILs) emerged as potential and alternative replacements for ordinary organic solvents, due to their negligible vapor pressures, general nonflammability, and typical high chemical and thermal stabilities. Moreover, a proper choice of the cation and/or anion composing the ionic liquid allows their properties to be tuned for specific applications. Gutowski et al.[3] were the first to show that imidazolium-based ionic liquids can also form ATPS in the presence of aqueous solutions of K_3PO_4, representing thus a step forward in the replacement of the conventional ATPS based on polymer/polymer and polymer/salt mixtures. The authors[3] additionally indicated that 1-butyl-3-methylimidazolium chloride, [C_4mim]Cl, can form ATPS with distinct "kosmotropic" salts, namely, KOH, K_2CO_3, Na_2HPO_4, and $Na_2S_2O_3$, while 1,3-dialkylimidazolium

triflate and tetrafluoroborate based ionic liquids form ATPS with $CaCl_2$ and NaCl. Hence, adequate inorganic salts can salt-out hydrophilic ionic liquids from aqueous solutions resulting in the formation of ATPS. This observation has lead, in the past few years, to the exploration of IL-based ATPS as novel extractive systems since a tailoring of the phase polarities could be achieved.[4−14] Most works, however, have been dealing with alkaline aqueous solutions, whereas the formation of IL-based ATPS through the use of neutral or acidic inorganic salts solutions is either contested or poorly understood. Nonetheless, the use of acidic aqueous solutions could be highly relevant in the extraction of biomolecules with low acid dissociation constants.

Phase diagrams containing several imidazolium-based ionic liquids and distinct alkaline aqueous solutions of salts, namely, KOH, K_2HPO_4, K_2CO_3, and K_3PO_4 were described in the literature.[8,11,15−21] Bridges et al.[21] reported ternary phase diagrams for imidazolium-, pyridinium-, ammonium-, and phosphonium-based chloride ionic liquids, water, and K_3PO_4, K_2HPO_4, K_2CO_3, KOH, and $(NH_4)_2SO_4$. In this study,[21] the only system capable of promoting ATPS with the slightly acidic aqueous solution of $(NH_4)_2SO_4$ was the ammonium-based ionic liquid. An additional work previously reported by our group[7] showed the higher aptitude of different phosphonium-based ionic liquids to undergo phase separation in the presence of aqueous solutions

of K_3PO_4. Sadeghi et al.[22] studied the salting-out effect in aqueous solutions of 1-butyl-3-methylimidazolium bromide with trisodium citrate. Recently, Wang et al.[23] published experimental data on ATPS formed by 1-butyl-3-methylimidazolium teterafluoroborate ($[C_4mim][BF_4]$) and Na_2CO_3, $(NH_4)_2SO_4$, NaH_2PO_4, $MgSO_4$, Na_2SO_3, and NaOH. The authors[23] also postulated the inability of Na_3PO_4, Na_2HPO_4, K_2HPO_4, NH_4Cl, $NaCH_3CO_2$, $NaNO_3$, NaCl, and KCl to induce the phase separation of the tetrafluoroborate-based ionic liquid. Subsequently, Li et al.[24] showed that it was possible to promote ATPS with aqueous solutions of $[C_4mim][BF_4]$ and Na_2CO_3, Na_3PO_4, Na_2SO_4, NaH_2PO_4, and NaCl. Curiously, contradictory results were found between the two research groups[23,24] for the formation of ATPS composed of $[C_4mim][BF_4]$ and the inorganic salts Na_3PO_4 and NaCl.

The effect of inorganic salts on IL-based ATPS formation has been widely studied,[3,5,6,21] and it was demonstrated that they typically follow the Hofmeister series (classification of ions based on their salting-out/salting-in aptitude).[25] Nevertheless, most of the inorganic salts studied present an alkaline or almost neutral character in aqueous solution.[3,7,8,15−23] Attempting to manipulate the pH values of IL-based ATPS, He et al.[5] showed that systems containing 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) can undergo phase separation by the addition of appropriate amounts of diverse alkaline aqueous salt solutions, such as K_2HPO_4, K_3PO_4, K_2CO_3, KOH, Na_2HPO_4, and NaOH. However, when acidic to neutral salt solutions, namely KH_2PO_4, K_2SO_4, $(NH_4)_2SO_4$, KCl, or NaCl, were added, the formation of IL-based ATPS was not observed.[5] In the same line of investigation, Li et al.[6] reported ternary phase diagrams between water, $[C_4mim]Cl$, and distinct inorganic salts. The authors[6] have shown that ATPS with $[C_4mim]Cl$ can be formed by the adequate addition of alkaline aqueous solutions of the following salts: K_3PO_4, KOH, K_2HPO_4, NaOH, K_2CO_3, and Na_2HPO_4. Nevertheless, when using acidic or neutral salts, such as KH_2PO_4, $(NH_4)_2SO_4$, NaCl, or KCl, no phase separation of the IL-rich phase was observed.[6] These reports[5,6] confirm that, besides the salting-in/salting-out aptitude of the inorganic salts (Hofmeister series rank), the creation of IL-based ATPS is strongly dependent on the pH of the aqueous solutions. For instance, if SO_4^{2-} is a stronger salting-out anion than HPO_4^{2-} or OH^-, ATPS making use of sulfate-based salts should be more easily formed. In fact, this was not verified,[5,6] meaning that the IL-based ATPS formation capability largely depends on the aqueous medium pH induced by the inorganic salt.

Although these previous works[5,6] have demonstrated the inability of acidic and neutral aqueous solutions to form IL-based ATPS, they have only focused on $[C_4mim]Cl$. The ability of ionic liquids to be tailored for specific applications suggests that adequate ionic liquids, capable of undergoing liquid−liquid demixing in aqueous solutions, can be found—if the molecular interactions at the basis of the demixing phenomenon are correctly understood. The results gathered in previous works by our group indicate that, for the formation of ATPS with weaker salting-out agents, such as carbohydrates[26] or amino acids,[27] more hydrophobic, yet water-soluble ionic liquids must be employed. Such ionic liquids are here defined as those fluids composed of long alkyl side chain lengths and/or anions with low hydrogen bond basicity values,[8,11] namely $[N(CN)_2]^-$, $[CF_3SO_3]^-$, and $[BF_4]^-$. Although it was previously[21] shown that $[C_4mim]$-$[BF_4]$ is capable of forming ATPS in the presence of sulfate-based salts, this ionic liquid is not water stable and particular care

should be taken when using these solutions for extraction purposes.[28] $[BF_4]$-based ionic liquids suffer hydrolysis in contact with water, releasing hydrofluoric acid even at room temperature.[28] Therefore, seeking water-stable ionic liquids capable of producing acidic ATPS is highly relevant.

