Salting-out in Aqueous Solutions of Ionic Liquids and K$_3$PO$_4$: Aqueous Biphasic Systems and Salt Precipitation

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**Abstract:** The salting-out effect produced by the addition of potassium phosphate, K$_3$PO$_4$ to aqueous solutions of water-miscible ionic liquids, viz. 1-ethyl-3-methylimidazolium ethyl sulfate, 1-butyl-3-methylimidazolium methyl sulfate, or 1-alkyl-3-methylimidazolium chloride (alkyl = butyl, octyl or decyl) is investigated. The effects are analyzed using both the corresponding temperature–composition pseudo-binary and composition ternary phase diagrams. Different regions of liquid-liquid and solid-liquid phase demixing are mapped. The phase behavior is interpreted taking into account the complex and competing nature of the interactions between the ionic liquid, the inorganic salt and water. In the case of solutions containing 1-octyl- or 1-decyl-3-methylimidazolium chloride, the smaller magnitude of the salting-out effects is explained in terms of the possibility of self-aggregation of the ionic liquid.

**Keywords:** ionic liquid, inorganic salt, salting-out effect, aqueous biphasic systems.
1. Introduction

Recently, Rogers and co-workers [1,2] demonstrated that the addition of potassium phosphate, \( \text{K}_3\text{PO}_4 \) – a water-structuring (kosmotropic) inorganic salt – to an aqueous solution of a hydrophilic ionic liquid produces a salting-out effect that leads to the formation of aqueous biphasic systems (ABS).

Besides their well-known biochemical use [3], the range of applications of ABS has recently been extended to various separation processes [4,5]. In fact ABS can be considered (just like ionic liquids often are) as novel, “green” extraction media [5]. The use of aqueous solutions of ionic liquids to promote the formation of ABS represents the meeting of two emergent areas of “green” chemistry.

The first studies on the solubility of ionic liquids in water appeared almost a decade ago [6,7]. In a recent work [8] we analyzed the effect of the addition of different inorganic salts on the phase behavior of 1-butyl-3-methylimidazolium tetrafluoroborate, \([\text{C}_4\text{mim}][\text{BF}_4]\), aqueous solutions, which are homogenous at room temperature but exhibit liquid-liquid demixing below 277.6 K [6,9,10]. Whereas Roger and co-workers [1,2] investigated the phenomenon of salting-out at room temperature, we studied the temperature dependence of the demixing loci upon the addition of the inorganic salt, namely the increase of the temperature-composition heterogeneous domains in quasi-binary mixtures of (water + \([\text{C}_4\text{mim}][\text{BF}_4]\) + inorganic salt) as compared to those observed in the corresponding binary (water + \([\text{C}_4\text{mim}][\text{BF}_4]\)) solutions.

In the current work, we focus on salting-out effects produced by the addition of the strong kosmotropic salt \( \text{K}_3\text{PO}_4 \) to aqueous solutions of several water-miscible ionic liquids, namely, 1-ethyl-3-methylimidazolium ethyl sulfate, \([\text{C}_2\text{mim}][\text{EtOSO}_3]\), 1-butyl-3-methylimidazolium methyl sulfate, \([\text{C}_4\text{mim}][\text{MeOSO}_3]\), or 1-alkyl-3-methylimidazolium chlorides, \([\text{C}_n\text{mim}][\text{Cl}]\) (with \( n = 4, 8 \) or 10). The temperature dependence of phase demixing was investigated by means of cloud-point temperature determinations as a function of composition. Solid-liquid equilibrium borders, whenever present, were also determined.

