Evaluation of the impact of phosphate salts on the formation of ionic-liquid-based aqueous biphasic systems

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ABSTRACT

The present study aims at evaluating the capability of phosphate-based salts, whose anions can coexist in water depending on the media pH, to promote aqueous biphasic systems (ABS) formation with 1-butyl-3-methylimidazolium-based ionic liquids, as well as to infer on the influence of the ionic liquid anion in the overall process of liquid–liquid demixing. In this context, novel phase diagrams of ABS composed of several imidazolium-based ionic liquids and three phosphate salts and a mixture of salts (K_3PO_4, K_2HPO_4, K_2HPO_4 + KH_2PO_4, and KH_2PO_4) were determined by the cloud point titration method at 298 K and atmospheric pressure. The corresponding tie-line compositions, tie-line lengths, and pH values of the coexisting phases were also determined. The ionic liquids ability to promote ABS is related with the hydrogen-bond basicity of the composing anion – the lower it is the higher the ability of the ionic fluid to undergo liquid–liquid demixing. Moreover, similar patterns on the ionic liquids sequence were observed with the different phosphate salts. The phosphate anion charge plays a determinant role in the formation of ABS. The two-phase formation aptitude (with a similar ionic liquid) decreases in the rank: K_3PO_4 > K_2HPO_4 > K_2HPO_4 + KH_2PO_4 > KH_2PO_4. Yet, besides the charge of the phosphate anion, the pH and ionic strength of the aqueous media also influence the phase separation ability.

1. Introduction

Ionic liquids (ILs) are salts with their ions loosely bound and which are liquid at temperatures below 100 °C. Their main physical and chemical properties are their wide liquid temperature range, a negligible volatility, enhanced chemical and thermal stabilities, good electrical conductivity, and their improved solvation ability for a large variety of compounds. ILs are actually considered tunable designer solvents since a myriad of physical and chemical properties can be obtained by introducing small changes in the cation or in the anion chemical structure. As such, they are amenable to be tailored according to the specific application in need [1]. Their unique characteristics make them a valuable choice for a number of industrial applications, namely in the conversion of biomass into added-value chemicals, in catalysis, in extraction and separation processes, among many others [2].

In recent years, aqueous solutions of ILs have been suggested as promising alternatives to polymer-rich phases in aqueous biphasic systems (ABS), mainly because of their lower viscosities, faster separation of the coexisting phases, and vast applicability in controlling the polarities of the phases [3–6]. The first reported system with this

family of ionic solvents used the hydrophilic 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) and K_3PO_4 as the salting-out inducing inorganic salt [7]. A wide range of studies using ILs in the formation of ABS have been performed since then, and attempts to understand the effect of the ionic liquid cation [8–11] and anion nature [3,12–14] have been carried out. Bridges *et al.* [15] were the first to evaluate the salt and ionic liquid cation effects by presenting phase diagrams for imidazolium-, pyridinium-, ammonium-, and phosphonium-based chloride ionic liquids combined with the salts K_3PO_4, K_2HPO_4, K_2CO_3, KOH, and $(NH_4)_2SO_4$. Wang *et al.* [16] studied ABS formed by 1-butyl-3-methylimidazolium tetrafluoroborate and the salts Na_2CO_3, $(NH_4)_2SO_4$, NaH_2PO_4, $MgSO_4$, Na_2SO_3, and NaOH. The authors [16] also reported 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. Li *et al.* [17] stated that ABS with 1-butyl-3-methylimidazolium chloride 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. In fact, on the literature, most of the reports have been focused on phosphate-based salts since they easily induce the formation of liquid–liquid biphasic systems. To provide a more complete perspective of the salt effect, Shahriari *et al.* [18] analyzed a large body of data to establish the effect of both the anion and cation of the inorganic/organic salt in the formation of ABS of a single ionic liquid: 1-butyl-3-methylimidazolium trifluoromethanesulfonate.

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In spite of the efforts carried by a number of authors, the formation of ionic-liquid-based ABS seems to be influenced by many variables besides the IL and salt identities and, as a result, a complete understanding of the mechanism and the underlying interactions has not yet been achieved. The picture more commonly accepted is that when a salt is dissolved in an aqueous solution, its ions are surrounded by a layer of water molecules, a process known as ionic hydration. In the present case, when an inorganic salt is added to an aqueous solution of an ionic liquid, the two solutes compete for the solvent molecules. The competition is won by the inorganic ions (with a stronger interaction with the solvent), and those of the ionic liquid lose. There is a "migration" of solvent molecules away from the ions of the ionic liquid towards those of the inorganic salt, which, in turn, decreases the hydration and therefore the solubility of the ionic liquid in water. As a consequence, a phase rich in ionic liquid separates from the rest of the solution [19,20]. Moreover, a more prominent effect of the salt anion is to be expected: having a more diffuse valence electronic configuration than cations, they are more polarizable and have a higher aptitude to be hydrated [9,19,21]. Most authors [15,17] stated that the Hofmeister series [22] is always obeyed and explained their ranks based on the Gibbs free energy of hydration of the ions [23], but there is considerable amount of evidence that the salting-out of ionic liquids by inorganic salts from aqueous media is driven by an entropic process resulting from the preferential formation of water-ion complexes [9,18,21,24]. Hydration and hydrogen-bond formation are thus processes particularly relevant for the anions involved, whether they come from the salt or from the IL. Those processes are naturally pH dependent and this variable must also be accounted for. However, changing the pH of the salt́s solution almost invariably leads to changes in both the charge of the ions and on the extent of the hydrogen-bonding. Therefore, an evaluation of each factor independently is not a straightforward matter.

Henceforth, a systematic approach stems as a most valuable tool to study these effects. Since salting-in/-out effects are more pronounced when different anions are compared [25,26] we propose now to study the IL anion influence in promoting ABS formation under different pH values obtained by the use of diverse phosphate-based salts. The cation 1-butyl-3-methylimidazolium was chosen due to its role as a model IL cation for which extensive data are available either from experimental studies [9,15,27–31] or from computer simulations [32–34]. In addition, the phosphate-based inorganic salts were selected because they are important ions in biological systems [35]. K_3PO_4 is indeed the most studied salt as a salting-out species [3,7,13,19,31,36–43] followed by KH_2PO_4 and KH_2PO_4/K_2HPO_4 mixtures which are also frequently used at the biotechnological field [19,33,43,45,46].

