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Sodium carbonate as phase promoter in aqueous solutions of imidazolium and pyridinium ionic liquids

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ABSTRACT

Several methylsulfate and chloride anion-based ionic liquids, such as 1-alkyl-3-methyl imidazolium methyl sulfate, $C_nMIM\ CH_3SO_4$ (n = 1, 2, and 4), 1-benzyl-3-methyl imidazolium methyl sulfate, BzMIM CH_3SO_4, 1-benzyl, or hexyl-3-methyl imidazolium chloride, XMIM Cl (X = Bz and Hx), and methylpyridinium methylsulfate, Mpy CH_3SO_4, with sodium carbonate, Na_2CO_3, as phase forming salt, have been investigated and discussed for their potential use in separations based on aqueous two-phase systems (ATPS). Phase diagrams have been experimentally ascertained at T = 298.15 K, and Merchuck equation and a variation of this model have been used for correlating the binodal data. The alkyl chain length in the cation and the type of anion and cation have been explored and discussed due to their decisive influence in the ATPS behavior. The consistence of tie-line data was ascertained by applying the Othmer–Tobias and Bancroft equations.

1. Introduction

During the last years, ionic liquids (ILs) have posed a breakthrough in the field of solvents. Special features such as chemical and thermal stability, recyclability, and tuneable physical and chemical properties, have made them to be considered as an attractive alternative for scientific community, which allows leaving behind the traditional chemistry and opening up new opportunities for reaching greener industrial processes [1]. These non-volatile molten salts are showing a tremendous growth on both fundamental and technological applications [2]. They are being used as solvents in separation techniques [3], media for biocatalysis [4], alternative electrolytes [5], and lubricants [6].

The concomitant effect of ILs and aqueous solutions of high charge-density inorganic salts led to the development of a specific technology based on aqueous two-phase systems (ATPS), which seek the formation of an upper IL-rich phase and a bottom inorganic salt-rich phase [7].

Globally, ATPS have been considered as an economical and efficient downstream separation technique which offer many advantages such as low viscosity, little emulsion formation, absence of organic volatile solvents, high extraction efficiency, low energy consumption, short process time, reliable scale-up, and a biocompatible environment [8]. The enormous potential of this separation process [9,10] has triggered a plethora of successful applications such as enzymes [4], antibiotics [11], biochemicals [12], and organic pollutants [13] extraction.

The aim of the present study is focused on the evaluation of the phase forming capacity of two families of ILs (imidazolium and pyridinium cations) containing two anions such as chloride and methylsulfate to form ATPS in the presence of sodium carbonate (Na_2CO_3) as model high charge density salt. The selection of this inorganic salt as phase promoter agent is supported by its high salting out ability in the light of the molar hydration entropy [14].

In general terms, thermophysical properties of ILs can strongly be affected by alkyl side chains, functional groups, and distinct anions and cations. For this reason, the second goal in this work is devoted to establish a diverse portfolio allowing the definition of novel ILs for more efficient and sustainable separation techniques. These results will preliminary serve as a first approach to map the final outcome of future new specific extraction processes without the need of going to the bench. The selection of these hydrophilic ILs raises from two main facts: (i) chloride-based ILs have been selected as models of traditional neoteric solvents which can be easily and economically produced; in fact, an imidazolium chloride-based IL was the first one to be used by BASF at industrial scale [15] and (ii) the mehylsulfate-based ILs have been chosen since they can also be easily synthesized in a halide-free way, at a reasonable cost, with relatively low viscosity, and they have been attributed a high affinity for alkyl hydrocarbons.

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The phase diagrams for the systems containing Na_2CO_3 and aqueous solutions of ILs formed by imidazolium and pyridinium as cations paired with methylsulfate and chloride as anions, *e.g.* C_nMIM CH_3SO_4 ($n = 1$, 2, and 4), BzMIM CH_3SO_4, XMIM Cl (X = benzyl and hexyl), and Mpy CH_3SO_4, have been determined experimentally. As far as we know, there are few reports in the literature related to binary aqueous IL solutions, and there is no report on the corresponding ATPS data for the selected systems. Two versions of the Merchuck model have been used to correlate the binodal data, one of them fixing two of the parameters (superscripts equal to 0.5 and 3, as usually reported) and the other option consisted of optimizing the five parameters defining the model. Additionally, the tie line data have been fitted to the Othmer–Tobias and Bancroft models to ascertain the reliability of the experimental data. The agreement between experimental and correlated data has been analyzed in terms of standard deviations.

2. Experimental

2.1. Chemicals

The 1-ethyl-3-methylimidazolium methyl sulfate (EMIM CH_3SO_4) was supplied by Merck (mass fraction purity > 0.98) with a chloride content less than $0.1 \cdot 10^{-6}$. Na_2CO_3 (mass fraction purity > 0.99) was procured from Fluka.

The ILs 1-benzyl-3-methyl imidazolium chloride (BzMIM Cl), 1-benzyl-3-methy-imidazolium methylsulfate (BzMIM CH_3SO_4), 1-butyl-3-methylimidazolium methyl sulfate (BMIMCH_3SO_4), 1-methylpiridinium methyl sulfate (Mpy CH_3SO_4), 1,3-dimethylimidazolium methyl sulfate (MMIM CH_3SO_4), 1-hexyl-3-methylimidazolium chloride (HxMIM Cl) were synthesized (mass fraction purity > 0.98) according to the procedure detailed elsewhere [16–20], with a chloride content between 2 and $15 \cdot 10^{-5}$, determined by potentiometry using a chloride specific electrode. All the ILs structures are shown in figure 1.