2. Results

Salting-out effects produced by the addition of \( \text{K}_3\text{PO}_4 \) to different aqueous solutions of water-miscible ionic liquids are depicted as temperature-composition \((T-w)\) phase diagrams in Figure 1 (sulfate-based ionic liquids) and Figure 2 (chloride-based ionic liquids). The liquid-liquid (L-L) and liquid-solid (L-S) equilibrium lines were constructed \( \text{via} \) the determination of the corresponding cloud-point temperatures. Several fixed concentrations of \( \text{K}_3\text{PO}_4 \) in water were considered. Data are also given in Table 1 (sulfate-based ionic liquids) and Table 2 (chloride based ionic liquids). It must be stressed that for practical reasons the ternary solutions were not prepared by addition of the inorganic salt to the ionic liquid aqueous solutions (addition of a solid to a liquid) but instead by adding the pure ionic liquid to pre-prepared \( \text{K}_3\text{PO}_4 \) aqueous solutions (liquid to liquid addition).
Table 1. Cloud-point temperature, \( T \), as a function of mass fraction, \( w \), of sulfate-based ionic-liquid solutions. The B and T subscripts denote the initial \( K_3PO_4 \) aqueous binary solutions and the ternary solutions. Data corresponding to salt precipitation are represented in bold.

| \( w_{\text{salt,B}} \) | \( w_{\text{sa}} \) | \( w_{\text{IL,T}} \) | \( T/K \) | \( w_{\text{salt,T}} \) | \( w_{\text{IL,T}} \) | \( T/K \) |
|---------------------|----------------|----------------|--------|----------------|----------------|--------|
| \( K_3PO_4 \text{(salt)} + [C_{2mim}]^{[EtSO_4]} (IL) + H_2O \) |
| 0.04889             | 0.02355        | 0.51828        | 298.2  | 0.01815        | 0.62886        | 348.7  |
|                     | 0.02321        | 0.52537        | 306.7  | 0.01636        | 0.66545        | 346.7  |
|                     | 0.02266        | 0.53650        | 316.9  | 0.01489        | 0.69548        | 342.6  |
|                     | 0.02226        | 0.54476        | 329.3  | 0.01165        | 0.76169        | 340.0  |
|                     | 0.02150        | 0.56029        | 345.8  | 0.00881        | 0.81977        | 335.5  |
|                     | 0.02134        | 0.56350        | 352.2  | 0.00703        | 0.85617        | 330.1  |
|                     | 0.02078        | 0.57505        | 351.8  | 0.00474        | 0.90309        | 320.4  |
|                     | 0.02005        | 0.59000        | 350.4  | 0.00295        | 0.93973        | 303.2  |
|                     | 0.01934        | 0.60442        | 350.7  | 0.00248        | 0.94931        | 291.4  |
|                     | 0.01840        | 0.62356        | 349.4  |                |                |        |
| 0.06313             | 0.03500        | 0.44551        | 295.6  | 0.02465        | 0.60950        | 348.8  |
|                     | 0.03410        | 0.45986        | 313.2  | 0.02179        | 0.65482        | 341.8  |
|                     | 0.03294        | 0.47820        | 333.6  | 0.01891        | 0.70039        | 339.5  |
|                     | 0.03180        | 0.49622        | 343.1  | 0.01599        | 0.74670        | 335.6  |
|                     | 0.03057        | 0.51581        | 351.6  | 0.01311        | 0.79229        | 329.2  |
|                     | 0.02903        | 0.54018        | 352.4  | 0.00915        | 0.85511        | 310.1  |
|                     | 0.02774        | 0.56056        | 351.3  | 0.00820        | 0.87018        | 291.7  |
| 0.10538             | 0.06571        | 0.37641        | 298.2  | 0.05824        | 0.44737        | 378.9  |
|                     | 0.06537        | 0.37970        | 313.2  | 0.05791        | 0.48000        | 332.2  |
|                     | 0.06386        | 0.39397        | 323.2  | 0.05190        | 0.52300        | 376.4  |
|                     | 0.06241        | 0.40774        | 337.9  | 0.04756        | 0.56333        | 358.2  |
|                     | 0.06165        | 0.41500        | 343.2  | 0.04315        | 0.60600        | 298.2  |
| 0.22670             | 0.18891        | 0.16610        | 297.8  | 0.03732        | 0.83526        | 298.8  |
|                     | 0.18791        | 0.17051        | 323.5  | 0.04023        | 0.82240        | 322.1  |
|                     | 0.18595        | 0.17919        | 346.4  | 0.04259        | 0.81201        | 345.5  |
|                     | 0.18402        | 0.18769        | 355.4  | 0.04534        | 0.79986        | 337.5  |
| \( K_3PO_4 \text{(salt)} + [C_{4mim}]^{[MeSO_4]} (IL) + H_2O \) |
| 0.02919             | 0.00389        | 0.86667        | 288.2  | 0.00317        | 0.89130        | 301.5  |
|                     | 0.00379        | 0.87013        | 296.3  | 0.00269        | 0.90794        | 309.0  |
|                     | 0.00321        | 0.88989        | 298.2  | 0.00231        | 0.92099        | 323.2  |
|                     | 0.00309        | 0.36604        | 284.7  | 0.02668        | 0.45326        | 333.2  |
|                     | 0.02984        | 0.38859        | 298.2  | 0.02594        | 0.46850        | 343.2  |
|                     | 0.02803        | 0.42558        | 317.5  | 0.02565        | 0.47445        | 364.2  |
| 0.10538             | 0.07298        | 0.30741        | 287.4  | 0.06799        | 0.35484        | 318.4  |
|                     | 0.07161        | 0.32044        | 298.2  | 0.06287        | 0.40339        | 351.7  |
|                     | 0.07057        | 0.33036        | 309.9  | 0.06022        | 0.42857        | 371.8  |
| 0.22670             | 0.20189        | 0.10944        | 287.9  | 0.18455        | 0.18592        | 362.2  |
|                     | 0.19496        | 0.14000        | 313.2  | 0.18368        | 0.18975        | 364.2  |
|                     | 0.19012        | 0.16137        | 333.3  | 0.18368        | 0.18975        | 322.2  |
|                     | 0.19012        | 0.16137        | 287.4  | 0.18148        | 0.19947        | 367.8  |
|                     | 0.18786        | 0.17132        | 351.2  | 0.18148        | 0.19947        | 331.4  |
|                     | 0.18555        | 0.18152        | 354.0  | 0.17465        | 0.22962        | 371.7  |
|                     | 0.18555        | 0.18152        | 313.8  | 0.17465        | 0.22962        | 367.4  |
Table 2. Cloud-point temperature, \( T \), as a function of composition (mass fraction, \( w \)) of chloride-based ionic-liquid solutions. The B and T subscripts denote the compositions of the initial \( K_3PO_4 \) aqueous binary solution and of the ternary solutions, respectively.