The present study aims at evaluating the ability of three phosphate salts, K_3PO_4, KH_2PO_4, and K_2HPO_4, and one of their mixtures (K_2HPO_4/KH_2PO_4), and whose anions can coexist in water depending on the media pH, to promote the formation of ionic-liquid-based ABS, and also infer on the influence of the IL anion in the overall process. The results here obtained, along with data from previous works using K_3PO_4 [19] and a buffered mixture KH_2PO_4/K_2HPO_4 [44] enabled us to gather a broader picture on the evaluation of the influence of both the salt's anion charge and ionic liquid anion towards the formation of ABS.

2. Experimental

2.1. Materials

The ionic liquids used in this work were 1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[C_4mim][CF_3SO_3]$; 1-butyl-3-methylimidazolium methanesulfonate, $[C_4mim][CH_3$-

$SO_3]$; 1-butyl-3-methylimidazolium acetate, $[C_4mim][CH_3CO_2]$; 1-butyl-3-methylimidazolium trifluoroacetate, $[C_4mim][CF_3CO_2]$; 1-butyl-3-methylimidazolium ethylsulfate, $[C_4mim][C_2H_5SO_4]$; 1-butyl-3-methylimidazolium methylsulfate, $[C_4mim][CH_3SO_4]$; 1-butyl-3-methylimidazolium 4-methylbenzenesulfonate (tosylate), $[C_4mim][TOS]$; 1-butyl-3-methylimidazolium chloride, $[C_4mim]Cl$; 1-butyl-3-methylimidazolium bromide, $[C_4mim]Br$; 1-butyl-3-methylimidazolium dicyanamide, $[C_4mim][N(CN)_2]$; and 1-butyl-3-methylimidazolium dimethylphosphate, $[C_4mim][DMP]$. Their ionic structures are presented in figure 1.

All ILs were supplied by Iolitec (Ionic Liquid Technologies, Germany). To reduce the volatile impurities content to negligible values, ILs individual samples were kept at constant agitation under vacuum and at a moderate temperature (323 K), for a minimum of 24 h. After this purification step, the purity of each IL was further checked by ^1H, ^{13}C and ^{19}F NMR (when applicable) spectra and found to be >98 wt% for all samples (water content < 1000 ppm as determined by Karl-Fischer titration and halogen content < 100 ppm). K_3PO_4 was from Sigma (purity > 98 wt%), K_2HPO_4 was from Riedel-de Haën (purity > 99 wt%), and KH_2PO_4 was from Panreac (purity > 99 wt%). The buffers used in the calibration of the pH meter equipment were the citric acid/sodium hydroxide/sodium chloride solution with a pH value of 4.00 (±0.02), and the potassium dihydrogenphosphate/disodium hydrogenphosphate solution with a pH value of 7.00 (±0.02), acquired from Fluka. Double distilled water, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification equipment, was used in all experiments.

2.2. Phase diagrams and tie-lines

The solubility curves of the systems composed of IL, water, and each of the phosphate salts were determined using the cloud point titration method at 298 K (±1 K). The experimental procedure adopted in this work follows the method already validated by us for ABS constituted by other ILs and inorganic salts [19,38,45].

Aqueous solutions of each salt with variable mass fractions (50 wt% for K_3PO_4 and K_2HPO_4, 18 wt% for KH_2PO_4, and 40 wt% for the phosphate buffer composed of a mixture of the salts K_2HPO_4 and KH_2PO_4 with pH = 7.0 and Henderson–Hasselbalch equation equivalents = 1.09), and aqueous solutions of each ionic liquid in a range between 35 and 70 wt%, were prepared and used for the determination of the corresponding solubility curves. Repetitive drop-wise addition of the aqueous salt solution to each ionic liquid aqueous solution was carried out until the detection of a cloudy solution (the biphasic region), followed by the drop-wise addition of water until the formation of a clear and limpid solution (the monophasic region). To complete the phase diagrams the opposite addition of the ionic liquid aqueous solution to the salt solutions was also carried out. Drop-wise additions were carried out under constant stirring. The ternary systems compositions were determined by weight quantification of all components within ±10^{-7} kg.

The experimental binodal curves were fitted by least-squares regression according to equation (1) [46]:

$$[IL] = A\exp[(B \times [Salt]^{0.5}) - (C \times [Salt]^3)], \tag{1}$$

where [IL] and [Salt] are the ionic liquid and the inorganic salt mass fraction percentages, respectively, and A, B and C are fitted constants obtained by the regression of the experimental data.

For the determination of each tie-lines (TL), a ternary mixture composed of phosphate salt + water + ionic liquid at the biphasic region was gravimetrically prepared within ±10^{-7} kg, vigorously stirred, and left to equilibrate for at least 12 h at 298 K, aiming for a complete separation of the coexisting aqueous phases. The
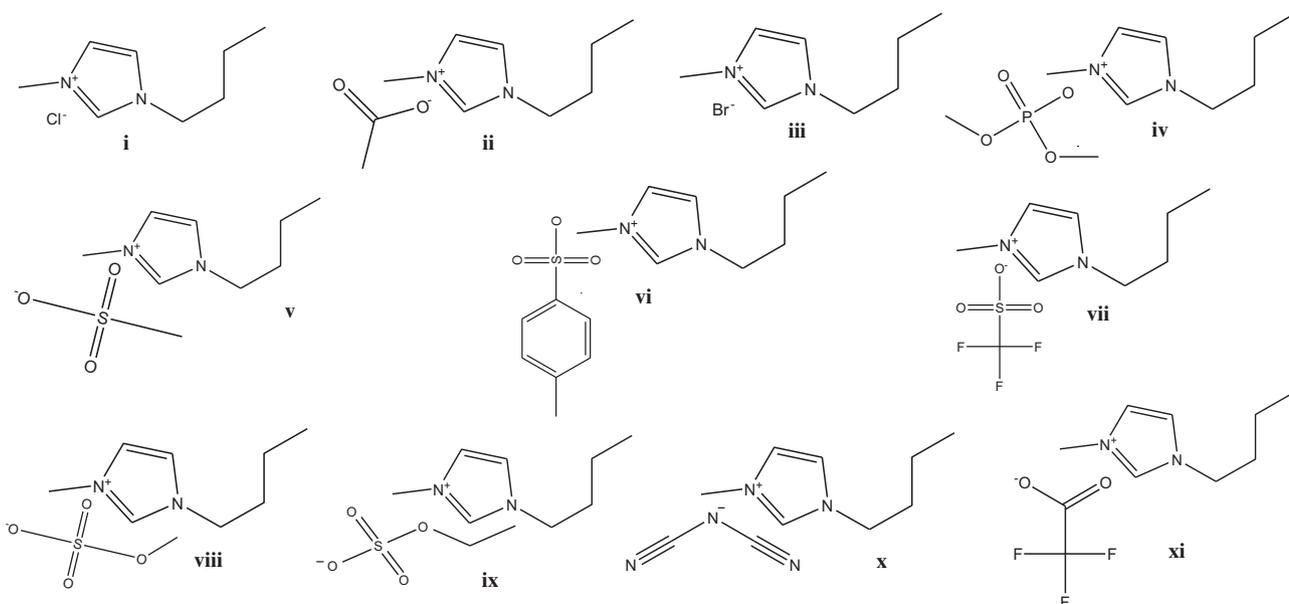
FIGURE 1. Chemical structures of the studied ILs: (i) [C$_4$mim]Cl; (ii) [C$_4$mim][CH$_3$CO$_2$]; (iii) [C$_4$mim]Br; (iv) [C$_4$mim][DMP]; (v) [C$_4$mim][CH$_3$SO$_3$]; (vi) [C$_4$mim][TOS]; (vii) [C$_4$mim][CF$_3$SO$_3$]; (viii) [C$_4$mim][CH$_3$SO$_4$]; (ix) [C$_4$mim][C$_2$H$_5$SO$_4$]; (x) [C$_4$mim][N(CN)$_2$]; (xi) [C$_4$mim][CF$_3$CO$_2$].

