Mutual solubility of betainium-based ionic liquid and water in the presence of hydrochloric acid and zwitterionic betaine

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Ionic liquids (ILs) are salts which have melting temperatures below 100 ^{o}C and many of them are liquid at room temperature.[1] The ILs have been widely used as alternative solvents due their unique physicochemical properties that can be tuned to meet specific needs in various fields. In the past few years our group has been investigating the ability ILs, in particular imidazolium- and pyrrolidinium-based ILs, to extract indium (In) and thallium (Tl), the two lighter homologs of the super-heavy element nihonium, from aqueous acidic media by using the liquid-liquid extraction method.[2-3] From these studies, it was found that the extraction of In and Tl into ILs was initiated by the solubility of the ILs in the aqueous phase. Thus, understanding the solubility of the ILs in the aqueous phase is considered as one of the keys to elucidating the mechanism of metal extraction into the ILs.

Recently, our group studied the extraction of In(III), Tl(I), and Tl(III) into betainium bis(trifluoromethanesulfonyl)imide ([HBet][Tf$_2$N]) from hydrochloric acid media.[4] It was found that In(III) was extracted at low acid concentrations and that the addition of zwitterionic betaine as the extractant improved the extraction efficiency. Tl(III) was also extracted but with lower extraction efficiency compared to that of In(III).

In order to understand the mechanism of In and Tl extraction into this ionic liquid, the mutual solubility of [HBet][Tf$_2$N] and water in the presence of hydrochloric acid was studied. The influence of the presence of zwitterionic betaine in the aqueous phase to the solubility was also investigated. Preliminary results are reported here.

The solubility experiments were carried out by the standard liquid–liquid extraction technique and performed in room temperature. The biphasic system was shaken for 5 min and centrifuged for 1 min, and the two phases were separated for further analysis. The water content in the ionic liquid phase was analyzed by the Karl-Fischer technique. The aqueous phase was analyzed to determine the equilibrium concentration of proton and chloride ions by using NaOH and AgNO$_3$ titrations, respectively. Preliminary results showed the change in the equilibrium concentrations of D$^+$ and Cl$^-$ [in this experiment we used deutero-hydrochloric acid (DCl)] in the aqueous phase compared to the initial ones (Fig. 1). The solid line in the figure represents the reference value when the equilibrium concentrations are equal to the initial ones.
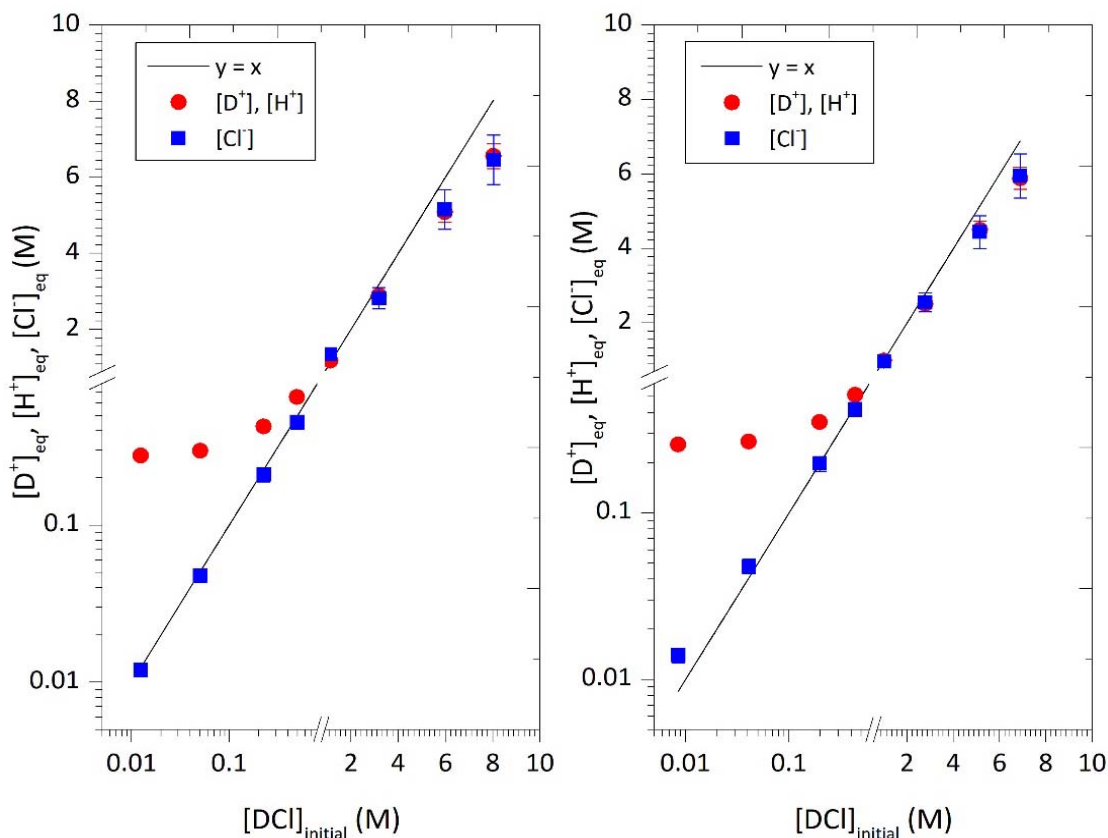
FIG. 1. The equilibrium concentrations of DCl was plotted as the function of the initial DCl concentrations. The solid line indicates the reference value when the equilibrium concentrations are equal to the initial ones. Figure (a) shows the result of $[D^+]$, $[H^+]$, and $[Cl^-]$ equilibrium concentrations without the presence of zwitterionic betaine, and figure (b) shows the result $[D^+]$, $[H^+]$, and $[Cl^-]$ equilibrium concentrations when zwitterionic betaine was added into the aqueous phase. Both figures show a similar trend.