| \( W_{\text{salt,B}} \) | \( W_{\text{salt,T}} \) | \( W_{\text{IL, T}} \) | \( T/K \) | \( W_{\text{salt,T}} \) | \( W_{\text{IL, T}} \) | \( T/K \) |
|-----------------|-----------------|-----------------|-------|-----------------|-----------------|-------|
| \( K_3PO_4 \) (salt) + \([\text{C}4\text{mim}]\text{Cl} \) (IL) + H\(_2\)O |
| 0.03604 | 0.01979 | 0.45086 | 270.2 | 0.01480 | 0.58942 | 326.6 |
| | 0.01964 | 0.45522 | 270.9 | 0.01429 | 0.60341 | 332.5 |
| | 0.01904 | 0.47167 | 285.2 | 0.01332 | 0.63045 | 339.4 |
| | 0.01865 | 0.48246 | 292.8 | 0.01237 | 0.65672 | 341.5 |
| | 0.01802 | 0.49992 | 308.7 | 0.01098 | 0.69536 | 341.3 |
| | 0.01617 | 0.55142 | 320.2 | 0.00942 | 0.73873 | 341.0 |
| 0.10538 | 0.07703 | 0.26904 | 268.7 | 0.07193 | 0.31744 | 328.8 |
| | 0.07572 | 0.28143 | 275.8 | 0.07167 | 0.31986 | 366.8 |
| | 0.07522 | 0.28625 | 278.7 | 0.03487 | 0.66915 | 357.9 |
| | 0.07413 | 0.29654 | 294.1 | 0.03250 | 0.69161 | 353.9 |
| | 0.07248 | 0.31223 | 322.9 | 0.02884 | 0.72634 | 343.8 |
| | 0.07197 | 0.31707 | 351.2 | 0.07197 | 0.31707 | 351.2 |
| \( K_3PO_4 \) (salt) + \([\text{C}8\text{mim}]\text{Cl} \) (IL) + H\(_2\)O |
| 0.10538 | 0.06320 | 0.40022 | 297.7 | 0.01626 | 0.84566 | 367.1 |
| | 0.06265 | 0.40548 | 305.5 | 0.01478 | 0.85979 | 350.4 |
| | 0.06079 | 0.42314 | 333.2 | 0.01164 | 0.88952 | 327.6 |
| | 0.05823 | 0.44747 | 364.4 | 0.05823 | 0.44747 | 364.4 |
| 0.15324 | 0.10905 | 0.28839 | 298.2 | 0.01519 | 0.90090 | 365.4 |
| | 0.10405 | 0.32098 | 323.4 | 0.01329 | 0.91324 | 345.5 |
| | 0.10086 | 0.34181 | 365.5 | 0.00730 | 0.95238 | 307.9 |
| \( K_3PO_4 \) (salt) + \([\text{C}10\text{mim}]\text{Cl} \) (IL) + H\(_2\)O |
| 0.15324 | 0.09676 | 0.36859 | 275.4 | 0.02280 | 0.85121 | 375.3 |
| | 0.09547 | 0.37696 | 282.4 | 0.02096 | 0.86320 | 351.1 |
| | 0.09388 | 0.38736 | 299.6 | 0.01824 | 0.88099 | 343.4 |
| | 0.09296 | 0.39339 | 307.4 | 0.09296 | 0.39339 | 307.4 |
| 0.22670 | 0.19130 | 0.15616 | 289.0 | 0.18526 | 0.18278 | 337.6 |
| | 0.19064 | 0.15906 | 292.5 | 0.03221 | 0.85793 | 369.4 |
| | 0.19001 | 0.16186 | 303.1 | 0.02885 | 0.87273 | 353.2 |