In this work, the ability of Na_2SO_4 (with a pH value ca. 7 in aqueous solution) for the formation of IL-based ATPS is presented and discussed. For such a purpose, novel ternary phase diagrams composed of different water-stable ionic liquids, water, and Na_2SO_4, at 298 K and atmospheric pressure, were determined. A large array of ionic liquids was explored, and it was verified that a proper selection of the ionic liquid structural features can lead to liquid−liquid demixing, and to different pH values at their coexisting phases. Most of the investigated ionic liquids were shown to produce acidic aqueous systems. Finally, a close relation between the ionic liquid aptitude to create ATPS and their hydrogen bond basicity values is presented. This close pattern is shown to provide an a priori qualitative method to identify ionic liquids that are capable of forming ATPS with Na_2SO_4 (if hydrogen bond basicity values are previously known).

■ EXPERIMENTAL SECTION

Materials. The ionic liquids used in this work to study the formation of acidic ATPS were the following: 1-ethyl-3-methylimidazolium methylsulfate, $[C_2mim][CH_3SO_4]$; 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, $[C_2mim][CF_3SO_3]$; 1-butyl-3-methylimidazolium chloride, $[C_4mim]Cl$; 1-hexyl-3-methylimidazolium chloride, $[C_6mim]Cl$; 1-heptyl-3-methylimidazolium chloride, $[C_7mim]Cl$; 1-butyl-3-methylimidazolium bromide, $[C_4mim]Br$; 1-butyl-3-methylimidazolium acetate, $[C_4mim][CH_3CO_2]$; 1-butyl-3-methylimidazolium methylsulfate, $[C_4mim][CH_3SO_4]$; 1-butyl-3-methylimidazolium ethylsulfate, $[C_4mim][C_2H_5SO_4]$; 1-butyl-3-methylimidazolium trifluoromethanesulfonate, $[C_4mim][CF_3SO_3]$; 1-butyl-3-methylimidazolium dicyanamide, $[C_4mim][N(CN)_2]$; 1-butyl-3-methylimidazolium hydrogensulfate, $[C_4mim][HSO_4]$; 1-butyl-3-methylimidazolium tosylate, $[C_4mim][TOS]$; 1-butyl-3-methylimidazolium dimethylphosphate, $[C_4mim][DMP]$; 1-butyl-3-methylimidazolium trifluoroacetate, $[C_4mim][CF_3CO_2]$; 1-butyl-3-methylimidazolium octylsulfate, $[C_4mim][OctylSO_4]$; 1-butyl-3-methylimidazolium thiocyanate, $[C_4mim][SCN]$; 1-benzyl-3-methylimidazolium chloride, $[C_7H_7mim]Cl$; 1-benzyl-3-methylimidazolium ethylsulfate, $[C_7H_7mim][C_2H_5SO_4]$; 1-allyl-3-methylimidazolium ethylsulfate, $[amim][C_2H_5SO_4]$; 1-butyl-3-methylpyridinium chloride, $[C_4mpy]Cl$; 1-butyl-1-methylpiperidinium chloride, $[C_4mpip]Cl$; 1-butyl-1-methylpyrrolidinium chloride, $[C_4mpyr]Cl$, and 1-octylpyridinium dicyanamide, $[C_8py][N(CN)_2]$. All ionic liquids were supplied by Iolitec. To reduce the volatile impurities to negligible values, ionic liquid individual samples were purified under constant agitation, under vacuum, and at moderate temperature (343 K), for a minimum of 24 h. After this step, the purity of each ionic liquid was further checked by ^1H, ^{13}C, and ^{19}F (whenever applicable) NMR spectra and found to be >99 wt % for all samples.

The inorganic salt Na_2SO_4 was from LabSolve (purity >99.8 wt %). The water employed was double distilled, passed across a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification equipment. The buffers used in the calibration of the pH meter equipment were a citric acid/sodium hydroxide/sodium chloride solution with a pH value of 4.00 ($\pm$0.02), and
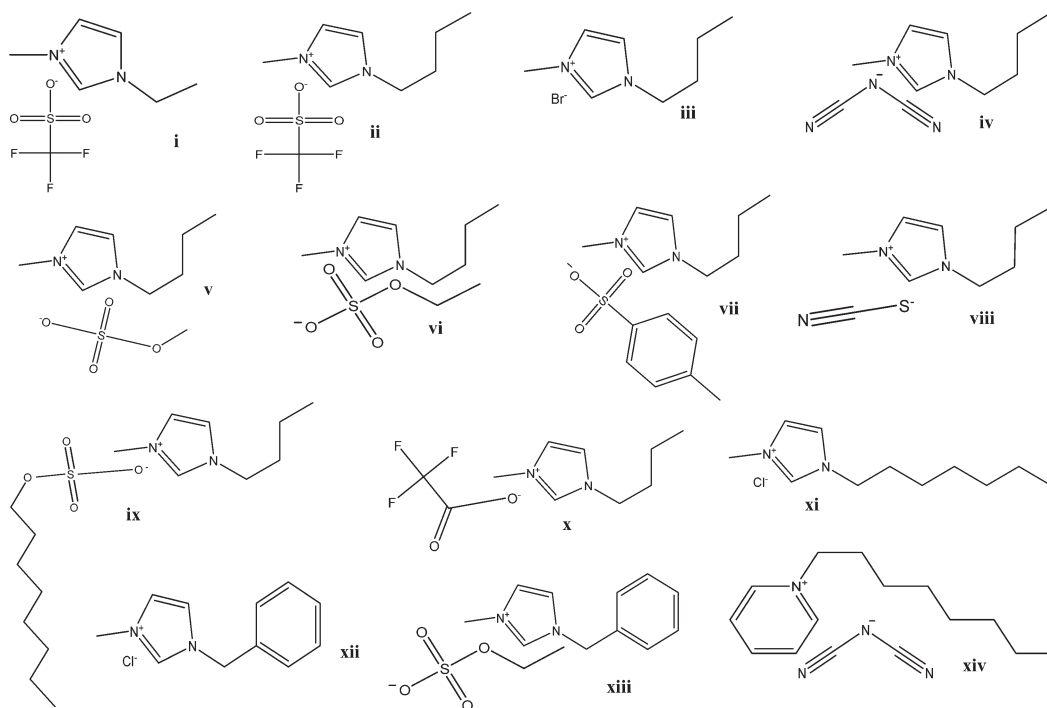
Figure 1. Ionic structures of the studied ionic liquids capable of forming ATPS with Na_2SO_4 aqueous solutions: (i) $[C_2mim][CF_3SO_3]$; (ii) $[C_4mim][CF_3SO_3]$; (iii) $[C_4mim]Br$; (iv) $[C_4mim][N(CN)_2]$; (v) $[C_4mim][CH_3SO_4]$; (vi) $[C_4mim][C_2H_5SO_4]$; (vii) $[C_4mim][TOS]$; (viii) $[C_4mim][SCN]$; (ix) $[C_4mim][OctylSO_4]$; (x) $[C_4mim][CF_3CO_2]$; (xi) $[C_7mim]Cl$; (xii) $[C_7H_7mim]Cl$; (xiii) $[C_7H_7mim][C_2H_5SO_4]$; (xiv) $[C_8py][N(CN)_2]$.