phases were further separated and individually weighed within $\pm 10^{-7}$ kg. Each TL was determined through the relationship between the weight of the top phase and the overall weight by the lever-arm rule [46], and for which the following system of four equations (equations (2)–(5)) and four unknown values ([IL]$_T$, [IL]$_B$, [Salt]$_T$ and [Salt]$_B$) was solved:

$$[IL]_T = A\exp[(B \times [Salt]_T^{0.5}) - (C \times [Salt]_T^3)], \tag{2}$$

$$[IL]_B = A\exp[(B \times [Salt]_B^{0.5}) - (C \times [Salt]_B^3)], \tag{3}$$

$$[IL]_T = \frac{[IL]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [IL]_B, \tag{4}$$

$$[Salt]_T = \frac{[Salt]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [Salt]_B, \tag{5}$$

where "T", "B", and "M" designate the top phase, the bottom phase and the mixture, respectively, [Salt] and [IL] represent the weight fraction of inorganic salt 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 mass fraction percentage of the ionic liquid and inorganic salt in the top and bottom phases, and thus represents the TLs of each system.

The tie-line length (TLL) was determined using equation (6),

$$TLL = \sqrt{\left([Salt]_T - [Salt]_B\right)^2 + \left([IL]_T - [IL]_B\right)^2} \tag{6}$$

and corresponds to the distance between the point in the binodal curve at the bottom phase composition to that at the top phase.

2.3. pH measurements

The pH values of the IL- and inorganic-salt-rich aqueous phases were measured at 298 K (± 1 K) using an HI 9321 Microprocessor pH meter (HANNA instruments) with an uncertainty of ± 0.02. The calibration of the pH meter was carried out with two buffers (pH values of 4.00 and 7.00). The ternary mixtures were prepared by weight, vigorously stirred, and further kept still in small ampoules for phase separation for at least 12 h, and as previously described for the determination of TLs. After the careful separation of

the phases, the pH of each aqueous phase was measured. The compositions at which the pH was measured correspond to the same compositions adopted for the TLs determination.

3. Results and discussion

Since all systems studied on this work share the same IL cation, and the temperature (298 K) and pressure (1 bar) are also common, the comparison of the data allows the evaluation of the effect of the anion of the IL as well as the effect of the salt on the ABS formation.

Albeit ionic species are present in ionic liquid + inorganic salt ABS, and thus ion exchange might be expected, Bridges *et al.* [15] have shown that the ions migration in the coexisting phases of the ABS composed of [C$_4$mim]Cl + K$_3$PO$_4$ is not significant to yield inaccurate results on the concentration of each salt at both aqueous phases – taking into account the uncertainty already associated to the experimental procedure. This has been confirmed later on by Zafarani-Moattar and Hamzehzadeh [43] and by Neves *et al.* [47]; therefore, it may be assumed that the same is valid for the phosphate systems here studied.

Making use of the experimental data obtained in this work and those already published [19,44], the main results can be grouped in four sets of phosphate-based ABS from highest to the least charge bearer salt: (1) potassium phosphate, K$_3$PO$_4$; (2) potassium hydrogenphosphate, K$_2$HPO$_4$; (3) phosphate buffer composed of potassium hydrogenphosphate + dihydrogenphosphate, K$_2$HPO$_4$ + KH$_2$PO$_4$; (4) potassium dihydrogenphosphate, KH$_2$PO$_4$. The weight fraction data for all the solubility curves measured in this work are presented in Supplementary data.

3.1. Effect of ionic liquid on ABS formation

3.1.1. Systems composed of potassium phosphate, K$_3$PO$_4$

The binodal curves for [C$_4$mim][CF$_3$SO$_3$], [C$_4$mim]Br, [C$_4$mim][CH$_3$SO$_3$], [C$_4$mim][N(CN)$_2$], [C$_4$mim][CF$_3$SO$_3$], [C$_4$mim]Cl, [C$_4$mim][CH$_3$CO$_2$], and [C$_4$mim][CF$_3$CO$_2$] were reported in a previous paper [19] while new data for [C$_4$mim][TOS], [C$_4$mim][CH$_3$SO$_4$], [C$_4$mim][C$_2$H$_5$SO$_4$] and [C$_4$mim][DMP] are shown in figure

2. It should be stressed that all the phase diagrams are displayed in molality units to allow a more direct comparison among the different ionic liquids and salts effects. The parameters obtained for the regression of the solubility curves of the IL + K$_3$PO$_4$ + H$_2$O systems using equation (1) are presented in table 1. The ternary system compositions used at the biphasic region and the TL compositions, the respective tie-line lengths, and pH values are reported in table 2.

In figure 2, the closer the curve is to the axes the larger the biphasic area and the stronger the demixing ability of the ionic liquid anion. On the systems here studied we found that ability to increase in the order: [C$_4$mim][TOS] > [C$_4$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim][DMP] ≈ [C$_4$mim][CH$_3$SO$_4$].