The main feature of the \((K_3PO_4 + [\text{C}4\text{mim}][\text{MeOSO}_3] + \text{H}_2\text{O})\) phase diagram depicted in Figure 1a, is the precipitation of the inorganic salt from the homogeneous solution and the absence (except in one case) of ABS formation. For the three solutions with lower inorganic salt concentration (cf. Table 1) one passes directly from a homogeneous solution (when the amount of ionic liquid is low) to a two-phase system (when the ionic liquid concentrations are higher) constituted by precipitated \(K_3PO_4\) and an aqueous ionic liquid solution. For the solution with 22.7 wt % of \(K_3PO_4\), the addition of ionic liquid leads to the formation of an ABS (two-phase region), but further addition of ionic liquid results in inorganic salt precipitation (three-phase region).
Figure 1. Cloud-point temperature as a function of ionic liquid concentration (weight fraction) in (a) $\text{K}_3\text{PO}_4 + [C\text{2mim}][\text{MeSO}_4] + \text{H}_2\text{O}$, and (b) $\text{K}_3\text{PO}_4 + [C\text{2mim}][\text{EtSO}_4] + \text{H}_2\text{O}$. In bold are the weight percentages of $\text{K}_3\text{PO}_4$ in the initial ($\text{K}_3\text{PO}_4 + \text{H}_2\text{O}$) solutions. The 1, 2 and 3 numerals on each side of the lines represent the number of phases at equilibrium. The solid lines indicate transitions to ABS; the dashed lines the occurrence of $\text{K}_3\text{PO}_4$ precipitation.

