

Mechanism of indium and thallium extraction into [Hbet][Tf₂N] ionic liquid

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Our research group has been actively studying the liquid-phase chemistry of indium and thallium, the predicted homologs of the superheavy element nihonium (Nh), by using the liquid-liquid extraction technique. This study seeks to establish chemical systems that can potentially be used to investigate the chemical properties of Nh, which still remain largely unknown since this element was first discovered in 2004. Due to its low production rate, Nh chemistry must be studied at a one-atom-at-a-time level. To mimic this condition, the study of the homologs was carried out using radiochemistry techniques, which allow the experiments to be done with ultra-trace In and Tl concentrations. Preliminary results are reported here.

The liquid-liquid extraction technique, also commonly known as solvent extraction, is based on preferential distribution of solutes between two immiscible liquid phases. Our study involves hydrochloric acid as the aqueous phase and an ionic liquid, a type of salt with melting temperature below 100 °C [1], as the organic phase. Previously, we have reported the preliminary results of In(III) and Tl(I, III) extraction into water-saturated [Hbet][Tf₂N] ionic liquid (IL) [2]. [Hbet][Tf₂N] is a protic and hydrophobic IL composed of a betainium cation and a bistriflimide anion [3]. Betainium is the protonated form of glycine betaine (bet), a zwitterionic compound with a carboxylic acid group in its structure [3]. The structure of this IL is shown in Fig. 1.

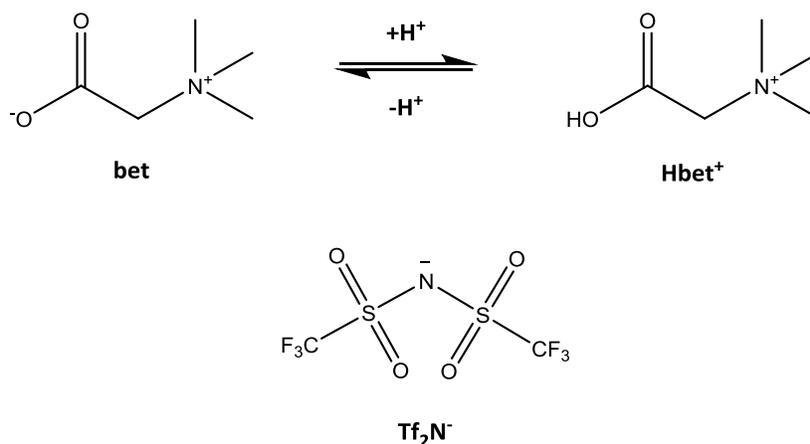


FIG. 1. Chemical structure of [Hbet][Tf₂N] components: zwitterionic betaine and betainium cation (top) and bistriflimide anion (bottom).

The previously reported results showed that the extraction yield of the In(III) and Tl(I, III) was better at lower acid concentrations and it decreased with increasing acidity. Having obtained these data, the mutual solubility between [Hbet][Tf₂N] and the acidic aqueous phase was studied in order to understand the chemical interactions in the system, and these results are reported in Ref. [4]. All this information allowed us to develop mathematical models to explain the extraction mechanisms of In(III) and Tl(I, III) into [Hbet][Tf₂N]. These models are based on the formation of betaine-containing metal complexes as the extracted species. The number of betaine molecules and the structure of the complexes were determined using a slope analysis method. An attempt to estimate the extraction constants of the extracted species and the constants of complexes formed in the aqueous phase was also made. These quantities, combined with the results of the slope analysis as well as the expected chemical behavior of the metals, ultimately led to the following conclusions:

1. In(III) was mostly extracted as InCl₂⁺ through an ion pair formation mechanism with [Tf₂N]⁻ anion. The structure of the extracted complex at low acidity and without additional betaine added is most likely [InCl₂(bet)₄][Tf₂N]. Meanwhile, in the presence of 15% (w/v) betaine, the extracted complex contains approximately three betaine molecules. Therefore, we considered the possibility that betaine binds with indium as a bidentate ligand when it is present in excess. At higher HCl concentrations, in both systems with and without betaine added, the predominant extracted complex is likely to be InCl₂[Tf₂N].
2. Tl(III) was predominantly extracted through ion pair formation with [Hbet⁺]. The extracted species is most likely TlCl₄⁻ in the entire range of HCl concentrations studied, with the possibility of betaine molecules incorporated in the extracted complex at low acidity. Unfortunately the number of betaine molecules associated with Tl(III) complex cannot be determined due to insufficient data and the large uncertainty on the slope.
3. Tl(I) was mainly extracted through a cation exchange mechanism with [Hbet⁺], but we also considered the extraction of [Hbet][TlCl₂] complex at high acid concentrations. The extracted species are [Tl(bet)⁺] at <0.5 M HCl, bare Tl⁺ in 0.5 – 5 M HCl region and TlCl₂⁻ in > 5 M HCl.

The results of this mechanism study would be beneficial should Nh chemistry be studied in the same media. By comparing the extraction behavior of Nh to its lighter homologs, one ideally could infer whether a similar complex is formed and extracted through a particular mechanism, and eventually determine if these elements belong to same group. However, these current data are still preliminary and extensive work is required for a future experimental study of Nh chemistry. Nevertheless, these results provide baseline data that could be useful for that purpose.

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