In the systems studied here and in the ones reported previously [19] the IL cation and the ions of the salt are the same, so a more general sequence for the IL anion ability to promote demixing can be established and is presented in table 3. Anions interact with water molecules by an approximately linear hydrogen bond, suggesting that the dominant interactions are short range forces of a
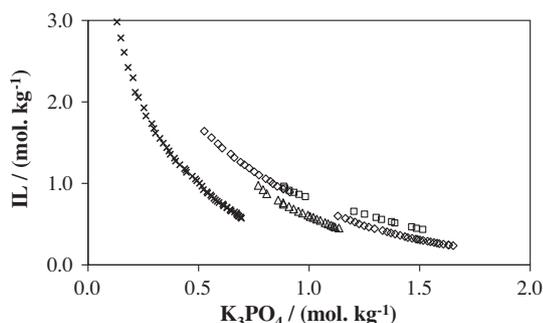

FIGURE 2. Ternary phase diagrams for [C$_4$mim]-based ILs + K$_3$PO$_4$ at 298 K and atmospheric pressure: ×, [C$_4$mim][TOS]; Δ, [C$_4$mim][C$_2$H$_5$SO$_4$]; □, [C$_4$mim][DMP]; ◇, [C$_4$mim][CH$_3$SO$_4$].

TABLE 1
Parameters *A*, *B* and *C* of equation (1) (and respective standard deviations, σ, and correlation coefficients, R^2) for the [C$_4$mim]-based ILs + phosphate salt + H$_2$O systems at 298 K.

	$A \pm \sigma$	$B \pm \sigma$	$10^5(C \pm \sigma)$	R^2
IL + K$_3$PO$_4$ + water				
[C$_4$mim][CH$_3$SO$_4$]	82.78 ± 1.90	−0.308 ± 0.007	6.67 ± 0.09	0.9998
[C$_4$mim][C$_2$H$_5$SO$_4$]	213.63 ± 57.22	−0.587 ± 0.079	5.48 ± 1.17	0.9984
[C$_4$mim][TOS]	89.88 ± 1.01	−0.378 ± 0.005	19.4 ± 0.53	0.9993
[C$_4$mim][DMP]	51.24 ± 12.04	−0.192 ± 0.065	4.57 ± 0.63	0.9996
IL + K$_2$HPO$_4$ + water				
[C$_4$mim]Cl	92.70 ± 3.29	−0.370 ± 0.012	1.80 ± 2.01	0.9919
[C$_4$mim]Br	73.80 ± 1.27	−0.267 ± 0.004	4.77 ± 0.36	0.9970
[C$_4$mim][CH$_3$SO$_4$]	81.48 ± 3.17	−0.284 ± 0.010	3.67 ± 0.07	0.9989
[C$_4$mim][C$_2$H$_5$SO$_4$]	87.20 ± 4.11	−0.322 ± 0.017	3.85 ± 0.74	0.9985
[C$_4$mim][N(CN)$_2$]	84.27 ± 0.73	−0.378 ± 0.004	17.34 ± 0.51	0.9986
[C$_4$mim][TOS]	89.88 ± 0.62	−0.347 ± 0.003	13.28 ± 0.02	0.9996
[C$_4$mim][DMP]	75.21 ± 1.00	−0.272 ± 0.004	2.28 ± 0.03	0.9996
[C$_4$mim][CH$_3$CO$_2$]	87.39 ± 2.54	−0.342 ± 0.009	1.64 ± 0.12	0.9992
[C$_4$mim][CH$_3$SO$_3$]	83.16 ± 0.40	−0.291 ± 0.002	2.16 ± 0.03	0.9996
[C$_4$mim][CF$_3$SO$_3$]	225.87 ± 8.38	−0.965 ± 0.021	1.00 ± 5.85	0.9962
[C$_4$mim][CF$_3$CO$_2$]	86.34 ± 0.62	−0.308 ± 0.003	6.17 ± 0.06	0.9997
IL + K$_2$HPO$_4$/KH$_2$PO$_4$ + water				
[C$_4$mim]Br	80.80 ± 0.77	−0.301 ± 0.004	2.31 ± 1.58	0.9994
[C$_4$mim][CH$_3$SO$_4$]	72.42 ± 2.38	−0.246 ± 0.008	3.22 ± 0.07	0.9996
[C4mim][DMP]	74.36 ± 2.96	−0.258 ± 0.011	2.07 ± 0.14	0.9996
[C$_4$mim][CF$_3$CO$_2$]	114.81 ± 2.80	−0.415 ± 0.010	2.88 ± 0.03	0.9977
IL + KH$_2$PO$_4$ + water				
[C$_4$mim][CF$_3$SO$_3$]	126.95 ± 5.51	−0.542 ± 0.025	39.93 ± 6.70	0.9977

chemical nature [48]. Thus, the ability for a given anion to be preferentially hydrated depends on its ability to hydrogen bond. In fact, the ionic liquid anion forming ability for ABS follows a trend most similar to the one presented by their H-bond basicity values [2,49]. This is a descriptor of solvation interactions at a molecular level that relies on empirical scales based on solvent interactions with a reference solute [50,51]. Those scales are usually based on solvatochromic probes, such as the Reichardt ET(30) [52] and the Kamlet-Taft [53]. If we consider the literature values using the ionic solvatochromic probe [Fe(phen)$_2$(CN)$_2$]ClO$_4$ in [51,54,55], we notice some discrepancy among them, so we considered values from the least number of authors (table 4). As it can be noticed the rank obtained from the binodal curves follows closely (although not accurately) the H-bond basicity values of the ionic liquids, and as previously discussed by us [19].

The PO$_4^{3-}$ equilibrium concentration values were determined from the corresponding values of the total phosphate concentration and the basicity constant, Kb$_3$, (the two successive hydrolysis reactions can be neglected, as well as water hydrolysis) and were always greater than 90% of the total amount. The triple charge and the ability of PO$_4^{3-}$ to act as a hydrogen acceptor towards water do certainly have an important contribution in extensive formation of complexes with water; the competition for water molecules will lead to the dehydration of IL ions which release water molecules, and to an increase of the surface tension of the IL cavity. Therefore, PO$_4^{3-}$ is a strong salting-out species and leads to the liquid–liquid demixing of a wide range of aqueous solutions of ionic liquids as shown in table 3.