a potassium dihydrogen phosphate/disodium hydrogen phosphate solution with a pH value of 7.00 (±0.02), acquired from Fluka.

■ EXPERIMENTAL PROCEDURE

Phase Diagrams and Tie-Line Determination. Aqueous solutions of Na_2SO_4 at ≈25 wt %, and aqueous solutions of the different hydrophilic ionic liquids at ≈60 wt %, were prepared and used for the determination of the binodal curves. The phase diagrams were determined at 298 (±1) K and at atmospheric pressure through the cloud point titration method (previously validated by us[7,8,11]). Dropwise addition of the aqueous inorganic salt solution to each ionic liquid aqueous solution was carried out until the detection of a cloudy (biphasic) solution, followed by the dropwise addition of ultrapure water until the formation of a clear and limpid solution (monophasic region). Dropwise additions were carried out under constant stirring. The ternary system compositions were determined by weight quantification of all components within $\pm10^{-4}$ g (using an analytical balance, Mettler Toledo Excellence XS205 DualRange).

The tie lines (TLs) were determined by a gravimetric method originally proposed by Merchuck et al.[29] For the determination of TLs, a ternary mixture composed of Na_2SO_4 + water + IL at the biphasic region was gravimetrically prepared within $\pm10^{-4}$ g, vigorously agitated, and left to equilibrate for at least 12 h and at 298 K, aiming at a complete separation of the coexisting phases. In this step small ampules (10 cm^3), specifically designed for the purpose, were used. Both phases were carefully separated and individually weighed within $\pm10^{-4}$ g. Each TL was determined by a mass balance approach through the relationship between the top mass phase composition and the overall system composition.

The experimental binodal curves were fitted according to eq 1:[29]

$$Y = A \exp[(BX^{0.5}) - (CX^3)] \tag{1}$$

where Y and X are the ionic liquid and the inorganic salt mass fraction percentages, respectively, and A, B, and C are constants obtained by the regression of the experimental binodal data.

For the determination of TLs, the following system of four equations (eqs 2−5) and four unknown values (Y_T, Y_B, X_T, and X_B) was solved:[29]

$$Y_T = A \exp[(BX_T^{0.5}) - (CX_T^3)] \tag{2}$$

$$Y_B = A \exp[(BX_B^{0.5}) - (CX_B^3)] \tag{3}$$

$$Y_T = \frac{Y_M}{\alpha} - \frac{1-\alpha}{\alpha} Y_B \tag{4}$$

$$X_T = \frac{X_M}{\alpha} - \frac{1-\alpha}{\alpha} X_B \tag{5}$$

where subscripts "T", "B", and "M" designate the top phase, the bottom phase, and the mixture, respectively; X and Y represent, respectively, the weight fractions of Na_2SO_4 and ionic liquid; and α is the ratio between the mass of the top phase and the total mass of the mixture. The system solution results in the composition (wt %) of the ionic liquid and inorganic salt in the top and bottom phases, and thus, TLs can be directly represented.

For the calculation of the tie-line length (TLL), the following equation was employed:
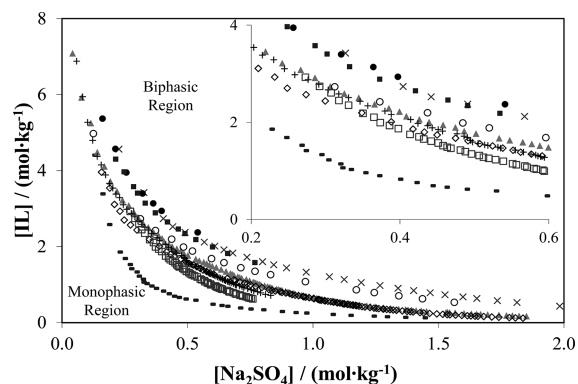
$$TLL = \sqrt{(X_T - X_B)^2 + (Y_T - Y_B)^2} \tag{6}$$

Figure 2. Ternary phase diagrams for [C₄mim]-based ILs at 298 K and atmospheric pressure: —, $[C_4mim][CF_3SO_3]$; ◇, $[C_4mim][TOS]$; +, $[C_4mim][SCN]$; ○, $[C_4mim][C_2H_5SO_4]$; × (gray), $[C_4mim]$-$[CH_3SO_4]$; ▲ (gray), $[C_4mim][N(CN)_2]$; □, $[C_4mim][OctylSO_4]$; ■, $[C_4mim][CF_3CO_2]$; ●, $[C_4mim]Br$.

where subscripts "T" and "B" symbolize, respectively, the top and bottom phases, and X and Y are the mass fraction percentages of inorganic salt and IL, as described before.

pH Determination. The pH values (±0.02) of the IL-rich and inorganic-salt-rich aqueous phases were measured at 298 (±1) K using an HI 9321 Microprocessor pH meter (HANNA instruments). The calibration of the pH meter was carried out with two buffers (pH values of 4.00 and 7.00). The compositions adopted at the biphasic region were composed of 15 wt % Na₂SO₄, 60 wt % water, and 25 wt % of each ionic liquid. All mixtures were gravimetrically prepared within $\pm10^{-4}$ g. The mixtures were prepared, vigorously stirred, and further kept still in small ampules for phase separation, and for at least 12 h at 298 (±1) K. After the careful separation of the phases, the pH of each aqueous phase was further measured.

