

Thallium transfer from hydrochloric acid media into pure ionic liquids

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Pure hydrophobic ionic liquids are known to extract metallic species from aqueous solutions. Here, we report on the systematic investigation of thallium (Tl) extraction from aqueous hydrochloric acid (HCl) solutions into six pure fluorinated ionic liquids, namely imidazolium- and pyrrolidinium-based ionic liquids with *bis*(trifluoromethanesulfonyl)imide and *bis*(fluorosulfonyl)imide anions.

It has been shown that distribution ratios attributed to Tl(I) are below 1. In the case of Tl(III), surprisingly high extraction efficiencies and fast kinetics have been observed, and equilibrium has been reached in seconds. Bromine water (Fig. 1a) or chlorine water (Fig. 1b) was used to oxidize Tl(I) to Tl(III). It has been found that the Tl(III) extraction ability of ionic liquids in this work increases in the order $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}] < [\text{C}_3\text{C}_1\text{pyrr}][\text{Tf}_2\text{N}] < [\text{C}_4\text{mim}][\text{Tf}_2\text{N}] < [\text{C}_2\text{mim}][\text{FSI}] < [\text{C}_3\text{C}_1\text{mim}][\text{Tf}_2\text{N}] < [\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$. The solubilities of the $[\text{Tf}_2\text{N}]$ -based ionic liquids in water decrease in the same order. The highest distribution value of Tl(III) was approximately 2000 (Fig. 1a). The charge of the Tl(III)

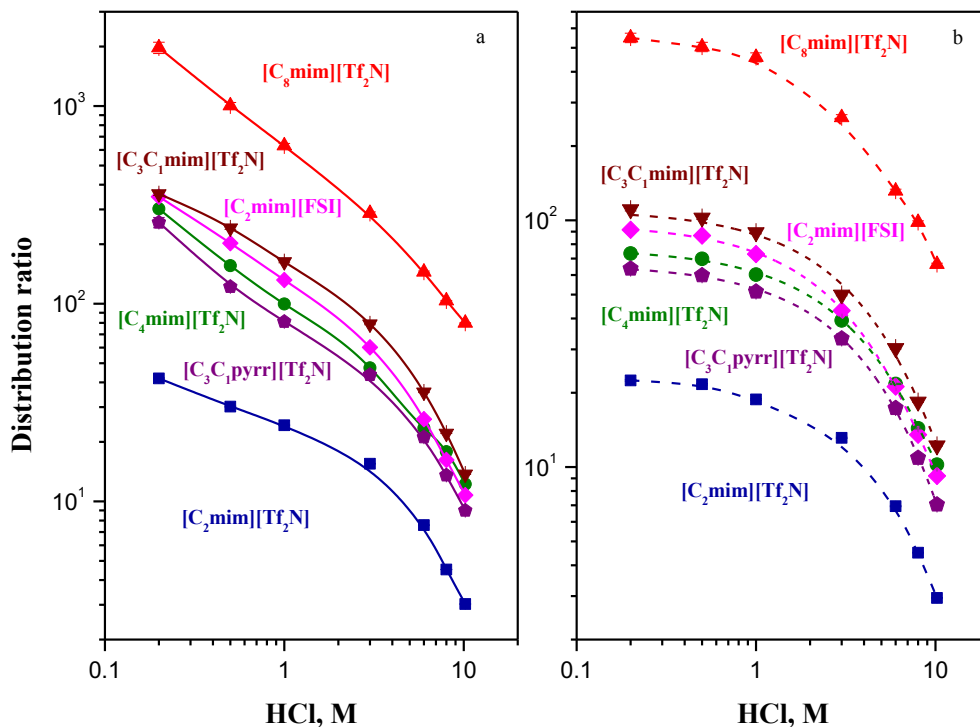


FIG. 1. Tl(III) extraction from HCl aqueous solutions into different ionic liquids: a) data with bromine water, b) data with chlorine water.

complexes has been determined by introduction of Li[Tf₂N] into the aqueous phase for experiments with [Tf₂N⁻]-based ionic liquids. The measured data indicated that the extraction of Tl(III) proceeds mainly *via* ion pair complex formation with IL cations, and that the extracted metallic species are TlCl₄⁻ in low acid concentrations and either TlCl₅²⁻ or a mixture of TlCl₄⁻ and TlCl₆³⁻ in high acid concentrations in the presence of chlorine water. Tl(III) extraction is quantitative for initial metal concentrations up to 1 × 10⁻³ M. Back-extraction of Tl(III) has been checked as a function of HCl concentration, and a successful decrease in distribution ratio values has been observed. In total, these results indicate that the use of pure ionic liquids for extraction of Tl from aqueous HCl solutions is feasible. A full publication on these results is available in Ref. [1].

[1] E.E. Tereshatov *et al.*, J. Phys. Chem. B **120**, 2311 (2016); doi:10.1021/acs.jpcc.5b08924