Furthermore, the equilibrium concentrations of $[HBet]^+$ and $[Tf_2N]^-$ in the aqueous phase were assayed by using ^{1}H-NMR and ^{19}F-NMR techniques, respectively. The results showed that $[HBet][Tf_2N]$ is soluble in the aqueous phase and that the equilibrium concentrations of $[HBet]^+_{aq}$ and $[Tf_2N]^-_{aq}$ were dependent on the initial acid concentration and on the presence of zwitterionic betaine (Fig. 2).

Based on the experimental results, these reactions were considered to occur upon dissolution of the ionic liquid into the aqueous phase:

$$[HBet][Tf_2N]_{IL} \leftrightarrow [HBet^+]_{aq} + [Tf_2N^-]_{aq} \tag{1}$$
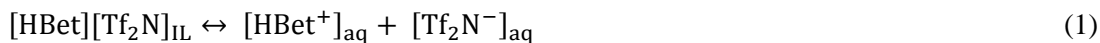
which is followed by an acid-base equilibrium where proton and zwitterionic betaine are formed:

$$[HBet^+]_{aq} \leftrightarrow H^+_{aq} + Bet_{aq} \tag{2}$$

and the protonation of anion [Tf$_2$N]$^-$ in the presence of acidic proton:

$$H^+_{aq} + [Tf_2N^-]_{aq} \leftrightarrow HTf_2N_{aq} \tag{3}$$

The study of the solubility mechanism is ongoing and this information will be used for further study of mechanism of In and Tl extraction into [HBet][Tf$_2$N] – HCl system.
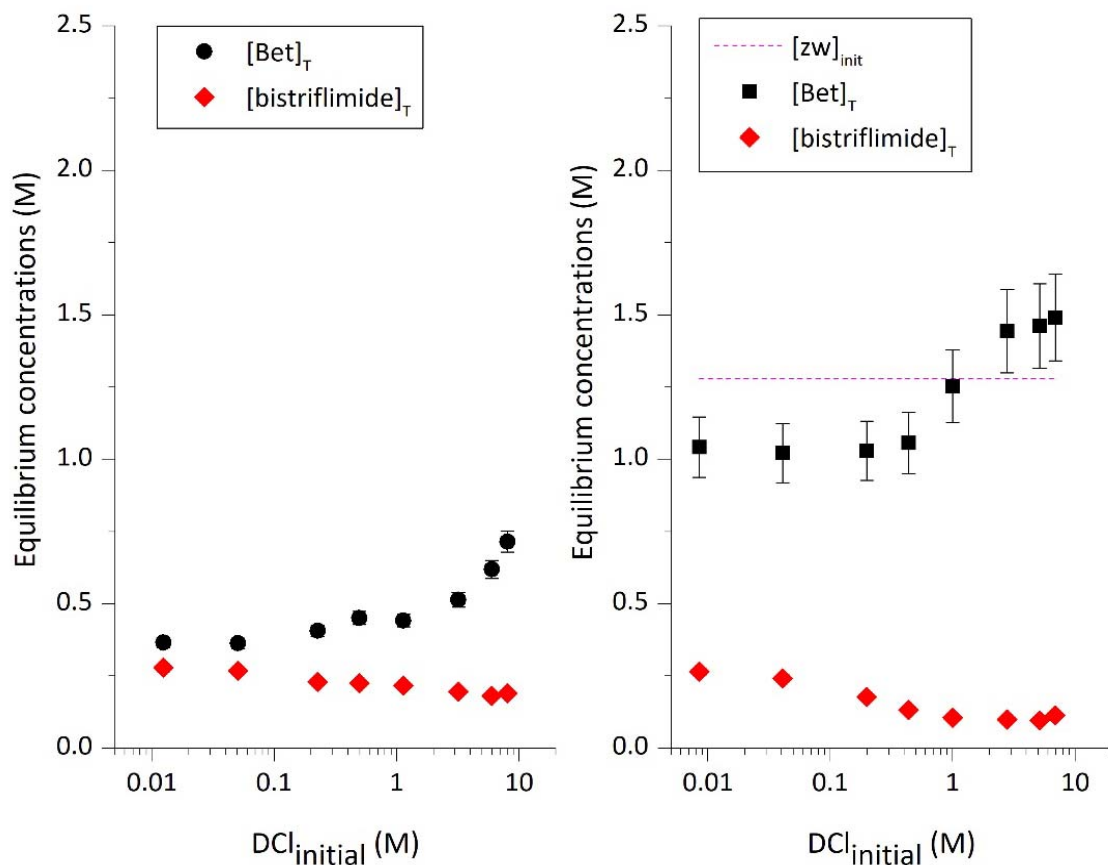

FIG. 2. The results of [HBet]$^+$ and [Tf$_2$N]$^-$ solubilities in the aqueous phase measured by ^{1}H NMR and ^{19}F NMR methods, respectively. Left: the solubility of [HBet]$^+$ and [Tf$_2$N]$^-$ in water containing DCl. Right: the solubility of [HBet]$^+$ and [Tf$_2$N]$^-$ in water containing DCl and zwitterionic betaine. The dashed line on the right figure represents the initial concentration of the zwitterionic betaine.

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