RESULTS AND DISCUSSION

Phase Diagrams. A broad range of ionic liquids was studied to identify the ionic liquid structural features responsible for the formation of ATPS in the presence of aqueous solutions of Na₂SO₄. The ionic liquids investigated were $[C_2mim][CH_3SO_4]$, $[C_2mim]$-$[CF_3SO_3]$, $[C_4mim]Cl$, $[C_4mim]Br$, $[C_4mim][CH_3CO_2]$, $[C_4mim][CF_3SO_3]$, $[C_4mim][N(CN)_2]$, $[C_4mim][HSO_4]$, $[C_4mim][CH_3SO_4]$, $[C_4mim][C_2H_5SO_4]$, $[C_4mim][TOS]$, $[C_4mim][DMP]$, $[C_4mim][SCN]$, $[C_4mim][CF_3CO_2]$, $[C_4mim]$-$[OctylSO_4]$, $[C_6mim]Cl$, $[C_7mim]Cl$, $[C_7H_7mim]Cl$, $[C_7H_7mim]$-$[C_2H_5SO_4]$, $[amim][C_2H_5SO_4]$, $[C_4mpip]Cl$, $[C_4mpy]Cl$, $[C_4mpyr]Cl$, and $[C_8py][N(CN)_2]$. The compositions used for the evaluation of the possibility of forming liquid−liquid biphasic systems are reported in the Supporting Information. The ionic liquids that were able to promote ATPS with Na₂SO₄ were the following: $[C_2mim][CF_3SO_3]$, $[C_4mim][CF_3SO_3]$, $[C_4mim]Br$, $[C_4mim][N(CN)_2]$, $[C_4mim][CH_3SO_4]$, $[C_4mim]$-$[C_2H_5SO_4]$, $[C_4mim][TOS]$, $[C_4mim][SCN]$, $[C_4mim]$-$[CF_3CO_2]$, $[C_4mim][OctylSO_4]$, $[C_7mim]Cl$, $[C_7H_7mim]Cl$, $[C_7H_7mim][C_2H_5SO_4]$, and $[C_8py][N(CN)_2]$. Therefore, despite the controversy found in the literature postulating that acidic and neutral inorganic salts are not able to promote IL-based ATPS, it is here shown that they can be created if an adequate choice of the ionic liquid is carried out.

The structures of the ionic liquids that were successful in creating ATPS with Na₂SO₄ are displayed in Figure 1. In
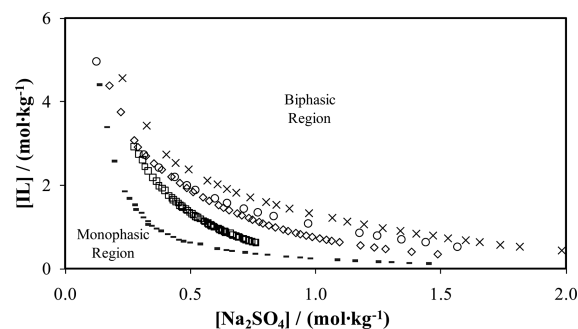

Figure 3. Ternary phase diagrams for selected ionic liquids at 298 K and atmospheric pressure (evaluation of the cation/anion alkyl chain length influence): —, $[C_4mim][CF_3SO_3]$; ◇, $[C_2mim][CF_3SO_3]$; ○, $[C_4mim][C_2H_5SO_4]$; × (gray), $[C_4mim][CH_3SO_4]$, □, $[C_4mim]$-$[OctylSO_4]$.
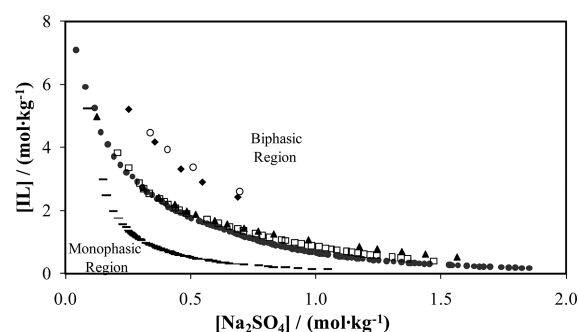

Figure 4. Ternary phase diagrams for selected ionic liquids at 298 K and atmospheric pressure (evaluation of the cation core and functionalized groups influence): —, $[C_8py][N(CN)_2]$; ▲, $[C_4mim][C_2H_5SO_4]$; ●, $[C_4mim][N(CN)_2]$; □, $[C_7H_7mim][C_2H_5SO_4]$; ● $[C_7H_7mim]Cl$; ○, $[C_7mim]Cl$.

agreement with the results previously reported,[6] we also found that it was not possible to create the $[C_4mim]Cl−Na_2SO_4$ ATPS, although an ATPS formation was observed with $[C_4mim]Br$. These data are in good agreement with our previous findings using the inorganic salt K_3PO_4[8,11] where $[C_4mim]Br$ was shown to be more able to undergo the formation of ATPS than the chloride counterpart.

The experimental phase diagrams obtained, at 298 K and at atmospheric pressure, for the ternary systems composed of Na₂SO₄ + water + ILs are presented in Figures 2−4. The phase diagrams are distributed by different figures to facilitate the individual analysis of the influence of the anion/cation structural effects. All phase diagrams are represented in molality units for a more comprehensive perception of the impact of diverse ionic liquids on the ATPS formation (thus avoiding differences that could merely be a result of different molecular weights).The experimental weight fraction data for each phase diagram are reported in the Supporting Information.