In spite of structural and chemical similarities, this behavior markedly contrasts with that of the ($\text{K}_3\text{PO}_4 + [C\text{2mim}][\text{EtSO}_3] + \text{H}_2\text{O}$) system depicted in Figure 1b; it also differs from the behavior of the ($\text{K}_3\text{PO}_4 + [C\text{4mim}][\text{Cl} + \text{H}_2\text{O}$) system depicted in Figure 2a and previously studied by Rogers and co-workers [1] (cf. discussion below) – where the formation of ABS is present for all studied $\text{K}_3\text{PO}_4$ aqueous solutions. In the $[C\text{2mim}][\text{EtSO}_3]$ case, two-phase liquid regions (ABS) are present for weight fractions of ionic liquid ranging from around $w = 0.2$ to 0.9. The demixing phenomena are less extant at higher temperatures. No precipitation of $\text{K}_3\text{PO}_4$ was observed in any of the studied solutions. The difference between the phase behavior of the $[C\text{2mim}][\text{EtSO}_3]$ and of the $[C\text{4mim}][\text{MeSO}_3]$ containing system is, in fact, striking, mainly if one points out the similarity of the two ionic liquids: overall, they differ structurally by just one methylene, -CH$_2$-, group, with the alkyl side chains being more evenly distributed between the anion and cation in the former system and less so in the latter.

Salting-out effects in ternary aqueous solutions of $\text{K}_3\text{PO}_4$ and 1-alkyl-3-methylimidazolium chloride ionic liquids, $[C_{n\text{mim}}]\text{Cl}$ with $n = 4$, 8 or 10, are shown in Figure 2.
Precipitation of $K_3PO_4$ from an ABS was observed only in $(K_3PO_4 + [C_n mim]Cl + H_2O)$ mixtures with high concentrations of ionic liquid (Figure 2a). In those cases the liquid-solid equilibrium lines were not quantitatively determined, since it was difficult to detect the beginning of precipitation in an already phase-separated system (ABS): the dashed vertical line represented in Figure 2a only gives an indication of the composition of the last points of ABSs without precipitation. The absence of precipitation at the cloud-point temperature was verified by keeping the respective samples at a temperature close to the lowest cloud point detected ($0 \, ^\circ C$), for a period of 24 hours.

The different panels of Figure 2 show that the formation of ABS (by salting out effect) is increased for: i) higher concentrations of $K_3PO_4$ in the solution (the two-phase envelopes on the left-hand side of each panel shift to the left with increasing concentrations of the $K_3PO_4$ aqueous solutions); ii) lower temperatures (the two-phase envelopes become narrower as temperature increases and in the case of the less concentrated $K_3PO_4$ aqueous solution in the $(K_3PO_4 + [C_n mim]Cl + H_2O)$ system, Figure 2a, one can even observe an UCST-like demixing domain) ; and iii) shorter alkyl side-chains in the $[C_n mim]^+$ cation (the two-phase envelopes on the left-hand side of each panel also shift to the left when one compares solutions with the same $K_3PO_4$ content but shorter alkyl-side chains in the $[C_n mim]^+$ cation. Note, for instance, the relative positions of the “11 %” lines in Figures 2a and 2b and the “15 %” lines in Figures 2b and 2c.
3. Discussion

3.1. ABS and precipitation

The phenomenon of inorganic salt precipitation associated with ABS formation was previously reported [8] in studies involving the hydrophilic ionic liquid [C₄mim][BF₄] and the inorganic salts Na₂SO₄ and Na₃PO₃. That fact did not affect the interpretation of salting out effects from the point of view of ABS formation and so it was not further examined in that work. In the current study, inorganic salt precipitation is present in the (K₃PO₄ + [C₄mim]Cl + H₂O) system and ubiquitously in the (K₃PO₄ + [C₄mim][MeOSO₃] + H₂O) system. In this case, a deeper analysis is needed.

Figure 3. Ternary diagrams of (K₃PO₄ + [C₄mim]Cl + H₂O) at 298 K and a nominal pressure of 0.1 MPa. (a) comparison of our data (red circles) with those of Rogers and co-workers (empty squares) [1] in the ABS region (I); (b) depiction of the three-phase (II) and solid-liquid (III) regions where K₃PO₄ precipitation occurs. The arrow in (b) marks the solubility limit of K₃PO₄ in water; the empty circles indicate experimental points where precipitation from ABS occurred. Concentrations are in weight fraction. The shaded area represents the homogeneous one-phase region.