3.1.2. Systems composed of potassium hydrogenphosphate, K$_2$HPO$_4$

A large range of ILs was studied using K$_2$HPO$_4$, and the experimental phase diagrams at 298 K and atmospheric pressure for the systems constituted by IL + K$_2$HPO$_4$ + H$_2$O are presented in figure 3. The parameters obtained for the regression of the corresponding solubility curves using equation (1) are presented in table 1. The TL compositions, tie-line lengths, and pH values of the coexisting phases are reported in table 2. An example of the tie-lines obtained in this work can be appreciated in figure 4 for the system composed of [C$_4$mim][N(CN)$_2$] + K$_2$HPO$_4$ + water.

When considering the basicity equilibrium for the HPO$_4^{2-}$ aqueous solutions (the species acidic character being negligible) small differences (<1%) between nominal and equilibrium values are to be expected and can be ignored.

If we choose the salt concentration of 1.0 mol·kg^{-1} to compare the relative ability of the IL for ABS formation we observe that it decreases according to the following order: [C$_4$mim][CF$_3$SO$_3$] > [C$_4$mim][TOS] ≈ [C$_4$mim][N(CN)$_2$] > [C$_4$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim][CF$_3$CO$_2$] > [C$_4$mim]Br ≈ [C$_4$mim][CH$_3$SO$_4$] ≈ [C$_4$mim][DMP] > [C$_4$mim][CH$_3$CO$_2$] > [C$_4$mim][CH$_3$SO$_3$] > [C$_4$mim]Cl. The systems formed by the addition of K$_2$HPO$_4$ closely follow the trend observed for the K$_3$PO$_4$ series presented above; yet, with higher values for their saturation solubilities. This is not an unexpected result considering the comparatively lower charge density of HPO$_4^{2-}$ and its inherent lower hydration capability.

Besides the general trend and that the ionic liquid extremes are almost the same, when comparing the sequences obtained with both salts, K$_3$PO$_4$ and K$_2$HPO$_4$, there are however slight differences in the ionic liquids rank (table 3). For instance, the acetate-based ionic liquid is more easily salted-out than [C$_4$mim]Cl when using K$_2$HPO$_4$. It should be noted that the interaction of IL with water is mainly dependent on the nature and concentration of the IL anion but also from the relative proportions of all players [56–58]. The processes seem to be surface phenomena and dominated by short range interactions with a marginal effect in the bulk water; the IL assumes therefore the prominent role [56]. Minor changes in pH may induce disturbances at the IL

TABLE 2
Compositions (mass fraction) for the [C$_4$mim]-based ILs + phosphate salt + H$_2$O systems at 298 K, and respective values of TLL, and pH of the coexisting phases.

IL	100 (mass fraction composition ± 2^{-4})^a						TLL ± 0.02^a	pH$_B$ ± 0.02^a	pH$_T$ ± 0.02^a
	[IL]$_T$	[Salt]$_T$	[Y]$_M$	[X]$_M$	[IL]$_B$	[Salt]$_B$			
				IL + K$_3$PO$_4$ + water					
[C$_4$mim][CH$_3$SO$_4$]	42.95	4.47	24.88	14.87	6.43	24.85	41.82	12.91	13.30
	52.07	2.27	29.54	14.51	3.22	28.82	55.60	12.94	13.07
[C$_4$mim][C$_2$H$_5$SO$_4$]	41.22	7.62	24.90	14.68	7.25	22.31	37.01	12.68	12.91
	53.46	5.49	29.99	14.68	5.37	24.32	51.64	12.67	12.90
[C$_4$mim][TOS]	52.82	1.96	29.79	10.27	3.93	19.58	52.00	12.56	12.99
	62.84	0.90	37.16	10.72	0.75	24.64	66.48	13.05	12.91
[C$_4$mim][DMP]	39.48	1.85	19.87	19.73	1.87	36.15	50.90	13.40	13.56
	46.53	0.25	24.65	19.87	0.58	41.45	61.72	13.54	13.77
				IL + K$_2$HPO$_4$ + water					
[C$_4$mim]Cl	37.86	5.81	33.37	9.81	4.58	35.45	44.57	9.46	9.46
	44.18	3.99	37.67	9.84	2.35	41.52	56.20	9.80	9.58
[C$_4$mim]Br	48.12	2.56	37.78	10.14	1.35	36.83	57.98	9.40	9.36
	57.78	0.84	44.76	10.60	0.22	44.02	71.96	9.60	9.57
[C$_4$mim][CH$_3$SO$_4$]	54.11	2.07	24.84	20.18	4.36	32.84	58.50	8.72	8.75
	60.39	1.11	29.93	20.07	2.11	37.39	68.65	8.81	9.08
[C$_4$mim][C$_2$H$_5$SO$_4$]	34.02	8.17	23.74	15.48	7.88	26.76	32.09	8.38	8.35
	49.48	3.08	25.29	19.90	2.08	36.03	57.73	8.52	8.72
[C$_4$mim][N(CN)$_2$]	49.50	1.97	30.00	10.14	2.50	21.65	50.95	8.46	9.25
	58.26	0.94	37.86	9.97	0.48	26.50	63.18	9.17	9.34
[C$_4$mim][TOS]	43.04	4.38	29.88	10.11	5.88	20.57	40.53	9.10	9.32
	53.76	2.19	25.35	14.90	1.75	25.46	56.98	9.18	9.59
	55.39	1.94	38.94	9.83	0.74	28.13	60.60	9.27	9.95
[C$_4$mim][DMP]	44.02	3.86	37.88	9.94	1.25	46.21	60.19	9.62	9.61
	57.26	1.01	29.52	24.87	0.68	49.75	74.64	10.02	10.20
[C$_4$mim][CH$_3$CO$_2$]	30.83	9.05	24.92	15.10	5.95	34.50	35.59	8.25	8.07
	38.61	5.65	29.88	15.08	1.90	45.27	54.01	8.07	8.08
[C$_4$mim][CH$_3$SO$_3$]	42.24	5.38	37.35	10.25	1.40	46.08	57.67	9.20	9.69
	44.79	4.50	30.64	19.74	0.47	52.25	65.15	9.44	9.89
[C$_4$mim][CF$_3$SO$_3$]	72.24	1.40	19.97	10.04	7.78	12.06	65.34	8.60	8.74
	69.50	1.49	37.91	9.95	3.03	19.30	68.81	9.09	9.26
				IL + KH$_2$PO$_4$/K$_2$HPO$_4$ + water					
[C$_4$mim]Br	46.00	3.49	37.89	10.03	3.77	37.56	54.26	7.45	7.47
	54.72	1.67	44.83	9.99	0.96	46.85	70.22	7.50	7.48
[C$_4$mim][CH$_3$SO$_4$]	43.95	4.08	24.98	19.98	2.32	38.95	54.31	7.09	7.27
	52.71	1.66	29.95	19.95	1.08	43.14	66.23	7.43	7.42
[C4mim][DMP]	44.58	3.91	38.00	9.98	2.82	42.50	56.87	7.50	7.53
	53.01	1.72	29.94	24.52	0.46	53.68	73.91	7.59	7.62
				IL + KH$_2$PO$_4$ + water					
[C$_4$mim][CF$_3$SO$_3$]	45.29	3.50	30.05	9.92	0.10	22.54	49.03	5.08	4.75
	53.91	2.47	37.67	9.92	0.00	27.21	59.32	5.96	4.83

^{a} Expanded uncertainty at the 0.95 confidence level evaluated from the standard deviation and applying a coverage factor $k = 2$.