Table 1 presents the parameters obtained by the regression of the experimental binodal curves (in weight fraction) using eq 1. In all phase diagrams, the top rich phase corresponds to the IL-rich phase while the bottom phase represents the Na₂SO₄-rich phase. A unique exception was observed with the $[C_4mim]$-$[CF_3SO_3]$ system. This inversion of phases is directly related to the high density of the fluorinated ionic liquid.[30] The tie lines and

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dx.doi.org/10.1021/jp204865a |*J. Phys. Chem. B* 2011, 115, 11145–11153

Table 1. Parameters (*A*, *B*, and *C*) Obtained by the Regression of the Experimental Binodal Data through the Application of eq 1 (and Respective Standard Deviations, σ) for the IL + Na$_2$SO$_4$ + H$_2$O Systems at 298 K

IL	$A \pm \sigma$	$B \pm \sigma$	$10^5 C \pm \sigma$	R^2
[C$_2$mim][CF$_3$SO$_3$]	106.1 ± 2.1	-0.439 ± 0.010	16.2 ± 2.0	0.9990
[C$_4$mim][CF$_3$SO$_3$]	190.0 ± 9.4	-0.965 ± 0.002	2.0 ± 3.9	0.9923
[C$_4$mim]Br	97.5 ± 2.6	-0.393 ± 0.016	1.0 ± 5.8	0.9989
[C$_4$mim][CH$_3$SO$_4$]	105.4 ± 2.4	-0.396 ± 0.009	4.4 ± 0.4	0.9963
[C$_4$mim][C$_2$H$_5$SO$_4$]	95.4 ± 0.7	-0.393 ± 0.004	5.7 ± 0.2	0.9980
[C$_4$mim][N(CN)$_2$]	88.8 ± 1.0	-0.446 ± 0.006	20.2 ± 0.7	0.9997
[C$_4$mim][TOS]	102.1 ± 0.7	0.421 ± 0.003	18.2 ± 0.2	0.9996
[C$_4$mim][SCN]	85.8 ± 0.5	-0.433 ± 0.003	49.0 ± 0.9	0.9995
[C$_4$mim][CF$_3$CO$_2$]	103.3 ± 1.6	-0.396 ± 0.008	5.0 ± 1.4	0.9995
[C$_4$mim][OctylSO$_4$]	158.0 ± 2.4	-0.575 ± 0.007	42.4 ± 1.1	0.9997
[C$_7$mim]Cl	91.6 ± 2.0	-0.287 ± 0.011	9.9 ± 1.5	1.0000
[C$_7$H$_7$mim]Cl	104.7 ± 7.4	-0.372 ± 0.036	4.9 ± 6.6	0.9982
[C$_7$H$_7$mim][C$_2$H$_5$SO$_4$]	100.6 ± 1.6	-0.383 ± 0.007	12.9 ± 0.5	0.9997
[C$_8$py][N(CN)$_2$]	195.2 ± 2.4	-1.079 ± 0.008	9.9 ± 2.3	0.9984

tie-line lengths for each system were determined through the application of eqs 2–6. Weight fraction compositions for the coexisting phases of each system (TLs), along with the respective tie-line lengths, are reported in Table 2.

The pH in the top and bottom phases of the ATPS investigated was determined to evaluate the formation of acidic IL-based ATPS (envisaging improved systems for the extraction of biomolecules with low acid dissociation constants). The pH values of the coexisting phases, displayed in Table 3, were measured in biphasic systems formed by 25 wt % of each IL + 15 wt % Na$_2$SO$_4$ + 60 wt % water. The respective compositions of each component at the IL- and Na$_2$SO$_4$-rich phases are reported in Table 2. Since the concentration of ionic liquid in each phase is not the same, the pH values at the coexisting phases are slightly different. Nevertheless, close pH values for a common system at both aqueous phases are observed.

A general trend in the pH values at the IL-rich phase was verified: an increase in the alkyl side chain length at the cation and/or anion leads to an increase in the pH values. At the salt-rich phase a straight pattern was not observed. The main differences in the pH values were observed with distinct [C$_4$mim]-based ionic liquids combined with several anions. As result, when using a neutral salt, such as Na$_2$SO$_4$, the pH values of IL-based ATPS are strongly dependent on the ionic liquid employed. Most IL-based ATPS here studied are acidic with the exception of the [N(CN)$_2$]-based systems that, due to anion basicity, produce alkaline aqueous phases.

In order to investigate the inorganic anion speciation into H$_2$SO$_4$/HSO$_4^-$/SO$_4^{2-}$ at the pH values induced by the different ionic liquids, the ratio of the concentrations of the pairs H$_2$SO$_4$/HSO$_4^-$ and HSO$_4^-$/SO$_4^{2-}$ was determined taking into account the acid dissociation constants of the corresponding polyprotic acid.[31] The ratio between the concentrations of the species SO$_4^{2-}$ and HSO$_4^-$ is provided in Table 3. The ratio of the ionic concentrations corresponding to the first dissociation of the protons was considered to be marginal since the pH values are well above the pK_{a1} of H$_2$SO$_4$ (these results are however provided in Supporting Information). From the results obtained it can be seen that there is not a close relationship between the

concentration of SO$_4^{2-}$ and the ability of the ionic liquids to be salted out. For instance, for the [C$_4$mim]-based ionic liquids, the highest concentration of the sulfate anion, at both aqueous phases, is observed with the ionic liquid [C$_4$mim][N(CN)$_2$]. Nonetheless, among the [C$_4$mim]-based series, [C$_4$mim][N(CN)$_2$] is not the ionic liquid with the highest ability to be separated from the aqueous mixture. Ionic liquids with anions such as [CF$_3$SO$_3$]$^-$, [SCN]$^-$, and [TOS]$^-$ are easily salted out from aqueous media albeit presenting lower pH values. Hence, for a common salt, the ability of the ionic liquids to undergo liquid–liquid demixing does not strictly depend on the inorganic salt speciation, but instead depends on the ionic liquid structural features or hydrogen bond ability as will be discussed below. On the other hand, the pH of the aqueous media seems to be an important factor in the creation of ATPS in the presence of a common salt. Contrary to the large array of ionic liquids that were able to produce ATPS in the presence of an alkaline aqueous solution of K$_3$PO$_4$,[8,11] in the presence of acidic or neutral aqueous solutions the number of ionic liquids that are capable of forming ATPS is largely reduced. Acidic or neutral salt solutions limit the range of ionic liquids that are able to create ATPS.

