Ionic liquid-based extraction of indium and thallium

E.E. Tereshatov, M.Yu. Boltoeva,[1,2] and C.M. Folden III
[1]*Université de Strasbourg, IPHC, Strasbourg, 67037 France*
[2]*CNRS, Strasbourg, 67037 France*

Indium and thallium are elements of interest for radiopharmaceuticals [1], manufacture of liquid crystal displays [2], and environmental protection [3]. The growing economic needs from high-tech industries support studies on efficient recovery of indium and development of new techniques for trapping of toxic thallium.

The goal of this work is to develop ionic liquid-based extraction procedures for indium and thallium. We investigated the extraction behavior of In and Tl from hydrochloric acid solutions into [C_4mim][Tf_2N], a well-characterized room temperature 1-butyl-3-methyl imidazolium *bis*(trifluoromethanesulfonyl)imide ionic liquid (IL) [4], with and without the widely used extracting agent tributyl phosphate, TBP (see Fig. 1). To the best of our knowledge, this extraction system has never been examined before for the extraction study of group 13 elements.
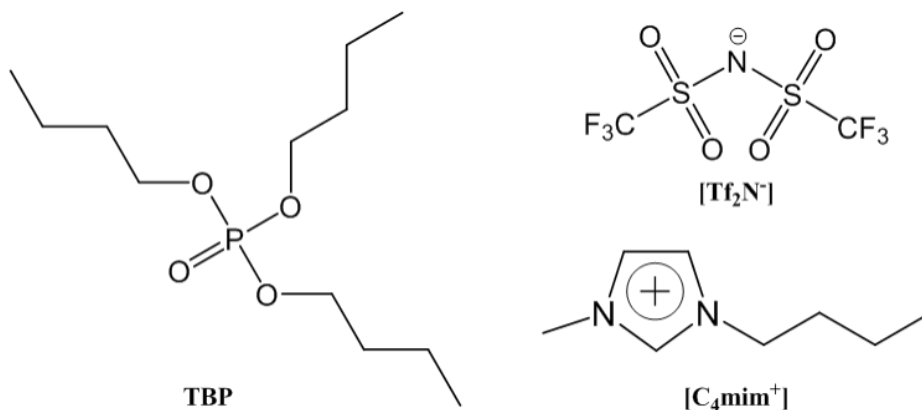

FIG. 1. Molecular structure and abbreviations of extractant and ionic liquid used in this work.