To reduce the water content to negligible values (mass fraction lower than $2 \cdot 10^{-4}$, determined using a 756 Karl Fisher coulometer), vacuum $P = 2 \cdot 10^{-1}$ Pa was applied to the ILs during several days, always immediately prior to its use. The ILs were kept in bottles under an inert gas.

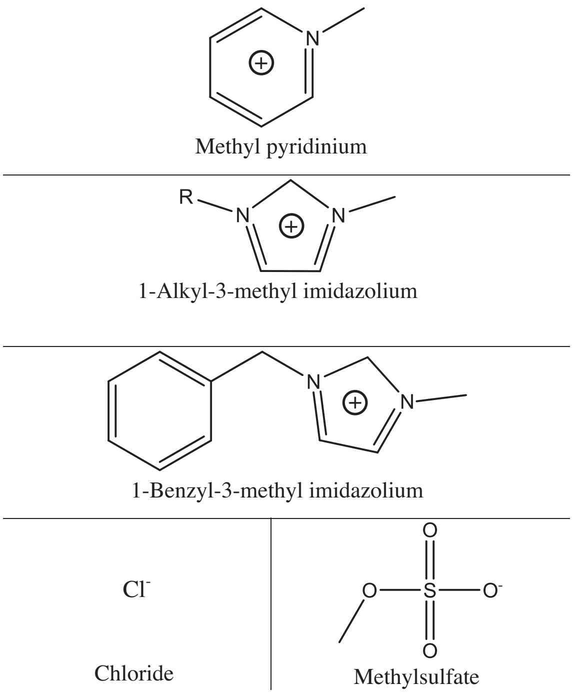

FIGURE 1. General schematic structure of the ILs used.

2.2. Experimental procedure

The cloud point titration method was used to determined the binodal data of the different ATPS at $T = 298.15$ K and atmospheric pressure according to the procedure described previously [4]. A known amount of salt was added to the different IL aqueous solution until the detection of turbidity, and then followed by the dropwise addition of ultra-pure water until a clear monophasic region was achieved. The system was always operating under constant stirring. The ternary system compositions were determined by the weight quantification of all components within an uncertainty of $\pm 10^{-4}$ g. The temperature was controlled with a F200 ASL digital thermometer with an uncertainty of ± 0.01 K.

The tie-lines (*TL*) determination was carried out by a gravimetric method, as proposed by Louros *et al.* [9], starting with the addition of a ternary mixture within the immiscibility region of known mass fraction to the ampoules. The temperature was kept constant and the mixture was stirred vigorously and left to settle for 24 h to ensure a complete separation of the layers. After a careful separation step, both top and bottom phases were weighed. The *TL* data were obtained by the lever arm rule taking into account the relationship between the upper phase and the overall system mass composition. The estimated uncertainty in the determination of the IL and salt phase mass compositions is less than $2 \cdot 10^{-4}$.

3. Results and discussion

The phase behavior involving the selected ILs and Na_2CO_3 as a segregation promoter was studied at $T = 298.15$ K and atmospheric pressure. The experimental binodal curve data in mass composition for the ternary mixtures of {IL + Na_2CO_3 + H_2O} are summarized in table 1, being the ILs C_nMIM CH_3SO_4 (n = 1, 2, and 4), BzMIM CH_3SO_4, XMIM Cl (X = benzyl and hexyl), and Mpy CH_3SO_4. In all cases, the top phase was rich in IL and poor in inorganic salt, while the bottom phase contained most of the high charge density salt and small IL quantities.

The first point addressed in this work consisted of comparing the different phase-forming abilities observed for methyl, ethyl, and butyl imidazolium methylsulfate. The results, shown in figure 2, allow the conclusion that larger biphasic regions are yielded when the length of the alkyl-chain is increased, meaning that less amount of Na_2CO_3 is needed to further phase segregation. The reason behind this behavior can underlie in the increased incompatibility between the phase-forming components, due to the more hydrophobic character of the IL moiety. Thus, it is possible to conclude that phase segregation is favoured by high alkyl chain length in the imidazolium cation. This finding further supports the possibility of including other cation families, as well as including other functional groups in the imidazolium ring to demonstrate the resulting IL potential associated with the salting out capacity.

In this sense, the next step was to explore the ATPS with Mpy CH_3SO_4, MMIM CH_3SO_4, and BzMIM CH_3SO_4. The aim of this task was to evaluate the differences in the salting out effect when a different cation is proposed (pyridinium vs. imidazolium) containing the same alkyl side chain (methyl), and when the benzyl group is added to the imidazolium cation (BzMIM CH_3SO_4). The binodal curves representing the minimum concentration necessary for the segregation of the phases at $T = 298.15$ K is shown in figure 3. It becomes apparent that MMIM CH_3SO_4 and Mpy CH_3SO_4 need almost identical amounts of Na_2CO_3 to trigger phase splitting,