TABLE 3
Ability of the various [C$_4$mim]-based ILs for phase separation (for 1 mol·kg^{-1} of phosphate salt).

Salts	Ability of [C$_4$mim]-based ILs for ABS formation
K$_3$PO$_4$	[C$_4$mim][CF$_3$SO$_3$] [19] > [C$_4$mim][N(CN)$_2$] [19] > [C$_4$mim][TOS] > [C$_4$mim][CF$_3$CO$_2$] [19] > [C$_4$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim]Br [19] ≈ [C$_4$mim][CH$_3$SO$_4$] > [C$_4$mim][DMP] > [C$_4$mim][CH$_3$SO$_3$] [19] > [C$_4$mim]Cl [19] > [C$_4$mim][CH$_3$CO$_2$] [19]
K$_2$HPO$_4$	[C$_4$mim][CF$_3$SO$_3$] > [C$_4$mim][TOS] > [C$_4$mim][N(CN)$_2$] > [C$_4$mim][C$_2$H$_5$SO$_4$] > [C$_4$mim][CF$_3$CO$_2$] ≈ [C$_4$mim][CH$_3$SO$_4$] ≈ [C$_4$mim][DMP] > [C$_4$mim]Br > [C$_4$mim][CH$_3$CO$_2$] ≈ [C$_4$mim][CH$_3$SO$_3$] > [C$_4$mim]Cl
K$_2$HPO$_4$/ KH$_2$PO$_4$	[C$_4$mim][CF$_3$SO$_3$] [44] > [C$_4$mim][TOS] [44] [C$_4$mim][N(CN)$_2$] [44] > [C$_4$mim][CF$_3$CO$_2$] > [C$_4$mim][C$_2$H$_5$SO$_4$] [44] ≈ [C$_4$mim][DMP] ≈ [C$_4$mim][CH$_3$SO$_4$] > [C$_4$mim][CH$_3$CO$_2$] [44] ≈ [C$_4$mim]Br > [C$_4$mim]Cl [44] > [C$_4$mim][CH$_3$SO$_3$] [44]
KH$_2$PO$_4$	[C$_4$mim][CF$_3$SO$_3$]

surface and in fact the difference in pH of both series is of several units, as can be seen in table 2. Impurities may also affect the IL surface, making reproducibility difficult to achieve [56]. Nevertheless, the presence of impurities affecting these experiments can be overruled by the close agreement between them and previous results from our group [19] as well as from others [31,59]. In Supplementary data the comparison of our results with literature ones for the systems [C$_4$mim]Cl, [C$_4$mim]Br and [C$_4$mim][CH$_3$CO$_2$] is presented.

3.1.3. Systems composed of potassium hydrogenphosphate + dihydrogenphosphate, K$_2$HPO$_4$ + KH$_2$PO$_4$

The combination of K$_2$HPO$_4$ + KH$_2$PO$_4$ (1.00 m + 1.09 m) to obtain a phosphate buffer solution at a neutral pH (7.0) and to be used in ABS formation was addressed in a previous study [44]. Nevertheless, to complete the study, new data for [C$_4$mim]Br, [C$_4$mim][CH$_3$SO$_4$], [C$_4$mim][DMP] and [C$_4$mim][CF$_3$CO$_2$] were obtained in this work. The regression parameters estimated by least-squares regression of the cloud-point data using equation
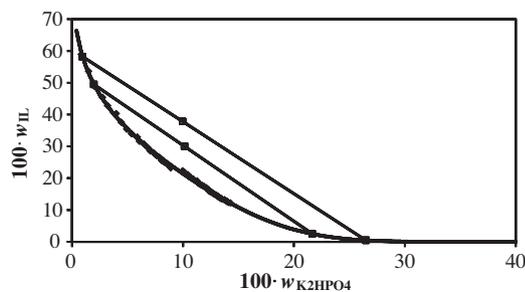
TABLE 4
Hydrogen bond basicity (β) of [C$_4$mim]-based ILs with the solvatochromic probe [Fe(phen)$_2$(CN)$_2$] ClO$_4$.

Ionic liquid	β
[C$_4$mim][CF$_3$SO$_3$]	0.49 [55]
[C$_4$mim][N(CN)$_2$]	0.60 [55]
[C$_4$mim][CH$_3$SO$_4$]	0.66 [55]
[C$_4$mim][CH$_3$SO$_3$]	0.85 [51]
[C$_4$mim]Br	0.87 [51]
[C$_4$mim]Cl	0.95 [51]
[C$_4$mim][DMP]	1.12 [55]
[C$_4$mim][CH$_3$CO$_2$]	1.20 [55]
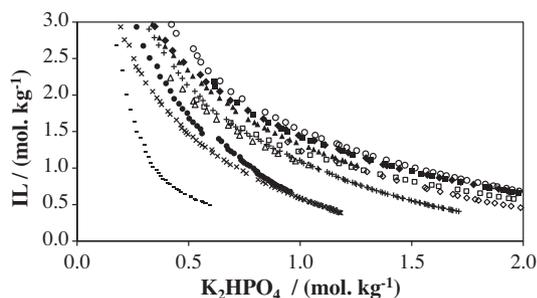
FIGURE 3. Ternary phase diagrams for [C$_4$mim]-based ILs + K$_2$HPO$_4$ at 298 K and atmospheric pressure: -, [C$_4$mim][CF$_3$SO$_3$]; ●, [C$_4$mim][N(CN)$_2$]; ×, [C$_4$mim][TOS]; △, [C$_4$mim][C$_2$H$_5$SO$_4$]; +, [C$_4$mim][CF$_3$CO$_2$]; □, [C$_4$mim][DMP]; ◇, [C$_4$mim][CH$_3$SO$_4$]; ▲, [C$_4$mim]Br; ◆, [C$_4$mim][CH$_3$SO$_3$]; ■, [C$_4$mim][CH$_3$CO$_2$]; ○, [C$_4$mim]Cl.
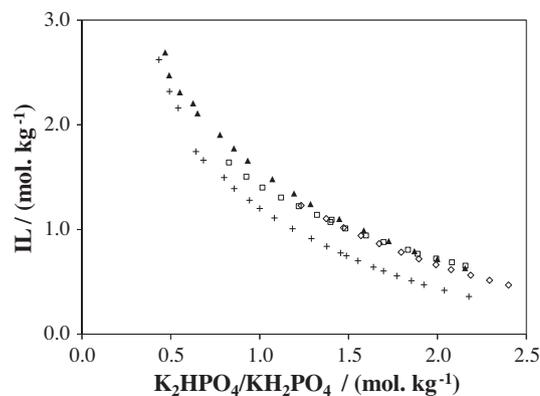