First, we have checked the ability of pure IL to extract Tl and In from the aqueous HCl solutions. Hereinafter, we describe the extraction system as M/HCl//L/[C_4mim][Tf_2N] where M is a metal ion and L is an extracting agent. The metal ion distribution between the IL and aqueous phases has been examined by varying the concentration of hydrochloric acid. The results of varying the HCl concentration are shown in Fig. 2. The distribution ratios of trivalent thallium are much higher than those of Tl(I) and In(III) in the whole acidity range. Moreover, the variation of acid concentration in the aqueous phase affects the extraction efficiency of trivalent thallium and indium differently. $D_{Tl(III)}$ decreases from 300 in 0.2 M HCl to 20 in 6 M, while $D_{In(III)}$ increases from 1×10^{-5} to 5×10^{-3}, respectively. There is no monotonic dependency on the acid concentration for extraction efficiency of Tl(I). This can indicate that Tl(I) extraction mechanism might be different for [HCl] > 1 M. The high extraction of Tl(III) without any extracting agents indicates that the IL is not an inert solvent and that it participates in the extraction process.
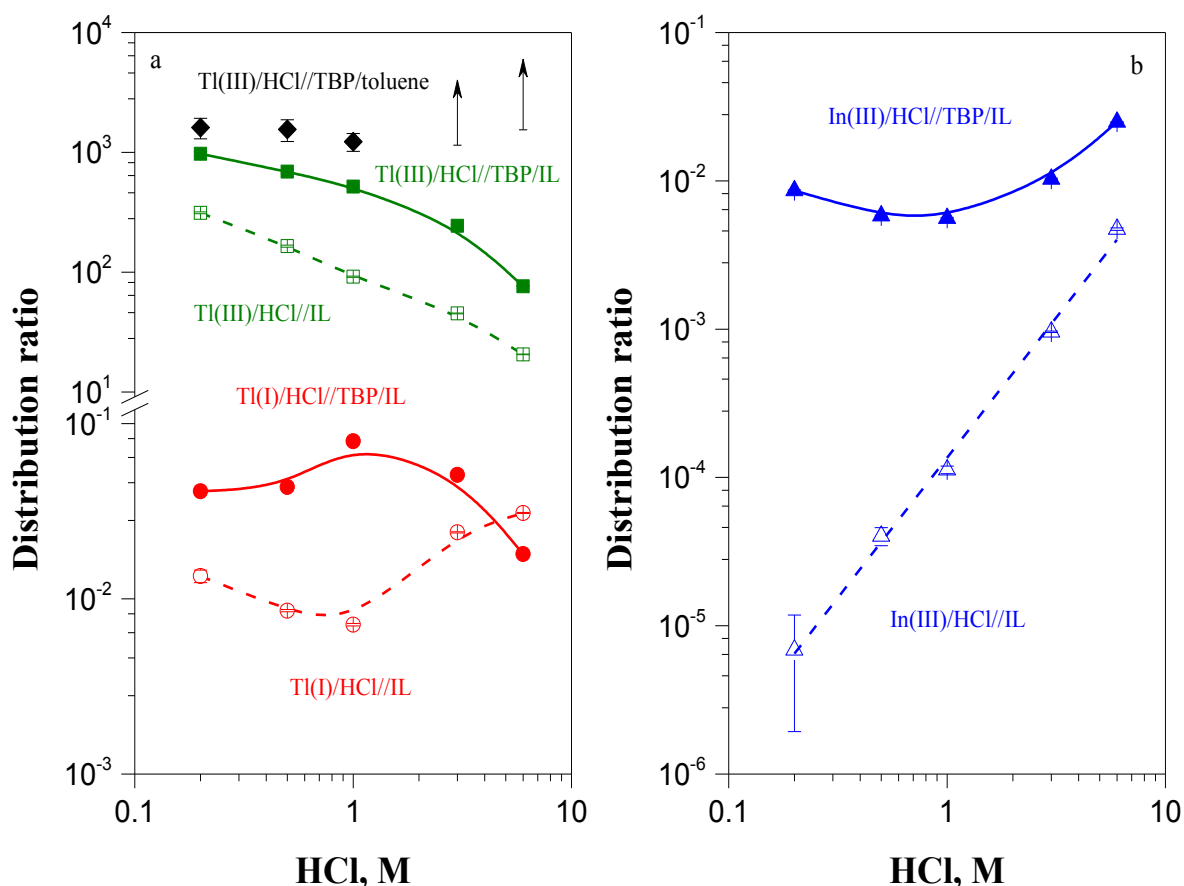
FIG. 2. Distribution ratio of: a – Tl(I) and Tl(III), b – In(III) from HCl solutions into IL (open symbols) and into IL or toluene with 30 % TBP (closed symbols).

The extraction of the individual metal ions has been also carried out in different initial hydrochloric acid concentrations in the aqueous phase (from 0.2 to 6 M HCl) with 30% TBP dissolved in IL or toluene (Fig. 2). As expected, the introduction of TBP, an organic ligand, in the extraction system results in a significant increase in the extraction efficiency of the metals. The extraction efficiencies of Tl(I) and In(III) by TBP and IL are greater than those for pure IL and the latter values are below 0.1. The extraction is quantitative for trivalent thallic ions into IL or toluene over the entire range of HCl concentrations. For the extraction into toluene, the highest $D_{Tl(III)}$ values have been found for [HCl] ≤ 1 M. In the case of further increase of acid concentration, only lower limits of distribution ratios have been measured. Our results are in agreement with literature data on the extraction of thallium and indium ions by TBP dissolved in molecular solvents. For example, De and Sen reported the complete extraction of trivalent thallium from 6 M HCl aqueous solution by 30% TBP in benzene, while In(III) is extracted much less efficiently ($D_{In(III)}$ = 3.57 at [HCl] = 2 M) [0]. Furthermore, the trend similarity of both distribution curves for Tl(III)/HCl//IL and Tl(III)/HCl//TBP/IL may indicate that the nature of extracted complexes stays the same, i.e. there are anionic species in both extraction systems. The

difference in shape of the curves for In(III) and Tl(I) reveals that composition of the extracted species is affected by the presence of TBP.

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