In complex mixtures, such as those containing high charge density salts with an enhanced capacity for creating ion–water hydration complexes (such as Na$_2$SO$_4$), the capability to induce ATPS increases with the decrease of the ionic liquid affinity for water: the ionic liquid is salted out by the inorganic ions. These hydrophobic ionic liquids are those composed of long alkyl side chains[8,11] or constituted by anions with lower hydrogen bond basicity values (anions with a low hydrogen bond acceptor strength).[8,11] The affinity of hydrogen bond donors or acceptors is influenced by steric factors (accessibility of the donor or acceptor groups), as well as by electronic factors, such as electronegativity and hybridization.[32] The hydrogen bonding ability of ionic liquids can be empirically estimated using a variety of solvatochromic probes as previously demonstrated in the literature.[33] The solvatochromic parameters are derived from spectroscopic techniques specifically designed to measure only a single interaction (hydrogen bonding). One of the most interesting and widely used set of solvatochromic parameters are the Kamlet–Taft parameters. These parameters comprise the solvent dipolarity/polarizability (π^*), the hydrogen bond acidity (α), and the hydrogen bond basicity (β).[33] The β scale is a measure of the ability of the solvent to accept a proton (or donate an electron pair) in a solute–solvent hydrogen bond. In ATPS, water is the most cohesive solvent, is dipolar, and is a strong hydrogen bond donor and acceptor. Ionic liquids display a complex combination of specific interactions including the ability to hydrogen bond. Thus, in this work, the Kamlet–Taft parameters (particularly, the hydrogen bonding basicity) will be used in the following discussion of the phase behavior since hydrogen bond interactions of the pairs IL–water and inorganic salt–water are competing for the creation of ATPS.

The larger the biphasic region, the higher is the ability of each ionic liquid to promote ATPS formation. From the gathered data, the overall tendency of the ionic liquids in creating ATPS, for instance in the presence of 0.5 mol·kg^{-1} Na$_2$SO$_4$, follows the order [C$_8$py][N(CN)$_2$] > [C$_4$mim][CF$_3$SO$_3$] $\gg$ [C$_4$mim]-[OctylSO$_4$] > [C$_4$mim][TOS] $\approx$ [C$_4$mim][SCN] > [C$_4$mim]-[N(CN)$_2$] > [C$_2$mim][CF$_3$SO$_3$] $\approx$ [C$_7$H$_7$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim][CF$_3$CO$_2$] $\approx$ [C$_4$mim]-[CH$_3$SO$_4$] > [C$_4$mim]Br > [C$_7$H$_7$mim]Cl > [C$_7$mim]Cl. The

Table 2. Mass Fraction Compositions (wt %) for the Coexisting Phases of the IL (Y) + Na$_2$SO$_4$ (X) + H$_2$O Systems at 298 K, and Respective Values of α and TLL

IL	weight fraction composition/ wt %						α	TLL
	Y_T	X_T	Y_M	X_M	Y_B	X_B		
[C$_2$mim][CF$_3$SO$_3$]	63.37	1.37	17.95	14.96	5.55	18.67	0.79	60.35
	71.67	0.80	24.88	15.28	2.22	22.30	0.33	72.70
	73.70	0.69	24.89	15.94	1.71	23.18	0.32	75.43
[C$_4$mim][CF$_3$SO$_3$]	3.89	15.60	20.10	11.96	68.31	1.12	0.75	66.03
	3.02	17.47	15.13	14.99	85.13	0.69	0.85	83.81
	2.15	20.00	24.95	14.97	90.03	0.60	0.74	90.00
[C$_4$mim]Br	34.62	6.90	23.05	14.97	15.07	20.53	0.59	23.83
	39.71	5.21	24.96	15.22	12.73	23.52	0.55	32.60
[C$_4$mim][CH$_3$SO$_4$]	45.93	4.36	24.69	14.52	11.88	20.64	0.62	37.74
	55.70	2.59	28.64	14.27	10.01	22.31	0.59	49.77
[C$_4$mim][C$_2$H$_5$SO$_4$]	30.58	7.98	14.01	18.44	8.05	22.21	0.27	26.65
[C$_4$mim][OctylSO$_4$]	50.40	3.79	9.73	15.45	1.23	17.88	0.17	51.15
	59.73	2.81	16.02	14.88	0.66	19.12	0.26	61.29
	73.70	1.75	24.98	14.95	0.14	21.68	0.34	76.20
[C$_4$mim][N(CN)$_2$]	53.19	1.32	15.08	14.93	2.97	19.26	0.24	53.33
	57.54	0.95	20.18	14.91	1.29	21.98	0.34	60.06
	60.82	0.56	25.00	15.00	0.40	24.92	0.41	65.15
[C$_4$mim][TOS]	44.64	3.78	15.00	15.07	4.69	19.00	0.26	42.75
	55.41	2.10	20.24	15.59	1.63	22.73	0.35	57.61
	57.41	1.87	24.80	14.93	0.87	24.52	0.42	60.91
[C$_4$mim][SCN]	47.27	1.87	15.14	10.06	9.14	11.59	0.16	39.35
	52.65	1.27	19.97	10.05	3.85	14.38	0.33	50.53
	63.19	0.50	24.93	14.94	0.01	24.35	0.39	67.53
[C$_4$mim][CF$_3$CO$_2$]	45.00	4.38	24.95	14.99	7.03	24.48	0.53	42.97
	51.80	3.04	27.17	14.96	6.67	24.88	0.55	50.14
[C$_7$mim]Cl	63.27	1.66	25.05	15.00	12.88	19.25	0.76	53.37
[C$_7$H$_7$mim]Cl	32.54	9.22	28.79	11.40	11.34	21.56	0.82	24.54
	46.78	4.63	25.08	15.13	10.72	22.08	0.60	40.06
	47.37	4.49	25.92	14.92	10.09	22.60	0.58	41.44
[C$_7$H$_7$mim][C$_2$H$_5$SO$_4$]	47.37	3.79	20.00	15.00	5.23	21.04	0.35	45.54
	55.92	2.33	25.01	15.00	2.43	24.27	0.42	57.81
[C$_8$py][N(CN)$_2$]	61.51	1.15	20.08	10.15	2.66	13.93	0.30	60.22
	68.44	0.94	20.58	12.07	1.56	16.50	0.28	68.66
	71.35	0.87	24.59	14.52	0.48	21.56	0.34	73.83

differences observed in the phase behavior for the different ionic liquids formed by distinct cation/anion combinations are a clear reflection of their commonly attributed epithet of "designer solvents". The appropriate selection of the cation and/or anion composing an ionic liquid could thus provide ATPS with tailored phase behavior and in acidic media.

