



# Copper extraction using protic ionic liquids: Evidence of the Hofmeister effect



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## ABSTRACT

Protic ionic liquids (PILs) have been used extensively in extractions of organic compounds but have seen relatively little use in the extraction of metals from aqueous phase. In this work, PILs based on trialkylammonium alkanooates are investigated for their capacity to extract copper from the aqueous phase. The results demonstrate a high degree of copper extraction, and the structures of the PILs make this possible even in the absence of chelating agents. Charge balance indicates that neutral extraction is the dominant mechanism in all cases, avoiding the degradation of the ionic liquid phase associated with ion exchange mechanisms. Further, we observe that the extent of copper extraction depends strongly on the identity of the anion of the copper salt, and that in the presence of multiple anions the PILs display a strong selectivity for particular species. The study presents strong evidence that this is a manifestation of the Hofmeister effect, and a review of literature studies indicates that this phenomenon may be quite common in IL-based extractions. We also demonstrate that the PILs used in this research are highly selective for copper from a mixture of alkali and alkaline earth metals, and that copper may be stripped from the IL phase using standard chelating agents.

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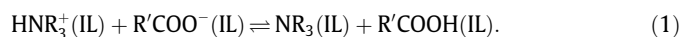
## 1. Introduction

The increasing global demand for metals requires the development of innovative technologies for extraction and recovery of metals from aqueous streams. Currently the most common technique for the extraction of commercially valuable metals from the aqueous phase is liquid-liquid extraction with molecular organic solvents [1–3]. Ionic liquids (ILs), salts that are molten at or near room-temperature, have recently emerged as very promising alternatives to conventional organic solvents.

Since the discovery of air and moisture stable ILs in the 1990s [4], an enormous range of IL species have been synthesized [5–8] and many studies have explored their application as media for the extraction of metals from aqueous phases [9–13]. As a class, ILs are largely non-flammable and non-volatile, potentially simplifying their use in commercial environments [5–7]. A more fundamental advantage is that while ionic metal complexes are generally insoluble in organic phases, ILs are capable of solvating ionic as well as neutral metal complexes [14,15]. This amounts to

the removal of a constraint on the coordination chemistry underlying extraction, offering researchers greater flexibility in process design. ILs therefore hold the potential for highly novel approaches to metal extraction.

Here, we consider protic ionic liquids (PILs) for the extraction of copper (II) from aqueous phase. PILs are a class of ionic liquids based on the mixture of a Brønsted acid and a Brønsted base, such that molecular and ionic forms exist in equilibrium. In the present study, we combine trialkylamines with linear alkanooic acids, so that the IL phase equilibrium can be written



Here, “(IL)” denotes solvation in the ionic liquid phase, and R and R' represent saturated, straight-chain alkyl groups. The fraction of ionic vs. molecular species in PILs is not easily measured, and the question of how to measure and define the “ionicity” of a PIL remains an active area of discussion [16,17]. However, there is evidence that while absolute pKa values are different in PIL and aqueous phases, the relative pKa values of the acid and base remain the same [18]. We are not aware of any literature reports of aqueous pKa values for the ammonium and carboxylic acids of interest in the present study, and the low aqueous solubility of these species would make their determination problematic. Generally, carboxylic

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acids typically display pKa values below 5, and organic ammonium species have pKa values above 9. Ionic forms should therefore predominate in the PIL.

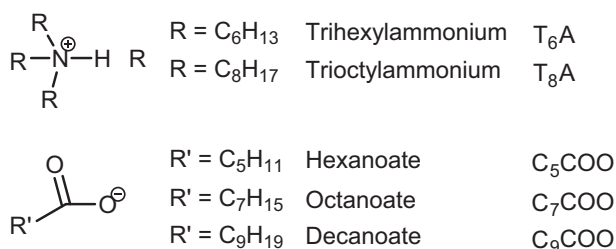
PILs have been studied in the extraction of organic [19–21] and biomolecular species [22,23] from aqueous phase, and have seen some application in electrodeposition of metals [24–26]. However, there has been relatively little study of PILs for metal extraction [27–30]. We report the results for the extraction of copper (II) from aqueous phase using PILs. While our focus in the present study is on mechanistic aspects rather than applications development, copper extraction is of significant current interest both for analytical processes [31–33] and for the treatment of waste streams [34–37]. A particular advantage of PILs in applications is that, as we discuss below, the coordination of the PIL with the metal ion eliminates the need for the inclusion of a chelating agent in the extraction. This is distinct from most previous studies of the extraction of Cu<sup>2+</sup> to ILs, as these studies generally employ non-protic ILs and require the use of a hydrophobic chelating agent to solubilize the metal in the IL phase [38–40]. Eliminating the need for such an agent offers significant potential advantages in cost and environmental impact in applications.