Note that the fair symmetry of the diagram indicates that the “salting-out effect” corresponds to a mutual exclusion of the two salts, the inorganic salt and the ionic liquid, i.e., they compete for being solvated by water molecules. Ionic liquids with non-bulky ions significantly “inherited” a good portion of what makes common inorganic salts different from other compounds: the Coulomb interactions [11-13].

As stated in the introduction, the (K₃PO₄ + [C₄mim]Cl + H₂O) system was previously studied by Rogers and coworkers [1]. Their study included the speciation of the species present in each phase of the ABS at 298 K, which allowed us to build the triangular ternary diagram presented in Figure 3a, and to compare their data with our results for the same system at that temperature. When adding the ionic liquid to the two K₃PO₄ aqueous solutions studied in this work (cf. Figure 3a starting at the arrows and moving down the dashed lines) one crosses the boundary into the ABS region (I) delimited by the green line. Our data (red circles) are in agreement with the results reported in Ref. [1].
In order to include the precipitation of $K_3PO_4$ one has to redraw diagram 3a as diagram 3b. The three-phase region (II) bounded by the orange triangle simply acknowledges two facts: i) Although $K_3PO_4$ is extremely soluble in water there is a solubility limit - one cannot move down indefinitely on the left side of triangles 3a or 3b without reaching a point where water becomes saturated in $K_3PO_4$ and the salt starts to precipitate. The arrow in Figure 3b indicates the approximate position of the solubility limit at 298 K [14]. The point identified by the arrow and the one corresponding to solid $K_3PO_4$ define two of the orange triangle’s tips. ii) When more ionic liquid is added to the ABS (moving further down the dashed line) eventually one starts to see the precipitation of $K_3PO_4$. This means that one has entered a three-phase region and (according to Gibbs rule) the compositions of each phase (for a given pressure and temperature) become fixed. The three phases in presence (liquid-liquid-solid equilibrium, LLS) are a saturated $K_3PO_4$ aqueous solution, solid $K_3PO_4$ and an ionic-liquid-rich aqueous solution. The composition of the latter defines the third tip of the triangle.

If more ionic liquid is added to the system then the amount of $K_3PO_4$-rich aqueous solution starts to diminish until it disappears. This means that the system exhibits again only two phases (liquid-solid equilibrium, LS): precipitated $K_3PO_4$ and an ionic-liquid-rich aqueous solution (region III).

The fluid phase behavior of the other studied (inorganic salt + ionic liquid + water) systems can now be discussed in terms of the relative positions of regions I (ABS), II (LLS) and III (LS). In the case of the sulfate-based ionic liquids the corresponding diagrams are depicted in Figure 4 (a and b).

![Figure 4. Ternary diagrams of (a) $(K_3PO_4 + [C_4mim][MeOSO_3] + H_2O)$ and (b) $(K_3PO_4 + [C_2mim][EtOSO_3] + H_2O)$ at 298 K and 0.1 MPa. Symbols and lines as in Figure 3.](image)

The marked difference between the two a priori “similar” systems (precipitation in the $[C_4mim][MeOSO_3]$-based system versus ABS formation in $[C_2mim][EtOSO_3]$-based system) is now evident from inspection of the two ternary diagrams. Although the homogeneous regions roughly remain on the same area of the diagrams (cf. also Figure 3b), the right tip of the triangle delimiting the three-phase region is, in the case of Figure 4a, shifted to the interior of the diagram, exposing a much larger SL (III) region and the corresponding precipitation (blue) line. On the other hand, Figure 4b depicts a system where the SL (III) region is practically absent. This shift in the position of the right tip
of the three-phase region explains, phenomenologically, the trend from a system showing only ABS formation (the \([C_{4}mim][EtOSO_{3}]\)-based systems depicted in Figures 1b and 4b) to a system showing \(K_{3}PO_{4}\) precipitation only for ionic liquid weight fractions near 80 % (the \([C_{4}mim]Cl\)-based system depicted in Figures 2a and 3b), and, finally, to a system where precipitation is the most conspicuous feature (the \([C_{4}mim][MeOSO_{3}]\)-based system depicted in Figures 1a and 4a).