The systems displayed in Figure 2 with a common cation, [C$_4$mim]$^+$, allow the investigation of the ability of the ionic liquid anions to promote ATPS. The results (at 0.5 mol·kg^{-1} Na$_2$SO$_4$) indicate that the anion influence follows the rank [CF$_3$SO$_3$]$^-$ > [OctylSO$_4$]$^-$ > [TOS]$^-$ ≈ [SCN]$^-$ > [N(CN)$_2$]$^-$ > [C$_2$H$_5$SO$_4$]$^-$ > [CF$_3$CO$_2$]$^-$ ≈ [CH$_3$SO$_4$]$^-$ > Br$^-$ (≫Cl$^-$ that does not form ATPS with Na$_2$SO$_4$ aqueous solutions). The trend displayed by the ionic liquid anions to induce ATPS agrees well with our previous results for ATPS formed with K$_3$PO$_4$ aqueous solutions.[11] This close agreement suggests that this trend is not dependent on the pH of the medium or on the ion speciation

(as discussed above) but is dependent only on the ionic liquid anion characteristics.[11] The anion rank obtained reflects thus the competition between the inorganic salt and the ionic liquid ions for the formation of water−ion hydration complexes.[34] Anions with highly dispersed charges tend to preferentially interact with hydrophobic moieties and do not form hydration complexes.[34] Thus, the hydrogen bonding accepting strength of an anion seems to be a main controlling factor in ATPS formation for a common inorganic salt. As previously observed, anions with low hydrogen bond basicity values are more prone to undergo liquid−liquid demixing in aqueous media.[11] While [C$_4$mim]-[CH$_3$CO$_2$] was not able to create Na$_2$SO$_4$-based ATPS, [C$_4$mim][CF$_3$CO$_2$] was capable of forming ATPS (the fluorination of the anion leads to lower β values).[11]

An increase in the alkyl side chain in both the ionic liquid cation and anion enhances the ability of the ionic liquid for ATPS formation, as observed by comparing the two following sets depicted in Figure 3:

Table 3. pH Values of the Coexisting Phases in IL–Na$_2$SO$_4$-Based ATPS at the Biphasic Composition of 25 wt % IL + 15 wt % Na$_2$SO$_4$ + 60 wt % Water (at 298 K), and the Na$_2$SO$_4$ Speciation[31] in Aqueous Solution

IL + Na$_2$SO$_4$ + water system			
IL		pH	[SO$_4$$^{2-}$]/[HSO$_4$$^{-}$]
[C$_2$mim][CF$_3$SO$_3$]	Na$_2$SO$_4$-rich phase	3.32	2.09×10^1
	IL-rich phase	2.71	5.13
[C$_4$mim][CF$_3$SO$_3$]	Na$_2$SO$_4$-rich phase	3.04	1.10×10^1
	IL-rich phase	3.12	1.32×10^1
[C$_4$mim]Br	Na$_2$SO$_4$-rich phase	5.22	1.66×10^3
	IL-rich phase	5.43	2.69×10^3
[C$_4$mim][CH$_3$SO$_4$]	Na$_2$SO$_4$-rich phase	1.57	3.72×10^{-1}
	IL-rich phase	1.88	7.59×10^{-1}
[C$_4$mim][C$_2$H$_5$SO$_4$]	Na$_2$SO$_4$-rich phase	1.29	1.95×10^{-1}
	IL-rich phase	2.29	1.95
[C$_4$mim][OctylSO$_4$]	Na$_2$SO$_4$-rich phase	3.52	3.31×10^1
	IL-rich phase	3.64	4.37×10^1
[C$_4$mim][N(CN)$_2$]	Na$_2$SO$_4$-rich phase	8.07	1.17×10^6
	IL-rich phase	8.54	3.47×10^6
[C$_4$mim][TOS]	Na$_2$SO$_4$-rich phase	5.16	1.45×10^3
	IL-rich phase	5.33	2.14×10^3
[C$_4$mim][SCN]	Na$_2$SO$_4$-rich phase	4.29	1.95×10^2
	IL-rich phase	4.49	3.09×10^2
[C$_4$mim][CF$_3$CO$_2$]	Na$_2$SO$_4$-rich phase	4.16	1.45×10^2
	IL-rich phase	4.18	1.51×10^2
[C$_7$mim]Cl	Na$_2$SO$_4$-rich phase	4.16	1.45×10^2
	IL-rich phase	4.15	1.41×10^2
[C$_7$H$_7$mim]Cl	Na$_2$SO$_4$-rich phase	4.64	4.37×10^2
	IL-rich phase	4.44	2.75×10^2
[C$_7$H$_7$mim][C$_2$H$_5$SO$_4$]	Na$_2$SO$_4$-rich phase	2.05	1.12
	IL-rich phase	2.08	1.20
[C$_8$py][N(CN)$_2$]	Na$_2$SO$_4$-rich phase	7.07	1.17×10^5
	IL-rich phase	6.94	8.71×10^5

Table 4. Hydrogen Bond Basicity Values (β) for Individual Ionic Liquids[a]

ionic liquid	β
[C$_4$mim][PF$_6$]	0.21[36]
[C$_4$mim][NTf$_2$]	0.24[36]
[C$_4$mim][BF$_4$]	*0.38[36]*
[C$_4$mim][CF$_3$SO$_3$]	*0.46[38]*
[C$_4$mim][N(CN)$_2$]	*0.60[38]*
[C$_4$mim][CH$_3$SO$_4$]	*0.67[38]*
[C$_4$mim][SCN]	*0.71[39,40]*
[C$_4$mim][CF$_3$CO$_2$]	*0.74[40,41]*
[C$_4$mim][OctylSO$_4$]	*0.77[40,41]*
[C$_4$mim]Br	*0.87[39,40]*
[C$_4$mim]Cl	0.95[37]
[C$_4$mim][DMP]	1.12[38]
[C$_4$mim][CH$_3$CO$_2$]	1.20[38]

[a] The rows in italics correspond to ionic liquids that are able to create Na$_2$SO$_4$-based ATPS.