### 1.1. Protic ionic liquids for metal extraction

The protic ILs used in the present study are based on trialkylammonium cations and linear alkanolate anions; the ions employed are shown in Fig. 1. The choice of this set of ionic liquids is motivated by the observation that Cu<sup>2+</sup> coordinates strongly with both carboxylate [41–43] and amine [44] ligands. Indeed, high levels of extraction to organic solvents are observed when carboxylate and amine ligands are used in tandem to produce mixed-ligand complexes [45]. Use of the protic IL based on a tertiary amine leaves a lone pair of electrons accessible to the metal (albeit in competition with IL phase protons), and facilitates coordination of Cu<sup>2+</sup> with the solvent. This eliminates the need for a molecular ligand as an extraction agent, simplifying the extraction process and potentially reducing the cost associated with such reagents.

Task-specific ionic liquids (TSILs), ILs with structures specifically tailored to coordinate metals of interest, also avoid the need for a chelating agent, but this often comes at the cost of a significant complication to their synthesis. The PILs employed here are formed by a mixture of inexpensive, commercially available chemicals without the need for synthetic modification. We do not believe it is appropriate to label these PILs as “task specific,” on the grounds that the use of the term for such generic structures would make the terminology so broad as to be meaningless.

#### Solvent Ions:



#### Copper Salts:

Cu(NO<sub>3</sub>)<sub>2</sub>  
CuCl<sub>2</sub>  
CuSO<sub>4</sub>

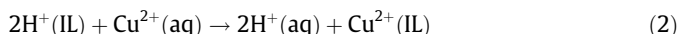
As noted above, relatively few studies have considered the use of PILs in metal extraction [27–30]. A relevant example is by Reyna-González et al. [30], who study the extraction of Cu<sup>2+</sup> using a protic IL based on a butylpyridinium cation and the bis(trifluoromethylsulfonyl)imide anion; we compare the observed processes in the next section. Bell and co-workers [46] dissolve small quantities of a protic IL in an aprotic IL solvent to promote the extraction of lanthanides. The protic species serve as extractants, just as the amine/carboxylate pairs do in the present study, but the mixture is not strictly a PIL.

While the formation of mixed ligand Cu<sup>2+</sup> complexes with amine and carboxylate groups is well-established [45,47,48], we do not characterize the complex (or complexes) present in the IL in the present study. Takemura et al. [49] report an extensive EXAFS and spectroscopic study of Cu<sup>2+</sup> coordination in N-hexylethylenediaminium bis(trifluoromethylsulfonyl)imide, a protic IL incorporating a primary amine. The authors infer that the metal is present as a stable mixed ligand species, incorporating both the amine and an anion. At low concentrations of copper salt in the IL, the anion in the metal coordination complex is the bis(trifluoromethylsulfonyl)imide of the IL; as the concentration of the copper salt increases, the IL anion is displaced by the inorganic anions (e.g. Cl<sup>-</sup>) that are introduced to the system in the copper salt. This scenario does not directly translate to the ILs reported in this study, because the IL carboxylate anions are far more strongly coordinating than any of the anionic species present in the Takemura et al. system.

### 1.2. Mechanism of extraction

The mechanism of ion extraction to ILs can be quite complicated [50–54]. Charged metal complexes are generally soluble in ILs, and Cu<sup>2+</sup> may therefore move from the aqueous to the IL phase without coordinating anions. However, because the electroneutrality of each phase must be preserved, transfer of a charged copper complex requires either concomitant transfer of uncoordinated anions from the aqueous phase, or ion exchange consisting of the transfer of cations from the IL phase into the aqueous phase.

Ion exchange mechanisms involving metals and IL cations have been studied extensively [55–60], and it is observed that strongly hydrophobic cations such as 1-decyl-3-methylimidazolium generally do not undergo extensive ion exchange [61]. The trialkylammonium species in the ILs used in the current study are sufficiently hydrophobic that it would be quite surprising if they engaged in ion exchange to a significant degree. However, the proton may dissociate, raising the possibility of ion exchange involving protons and copper ions according to the equation



This mechanism is observed by Reyna-González et al. [30], in their study of copper extraction. But as discussed in Section 3.2, charge balance demonstrates that little if any such ion exchange takes place in the systems reported here. The mechanism is likely suppressed by the basicity of the IL alkanolate anions, which limits removal of protons from the IL phase. The dominant extraction mechanism involves transfer of inorganic anions from the aqueous to the IL phase.

In addition to these mechanistic findings, our results demonstrate that PILs are very promising materials for metal extraction. We observe high levels of extraction without significant ion exchange that would degrade the IL or contaminate the aqueous phase, and this extraction is achieved without the use of a chelating agent, greatly simplifying the system. We also report promising results on the stripping of copper from the IL phase after extraction.

Fig. 1. Ionic structures of the IL cations and anions used in this research, and the copper salts studied in extraction. The actual ILs studied are listed in Table 1.

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