

## Indium and thallium extraction into a betainium-based ionic liquid

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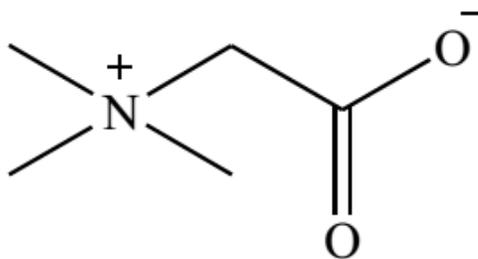
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Previously, our group has reported the extraction of indium (In) into imidazolium-based ionic liquids [1] and extraction of thallium (Tl) into several imidazolium-based and pyrrolidinium-based ionic liquids [2] using the liquid-liquid extraction (LLE) technique. This study is intended to provide the basis for a potential future chemistry study of nihonium, the heaviest homolog of In and Tl, with a focus on developing an effective and efficient separation of In and Tl.

The LLE technique used in this study is based on the distribution of the solute in two immiscible phases, an aqueous and an organic phase [3]. Our previous results showed that Tl was effectively extracted into the ionic liquids in the form of a negatively charged complex  $TlX_z^{3-z}$ , where X is either  $Cl^-$  or  $Br^-$ , and thus enabled effective separation with In, as the latter mainly remains in the aqueous phase. In the current work, we explore the ability of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide ([HBet][Tf<sub>2</sub>N]) to extract In and Tl from hydrochloric acid (HCl) media.

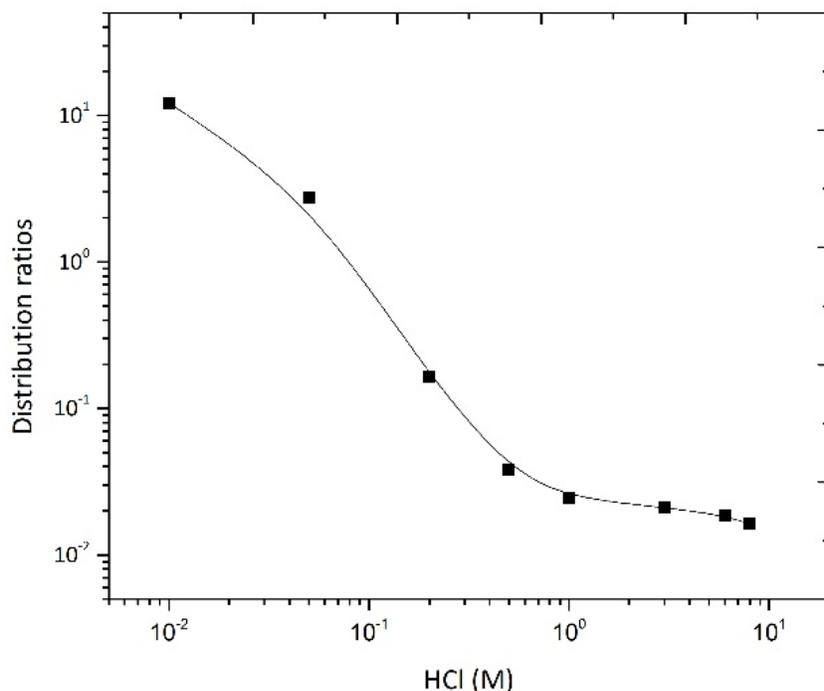
Unlike the previous ionic liquids that have been studied, [HBet][Tf<sub>2</sub>N] is not commercially available. The [HBet][Tf<sub>2</sub>N] ionic liquid was synthesized in our laboratory according to a procedure in the literature [4]. Betaine hydrochloride solution was mixed with lithium bis(trifluoromethylsulfonyl)imide solution with a 1:1 molar ratio. The mixture was stirred for 1 h at room temperature. Upon mixing, the solution was allowed to sit until it formed two distinct phases. Subsequently, the aqueous phase was dispensed and the organic phase was washed with deionized water several times to remove chloride impurities. The final product was used as a water-saturated ionic liquid to avoid uncontrollable water uptake during the extraction.

Betaine, which is also known as 1-carboxy- N,N,N-trimethylmethanaminium hydroxide, N,N,N-trimethylglycine, N-trimethylglycine, or trimethylglycine, is a zwitterion, and thus possesses both positive and negative charges within its molecule (Fig. 1) [3]. The zwitterionic form has a strong coordination site on the carboxylate group and this makes it a potential extractant to the metal ions [5].