The shift in the position of the right tip of the three-phase region can be analyzed in terms of the relative kosmotropic nature of the different salts involved in the three ternary systems. Potassium phosphate is one of the strongest kosmotropic salts available (producing intense salting-out effects) but when it comes to aqueous solutions of hydrophilic ionic liquids there is an issue: the ionic liquid will not precipitate (as a pure solid or otherwise) which means that what can be expected at most is the separation into two aqueous solutions (the ABS) with variable amounts of water being distributed between the \(K_{3}PO_{4}\)-rich and ionic-liquid-rich phases. This competition for water between the two salts (\(K_{3}PO_{4}\) and the ionic liquid) is influenced by the ability of each salt to make strong bonds with the water molecules and/or enhance its structure, i.e. their kosmotropicity. If the ionic liquid binds strongly to water, the IL-rich phase in the ABS can have a relatively large amount of water, which means that the \(K_{3}PO_{4}\)-rich phase can become saturated in \(K_{3}PO_{4}\) (depleted in water) and precipitation can occur.

In the case of the \([C_{4}mim][MeOSO_{3}]\) and \([C_{4}mim]Cl\) ionic liquids, which have a common cation, the results – extensive precipitation of \(K_{3}PO_{4}\) in systems containing the former ionic liquid – indicate that the methylsulfate anion is more kosmotropic than the chloride anion. This fact is corroborated by data taken from the literature which is based on viscosity (B-coefficients of the Jones-Dole equation) or NMR (B’-coefficients) measurements [15]. The data show that alkylsulfate anions are more kosmotropic than the chloride anion. When both the cation and anion change (like when one passes from \([C_{4}mim][MeOSO_{3}]\) to \([C_{2}mim][EtOSO_{3}]\)) it is harder to predict the relative kosmotropicity of the ionic liquids. The results show that even very small variations in the structure of the two ions composing the ionic liquid can have a dramatic effect in terms of the competition between the ionic liquid and the inorganic salt for the interactions with the water molecules.

### 3.2. ABS and Micelle formation

When interpreting the salting-out effects (ABS formation) in ternary mixtures containing \([C_{n}mim]Cl\) with \(n = 4, 8\) or 10 (Figure 2) one has to take into account the possibility of micelle formation in systems containing the former ionic liquid – indicate that the methylsulfate anion is more kosmotropic than the chloride anion. This effect is corroborated by data taken from the literature which is based on viscosity (B-coefficients of the Jones-Dole equation) or NMR (B’-coefficients) measurements [15]. The data show that alkylsulfate anions are more kosmotropic than the chloride anion. When both the cation and anion change (like when one passes from \([C_{4}mim][MeOSO_{3}]\) to \([C_{2}mim][EtOSO_{3}]\)) it is harder to predict the relative kosmotropicity of the ionic liquids. The results show that even very small variations in the structure of the two ions composing the ionic liquid can have a dramatic effect in terms of the competition between the ionic liquid and the inorganic salt for the interactions with the water molecules.
liquid rich phase (or micelle-rich phase) will retain a relatively small amount of water which means that the saturation of the $\text{K}_3\text{PO}_4$-rich solution is much more difficult and $\text{K}_3\text{PO}_4$ precipitation is not easy to obtain – it was never observed for the systems containing $[\text{C}_8\text{mim}]\text{Cl}$ or $[\text{C}_{10}\text{mim}]\text{Cl}$.

