

## Metal Extraction into Ionic Liquids and Hydrophobic Deep Eutectic Mixtures

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**Abstract :** Room temperature ionic liquids (RTILs) are a class of liquid organic salts with melting points below 20 °C that are considered to be environmentally friendly 'designers' solvents. Pure hydrophobic ILs are known to extract metallic species from aqueous solutions. The closest analogues of ionic liquids are deep eutectic solvents (DESs), which are a eutectic mixture of at least two compounds with a melting point lower than that of each individual component. DESs are acknowledged to be attractive for organic synthesis and metal processing. Thus, these non-volatile and less toxic compounds are of interest for critical metal extraction. The US Department of Energy and the European Commission consider indium as a key metal. Its chemical homologue, thallium, is also an important material for some applications and environmental safety. The aim of this work is to systematically investigate In and Tl extraction from aqueous solutions into pure fluorinated ILs and hydrophobic DESs. The dependence of the Tl extraction efficiency on the structure and composition of the ionic liquid ions, metal oxidation state, and initial metal and aqueous acid concentrations have been studied. The extraction efficiency of the TlX<sub>3</sub>-z anionic species (where X = Cl<sup>-</sup> and/or Br<sup>-</sup>) is greater for ionic liquids with more hydrophobic cations. Unexpectedly high distribution ratios (> 103) of Tl(III) were determined even by applying a pure ionic liquid as receiving phase. An improved mathematical model based on ion exchange and ion pair formation mechanisms has been developed to describe the co-extraction of two different anionic species, and the relative contributions of each mechanism have been determined. The first evidence of indium extraction into new quaternary ammonium- and menthol-based hydrophobic DESs from hydrochloric and oxalic acid solutions with distribution ratios up to 103 will be provided. Data obtained allow us to interpret the mechanism of thallium and indium extraction into ILs and DESs media. The understanding of Tl and In chemical behavior in these new media is imperative for the further improvement of separation and purification of these elements.

**Keywords :** deep eutectic solvents, indium, ionic liquids, thallium

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