FIGURE 4. Ternary phase diagram for [C$_4$mim][N(CN)$_2$] + K$_2$HPO$_4$ + water at 298 K and atmospheric pressure: ◆, experimental binodal curve data; □, TL data, —, fitting by equation (1).

(1) are presented in table 1. In table 2 are reported the ternary system compositions, and the respective tie-line lengths and pH values at the coexisting phases.

The experimental phase diagrams at 298 K and atmospheric pressure for the systems making use of the phosphate buffer are shown in figure 5.

From the solubility curves we can order the ILs according to their ability to form biphasic systems: [C$_4$mim][CF$_3$CO$_2$] > [C$_4$mim][DMP] $\approx$ [C$_4$mim][CH$_3$SO$_4$] > [C$_4$mim]Br. When considering also the ILs studied previously [44] with this mixture of salts a broader ranking is obtained and is displayed in table 3. All these systems present consistently higher saturation solubility values when compared with the corresponding ones using K$_2$HPO$_4$ salt solution alone, thus revealing the importance of pH in the interactions among all ions present in solution and/or the importance of substituting a stronger salting-out anion (HPO$_4^{2-}$) by a weaker one (H$_2$PO$_4^-$). The ranking obtained for the ILs ability to promote ABS with this mixture of salts is much similar to the ones
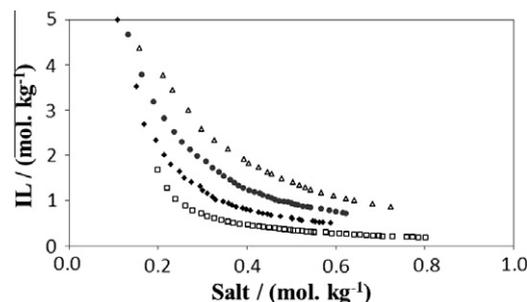

FIGURE 5. Ternary phase diagrams for [C$_4$mim]-based ILs + K$_2$HPO$_4$/KH$_2$PO$_4$ at 298 K and atmospheric pressure: +, [C$_4$mim][CF$_3$CO$_2$]; □, [C$_4$mim][DMP]; ◇, [C$_4$mim][CH$_3$SO$_4$]; ▲, [C$_4$mim]Br.

presented before using the other phosphate salt solutions. Since the cation is the same for all the ILs, that means that the IL anion demixing ability follows a trend close to the previous ones, indicating coincidental mechanisms of ABS formation for both phosphate salts.

3.1.4. Systems composed of potassium dihydrogenphosphate, KH$_2$PO$_4$

To complete the study of the phosphate salt series, the ABS formation using the most protonated phosphate species, KH$_2$PO$_4$, was further investigated. Although acidic in aqueous solutions, the equilibrium and the nominal concentrations of H$_2$PO$_4^-$ are not significantly different. All the ILs investigated were combined with this salt, yet only the [C$_4$mim][CF$_3$SO$_3$] was able to form a biphasic system. For the remaining systems solid-liquid phases were observed instead of liquid–liquid phases. Nevertheless, it should be remarked that although literature presents this phosphate anion as not amenable to inducing liquid–liquid demixing [16], it was here observed the formation of ABS with [C$_4$mim][CF$_3$SO$_3$] – an ionic liquid with low affinity for water. The binodal curve obtained with [C$_4$mim][CF$_3$SO$_3$] and KH$_2$PO$_4$ solutions, along with the curves obtained for the same IL and all the other different phosphate solutions, are presented in figure 6. The regression parameters obtained for the equation (1) estimated by least-squares regression of the cloud-point data are presented in table 1 and the ternary system compositions, tie-line lengths, and pH values are reported in table 2.

Considering all the salt series studied, whose results are summarized in table 3, we notice that [C$_4$mim][CF$_3$SO$_3$] consistently proved to be the IL most prone to form biphasic systems. This strong ability was already acknowledged as this IL had been able to undergo liquid–liquid demixing with other weak salting-out

FIGURE 6. Ternary phase diagrams for [C$_4$mim][CF$_3$SO$_3$] and different potassium-phosphate-based salts ABS at 298 K and atmospheric pressure: □, K$_3$PO$_4$ [19]; ◆, K$_2$HPO$_4$; ●, K$_2$HPO$_4$/KH$_2$PO$_4$ [44] (pH = 7.0); △, KH$_2$PO$_4$.

species, such as NaCl [18], polymers [60], carbohydrates [61] and amino acids [39]. The ILs ability to promote ABS systems follows approximately the same order independently of the salt, which seems to emphasize the prominent role of the ILs anion identity and its hydrogen-bonding donor ability in the two phase formation.

3.2. Effect of the phosphate salt on ABS formation

A comparison of the different sets of results is now carried out aiming at determine the influence of the salt in the ABS forming ability. Figure 6 shows the effect of the replacement of the highly basic and charged PO_4^{3-} anion by less alkaline and less charged anions, $H_2PO_4^-$ and the phosphate buffer mixture, $HPO_4^{2-} + H_2PO_4^-$, ending up with the slightly acidic anion, $H_2PO_4^-$. This pattern reflects curves successively more apart from both axes revealing a decreased ability for biphasic systems promotion that follows the order: $PO_4^{3-} > HPO_4^{2-} > (HPO_4^{2-} + H_2PO_4^-) > H_2PO_4^-$.