[C$_2$mim][CF$_3$SO$_3$]/[C$_4$mim][CF$_3$SO$_3$] and [C$_4$mim][CH$_3$SO$_4$]/[C$_4$mim][C$_2$H$_5$SO$_4$]/[C$_4$mim][OctylSO$_4$]. This trend is a direct outcome of solvophobic and entropic effects: increasing the alkyl side chain length of the ionic liquid cation and/or anion enhances the fluid overall hydrophobicity while increasing the entropy of solution of the ionic liquid in water, and therefore facilitates the phase separation.[35] Moreover, while [C$_4$mim]Cl was not able to induce the phase separation, the chloride combination with different cations, such as [C$_7$mim]$^+$, leads to the formation of ATPS with Na$_2$SO$_4$ aqueous solutions, as shown in Figure 4. The ability for ATPS formation of [C$_7$mim]Cl is also a direct consequence of the longer alkyl side chain cation.

Figure 4 illustrates additional information on the ionic liquid cation influence for liquid–liquid demixing using Na$_2$SO$_4$ aqueous solutions. Comparing [C$_4$mim][C$_2$H$_5$SO$_4$] and [C$_7$H$_7$mim]-[C$_2$H$_5$SO$_4$], it is observed that the later ionic liquid presents a slightly higher ability to induce the formation of ATPS. Although the benzyl group present in [C$_7$H$_7$mim][C$_2$H$_5$SO$_4$] enhances the ionic liquid affinity for water and the ability to hydrogen bond, this larger substituent also contributes to a decrease in the solubility of the ionic liquid in water when compared with [C$_4$mim][C$_2$H$_5$SO$_4$]. This pattern is also in close

agreement with the results observed between [C$_7$H$_7$mim]Cl and [C$_4$mim]Cl.

Figure 4 shows that the ionic liquid containing the cation [C$_8$py]$^+$ has the greatest capacity to promote ATPS among all the ionic liquids studied. This enhanced capacity in creating ATPS is a direct result of the anion low hydrogen bond basicity ([N(CN)$_2$]$^-$) coupled to a pyridinium cation that also contributes to a reduction of the overall hydrogen bond basicity of the ionic liquid. Although we were not able to find literature β values for this specific ionic liquid, a general trend between imidazolium- and pyridinium-based cations was found and support this statement. The hydrogen bond basicity values of pyridinium-based ionic liquids are consistently lower than their imidazolium-based counterparts (β values: [C$_4$py][BF$_4$] = 0.213 and [C$_4$mim][BF$_4$][36] = 0.376; [C$_8$py][BF$_4$] = 0.340 and [C$_8$mim][BF$_4$][37] = 0.630; [C$_4$py][NTf$_2$] = 0.123 and [C$_4$mim][NTf$_2$][37] = 0.420; [C$_8$py][NTf$_2$] = 0.115 and [C$_8$mim][NTf$_2$][37] = 0.470). Therefore, the lower the hydrogen bond basicity of an ionic liquid, the greater is its ability for promoting ATPS.

Most of the discussion on the ionic liquid aptitude for creating ATPS was based on their hydrogen bond basicities, since it was verified that with the salt Na$_2$SO$_4$ the ILs with lower β values are apt to promote ATPS.[36−41] The β values for the distinct ionic liquids investigated in this work are reported in Table 4. Table 4 reveals that a close relationship exists between the ability of each ionic liquid to form ATPS and their hydrogen bond basicity values: the lower the β value is, the more efficient the ionic liquid is in creating ATPS. However, it should be remarked that, although a qualitative trend is observed, the comparison of the solvatochromic parameters obtained by different authors and different techniques is not straightforward and general deviations exist.[36−41] To generalize this comparison, the ionic liquids that were not able to form ATPS were also included, as well as those at the opposite extreme: the [PF$_6$]- and [NTf$_2$]-based ionic liquids that present low hydrogen bond basicities and, as such, are not completely miscible with water,[35,42] and are thus unable to create ATPS.

The results compiled in Table 4 indicate that any ionic liquid with β values ranging between those displayed by [C$_4$mim][BF$_4$]

and $[C_4mim]Br$ should be able to form ATPS with Na_2SO_4, while those below this range will be not water soluble and those above will not be able to undergo liquid—liquid demixing in Na_2SO_4 aqueous solutions.

CONCLUSIONS

IL-based ATPS are new approaches for recycling or concentrating hydrophilic ionic liquids from aqueous solutions or to perform selective separations of added-value products. In particular, when dealing with the extraction of compounds with low acid dissociation constants from aqueous media, the use of acidic IL-based ATPS could be advantageous.

Contrary to most literature reports that have suggested that IL-based ATPS could not be formed with acidic or neutral salt aqueous solutions, it was here demonstrated that an adequate selection of the ionic liquid structural features can lead to ATPS formation in acidic media. Phase diagrams, tie lines, and tie-line lengths were determined and reported at 298 K and atmospheric pressure. The results obtained indicate that both the ionic liquid cation and anion structural features have a large impact on the phase diagram behavior. In general, an increase in the cation/anion alkyl chain length leads to an increase in the phase separation ability, whereas a decrease in the hydrogen bond basicity of the ionic liquid promotes the formation of ATPS. In particular, the ability of ionic liquids to create ATPS was found to be largely dependent on their hydrogen bond basicity values: a measure of their capability to hydrogen bond with water. This close relationship allowed us to state that ionic liquids with β values ranging between $[C_4mim][BF_4]$ and $[C_4mim]Br$ are able to form aqueous two-phase systems with Na_2SO_4, while those ionic liquids with β values outside this limited range will not form Na_2SO_4-based ATPS. Besides the effect of the ionic liquid structural features toward the formation of IL-based ATPS, the pH media of the inorganic salts were shown to be a determinant factor regarding the number of effective ionic liquids that are capable of undergoing liquid—liquid demixing.

ASSOCIATED CONTENT

S **Supporting Information.** Initial weight fraction compositions used in the determination of the phase diagrams; weight fraction binodal data for the ternary systems with ILs (1), Na_2SO_4 (2), and water (3) at 298 K; pH values of coexisting phases in IL—Na_2SO_4-based ATPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

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