Figure 5. Ternary diagrams of (a) ($\text{K}_3\text{PO}_4 + [\text{C}_4\text{mim}]\text{Cl} + \text{H}_2\text{O}$); (b) ($\text{K}_3\text{PO}_4 + [\text{C}_8\text{mim}]\text{Cl} + \text{H}_2\text{O}$); and (c) ($\text{K}_3\text{PO}_4 + [\text{C}_{10}\text{mim}]\text{Cl} + \text{H}_2\text{O}$); at 298 K and 0.1 MPa. Symbols and lines as in Figure 3.

4. Conclusions

The results presented in this work show that salting out effects produced by the addition of a kosmotropic inorganic salt to aqueous solutions of water-soluble ionic liquids can produce ABS formation but can also lead to the precipitation of the inorganic salt. Ionic liquids that form micelles in aqueous solution can also alter significantly the pattern of ABS formation, particularly in the ionic-liquid-rich regions of the corresponding ternary diagrams.

The diverse types of phase behavior observed for ternary systems based on different ionic liquids is explained phenomenologically by the analysis of the corresponding triangular ternary diagrams. From
a molecular point of view, salting-out effects can be understood as a delicate balance between the interactions between the two solutes (K$_3$PO$_4$ and the ionic liquid) and the solvent (water). Hydration theories (including the concept of kosmotropy) can explain in a semi-quantitative way the magnitude of the effects but the inbuilt complexity of aqueous solutions and ionic liquids make difficult the interpretation of such dramatic effects as those evidenced by the extensive precipitation of K$_3$PO$_4$ in the reported [C$_n$ mim][MeSO$_3$]-based system.

5. Experimental Section

5.1. Chemicals and Preparation of Solutions

1-ethyl-3-methyl imidazolium ethyl sulfate (ECOENG, [C$_2$mim] [EtSO$_3$]) was purchased from Solvent Innovation, Germany, with a stated purity better than 98 wt % and water and chloride contents of 153 ppm and 404 ppm, respectively. 1-buthyl-3-methylimidazolium methyl sulfate ([C$_4$mim] [MeSO$_3$]), produced by BASF, was purchased from Sigma-Aldrich, (stated purity 95 wt %; water content below 500 ppm and a very low chloride content (< 20 ppm). 1-alkyl-3-methylimidazolium chlorides ([C$_n$mim][Cl], where $n$ = 6, 8, 10) were synthesized at QUILL (The Queen’s University Ionic Liquid Laboratories, Belfast), where they underwent first-stage purification. All ionic liquid were further thoroughly degassed (freed of any small traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperatures (40 – 60 °C) for typically 48 h). Our purification of [C$_4$mim] [MeSO$_3$] improved its purity to at least 98 wt % as estimated by H-NMR. Mass spectra (MS) of the chloride ionic liquids did not reveal the presence of impurities at a detection level of about 1 %.

5.2. Experimental procedure

The onsets of phase demixing at a nominal pressure of 0.1 MPa were determined using a dynamic method with visual detection of the solution turbidity (cloud-point). For this purpose, top-narrow-necked Pyrex-glass vials equipped with a magnetic stirrer were used. After being encapsulated, the solutions were frozen under vacuum and the vials sealed at the narrow neck of the open end. On warming and melting, the mixture inside the vial always occupied almost its entire internal volume ($\pm$ 0.5 cm$^3$) leaving only a small dead-volume of vapor phase. The vials were placed in a glass thermostat beaker of 2 L filled with ethanol (from 253 K-293 K), water (from 293 K-333 K), or silicon oil (up to 400 K) as the thermostatic fluid. Providing continuous stirring, the solutions were cooled off or heated usually in two or three runs with the last run being carried out very slowly (the rate of temperature change near the cloud point was not greater than 5 Kh$^{-1}$). Starting in the heterogeneous region, upon heating, the temperature at which the last sign of the turbidity disappeared was taken as the temperature of the phase transition. On the other hand, beginning in the homogeneous region, upon cooling, the temperature at which the first sign of turbidity appeared was taken as the temperature of the phase transition. Temperature (± 0.1 K) was monitored using a four-wire platinum resistance thermometer coupled to a Keithley 199 System DMM/Scanner.
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