The results shown in figure 6 corroborate the qualitative trend on the salt anions ability to induce the salting-out of the ionic liquid that closely follows the Hofmeister series [22]. The anion which induces the strongest salting-out effect is PO_4^{3-} as previously observed by us [9] and others [15]. Moreover, the salts ion charge plays a significant role being responsible for the formation of hydration complexes [18]. Although the hydration sphere of PO_4^{3-} ion seems to have less water molecules than those of HPO_4^{2-} and $H_2PO_4^-$ [62,63], which, in a superficial analysis, could suggest a comparatively weaker interaction of the PO_4^{3-} with water and a lower capability to create ABS, it should be stressed that the data refer to the number of water molecules in the first hydration shell (not the whole hydration sphere), and not to the strength of their interaction. Due to its higher charge, PO_4^{3-} will more strongly and readily hydrogen bond with water than the less charged phosphate species. Those studies [62,63] also suggest that the hydration sphere for both hydrogen and dihydrogen phosphate anions are similar, as far as the number of water molecules and their geometry are concerned; however, as shown here, a drastic reduction in the ABS formation ability is observed when changing from hydrogen to dihydrogen phosphate salt. A possible explanation for those results is to consider that the higher the charge of the anion the more intense is the electric field, and the more aligned are the dipoles of the water molecules around the anion, with the exact number of hydrogen bonds being less important than the cohesion brought by the alignment of the dipoles of the surrounding water molecules. This would rank the interaction anion/water as obtained by us: $PO_4^{3-} > HPO_4^{2-} > H_2PO_4^-$. Other factors being equal, water molecules are held more strongly by molecules with a net charge than by molecules with no net charge [64].

Apart from the charge of the salts anion, the replacement of PO_4^{3-} anions with increasingly protonated phosphate species carries other significant changes along, namely a decrease of the medium ionic strength and a decrease in solution's pH. According to Tomé et al. [20] salting-in/-out effects are considerably dependent on the ionic strength and, in fact, when displacing K_3PO_4 with KH_2PO_4, the ionic strength varies six-fold from 6 m to 1 m. This in turn will cause significant changes in the surface tension that, together with the formation of hydration complexes, are particularly relevant to the solution behavior of high charge density ions such as PO_4^{3-} and HPO_4^{2-} [9]. Another dramatic change occurs concurrently when K_2HPO_4 replaces K_3PO_4: the OH^- concentration decreases nearly four orders of magnitude, and the corresponding decrease is close to five orders when the salt KH_2PO_4 replaces K_2HPO_4, as can be appreciated in table 2. In fact, the pH difference between the two phases in equilibrium for the systems herein studied is usually smaller than 0.5 pH units. Identical differences were reported by Cláudio et al. [65] in a study of ionic-liquid-based

ABS formed by the addition of Na_2SO_4 evidencing a considerable extension of the hydrogen ion equilibrium between both aqueous phases. Although the migration of ions in the coexisting phases of ABS might accomplish an irrelevant mass transfer to affect major ions [15], for the most mobile ions in solution, hydronium and hydroxide, it is sufficient to allow convergent pH values for both phases. Since the pH of the IL solution follows closely the pH values of the solution of the salt, the hydroxide ion concentration in the IL solution decreases abruptly when changing the salt from K_3PO_4 to K_2HPO_4, and then to the buffer and to KH_2PO_4. The C2 carbon atom of the imidazolium cation shows a higher affinity for OH^- ions than for the identically charged monovalent anions [66]. The decrease of hydroxide ions in solution will reduce the competition with the IL anions, making more difficult to bring the IL ions apart, and thus the ability of ABS formation is highest for PO_4^{3-} and severely reduced for the acidic $H_2PO_4^-$. The media pH may have a steady although small influence on ABS formation; the lower it is, the higher the saturation solubility values, but the effect turns from quantitative to qualitative when the pH goes from alkaline or neutral to moderately acidic (see table 2).

The precise mechanism of salting-out is not fully understood, and different interactions have been proposed to explain the mechanisms involved [23,67] and where hydration phenomena stem as having a key role; specific hydration values for each ion in different pairs are acknowledged, but no real predictability exists yet [68]. Several studies however relate the IL salting-out with the Gibbs free energy and the entropy of hydration of the ions of the inorganic salt [18,69]. It was shown elsewhere by us that solubility data of hydrophobic IL in aqueous salt solution correlates well with the molar entropy of hydration of the salt ions [9,21,24]. Shahriari et al. [18] in a recent study using $[C_4mim][CF_3SO_3]$ and an extensive range of salts concluded that the entropy of hydration of the inorganic salts, and not the free Gibbs energy, has a dominant role in the formation of ion-water complexes and in promoting ionic-liquid-based ABS. However caution should be used when generalizing theses results, since when different salts are used discrepancies may occur [67,68,70]. Additionally it has to be considered that the aqueous solutions in ABS may be so concentrated that there is no 'bulk' water present and all water molecules are interacting with one or more ions [71].

4. Conclusions

Novel phase diagrams of ABS for several imidazolium-based ILs and three phosphate salts and a mixture of salts (K_3PO_4, K_2HPO_4, $K_2HPO_4 + KH_2PO_4$, and KH_2PO_4) were determined by the cloud point titration method at 298 K. From the gathered results, the ability of different IL anions, as well as the salt employed, to promote the formation of ABS was presented and discussed.

As far as the ability of creating ABS is concerned it was observed that the sequences of ILs follow similar patterns for the different phosphate salts series. In general, the lower the hydrogen bond basicity of the IL (i.e., less affinity of the IL anion to interact with the protons of water), the higher the ability of the ionic fluid to undergo liquid−liquid demixing in the presence of the phosphate salt.

When considering the different forms of the phosphate anions as salting-out agents it was found that the charge of the phosphate anion plays the most determinant role (the higher it is the better the salting-out agent) and the liquid–liquid demixing of a similar ionic liquid decreases in the rank: $K_3PO_4 > K_2HPO_4 > K_2HPO_4 + KH_2PO_4 > KH_2PO_4$. However, this effect is attributable not only to the salts anion charge but also to pH and ionic strength changes. In fact there was a considerable reduction in the number of ABS formed when the acidic phosphate salt, KH_2PO_4, was used. Only $[C_4mim][CF_3SO_3]$ was able to form ABS with this acidic salt.

Although the interactions among all players in a given ABS (water/IL/salt) are not yet completely understood we put forward a thorough set of results for the IL/phosphate salts based systems. The establishment of this correlation pattern, even if fraught with some empiricism, is of paramount importance as it provides a grounded basis for a proper choice of a system according to its purpose or application, as well as a guidance when pursuing further studies aiming at unveiling the intricate interactions in these systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2012.05.019.

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