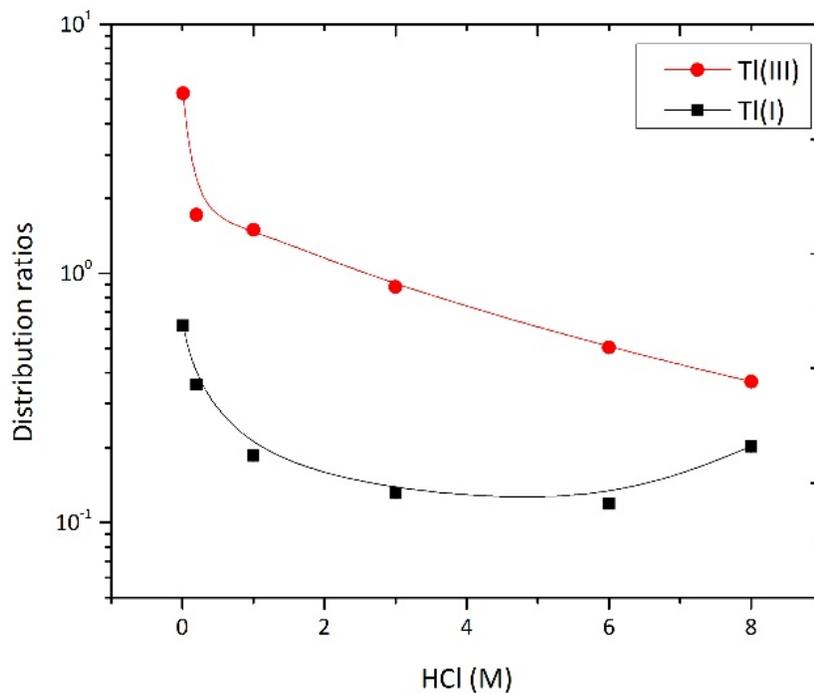
**FIG. 1.** The structure of zwitterionic betaine.

The mechanism of metal extraction into [HBet][Tf<sub>2</sub>N] can occur via several pathways, i.e., complex formation, ion exchange, or ion-pair formation. This extraction mechanism will be one of the subjects of a future study. Extraction experiments were performed following the previous procedure used in our work [6]. The result of extraction is presented in the form of a distribution ratio, that is, the ratio of activity of the solute in the organic phase to that of in the aqueous phase. Preliminary results of the current study indicate that the distribution ratios of In and Tl extraction are affected by several factors such as the acid concentration and the speciation of metal complexes in the aqueous solution.



**FIG. 2.** Indium extraction into [HBet][Tf<sub>2</sub>N].

As shown in Fig. 2, the distribution ratios of In extraction decrease as the HCl concentration increases. Also the distribution ratios of Tl(I) and Tl(III) decrease with the same trend (Fig. 3). Considering the pK<sub>a</sub> of betaine is 1.82 [7], deprotonation of [HBet]<sup>+</sup> may occur in 0.01 M HCl and enable the formation of zwitterion betaine compound in the organic phase. Indium is known to form InCl<sub>2</sub><sup>+</sup>, InCl<sub>3</sub>, and InCl<sub>4</sub><sup>-</sup> in chloride solution, depending on the chloride ion concentration [1, 8]. It is likely that at lower chloride concentrations (HCl concentration < 0.05 M), In is extracted as an InCl<sub>2</sub><sup>+</sup> complex, while at higher chloride concentrations (>0.5 M), the speciation of In is InCl<sub>3</sub> or InCl<sub>4</sub><sup>-</sup>, resulting in much poorer extraction.



**FIG. 3.** Thallium extraction into [HBet][Tf<sub>2</sub>N].

In the case of Tl(I), Tl<sup>+</sup> is the dominant species in dilute HCl, while it may present in the form of TlCl or TlCl<sub>2</sub><sup>-</sup> at higher acid concentrations [2]. Based on Fig. 3, the extraction curves of Tl(I) and Tl(III) show a similar trend, although Tl(I) mostly remains not extracted. This phenomena suggests that the extraction mechanism of Tl(I) and Tl(III) follow the same pathways (specifically at HCl concentrations < 3 M), but further experiments will be performed to test this assumption.

These preliminary results provided good indication of the ability of [HBet][Tf<sub>2</sub>N] ionic liquid to extract In and Tl from HCl media. Based on these findings, potential separation of In and Tl can be achieved by controlling the acid concentration and the speciation of the metal ions. Further experiments will be conducted to confirm these results as well as to elucidate the extraction mechanisms. In addition, future experiments will be aiming toward improving the extraction efficiency by introducing an additional extractant into the existing chemical system.

- [1] E.E. Tereshatov, M.Y. Boltoeva, and C.M. Folden III, *Solv. Extr. Ion Exc.* **33**, 607 (2015).
- [2] E.E. Tereshatov, M.Y. Boltoeva, V. Mazan, M.F. Volia, and C.M. Folden III, *J. Phys. Chem. B* **120** 2311 (2016).
- [3] T.V. Hoogerstraete, B. Onghena, and K. Binnemans, *Int. J. Mol. Sci.* **14**, 21353 (2013).
- [4] P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. van Hecke, L. van Meervelt, B. Kirchner, and K. Binnemans, *J. Phys. Chem. B* **110**, 20978 (2006).

- [5] B. Onghena and K. Binnemans, *Ind. Eng. Chem. Res.* **54**, 1887 (2015).
- [6] M.F. Volia, E.E. Tereshatov, M.Y. Boltoeva, and C.M. Folden III, *Progress in Research*, Cyclotron Institute, Texas A&M University (2015-2016) p. II-3. [https://cyclotron.tamu.edu/progress-reports/2015-2016/cyclotron\\_progress\\_2016.pdf](https://cyclotron.tamu.edu/progress-reports/2015-2016/cyclotron_progress_2016.pdf).
- [7] R.M.C. Dawson, D.C. Elliott, W.H. Elliott, and K.M. Jones, *Data for biochemical research* (Oxford University Press: New York, 1986) p. 8-9.
- [8] E.A. Burns and D.N. Hume, *J. Am. Chem. Soc.* **79**, 2704 (1957).