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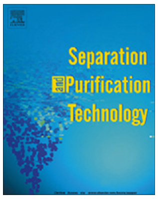

Ionic liquid anion effects in the extraction of metal ions by macrocyclic polyethers

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ABSTRACT

As part of a broader effort to determine the factors governing the relative contributions of ion-exchange processes and neutral complex/ion-pair partitioning in the extraction of metal ions into room-temperature ionic liquids by neutral extractants, the effect of ionic liquid (IL) anion on the extraction of alkali and alkaline earth cations by a crown ether from acidic nitrate and chloride media has been systematically examined. Results for a series of 1,3-dialkylimidazolium ($\mathrm{C_nmim^+}$)-based ILs incorporating hexafluorophosphate ($\mathrm{PF_6^-}$), bis[(trifluoromethyl)sulfonyl] imide ($\mathrm{Tf_2N^-}$), or bis[(perfluoroethyl)sulfonyl]imide ($\mathrm{BETI^-}$) as the counterion indicate that the choice of anion, in particular its hydrophobicity, can influence the balance among the various possible pathways for extraction, as well as both the extraction efficiency and selectivity. Overall, higher IL anion hydrophobicity is accompanied by a greater tendency toward ion exchange as the predominant mode of extraction. The effect upon extraction efficiency and selectivity is more complex, however, varying markedly with aqueous acidity.

1. Introduction

In the nearly two decades that have passed since the introduction of the first air- and water-stable ionic liquids (ILs) [1], countless studies have explored the influence of cation and anion structure on the physicochemical properties of these unique solvents and on their utility in a wide variety of applications. It is by now well-established, for example, that 1,3-dialkyl-imidazolium ionic liquids can be made progressively more water soluble by shortening the alkyl moieties appended to the imidazolium cation [2]. Similarly, incorporation of a sufficiently hydrophilic anion (e.g., $\mathrm{Cl^-}$) into these same ionic liquids can render them completely water miscible [3]. Analogous studies on these and a host of other ionic liquids have demonstrated the importance of the precise nature of the cationic and anionic constituents of the ionic liquid in determining such properties as density [4], water content [5], thermal [5,6] and radiolytic [7] stability, lubricity [8], toxicity [9], and conductivity [10], among others. In addition, various IL cation and anion characteristics have been found to be critical in determining the suitability of these solvents as media for electrochemistry [11], synthesis [12], and catalysis [13].

Our own work has examined the relationship between the properties of ionic liquids and their performance as solvents in the extraction of metal ions from aqueous solution by various neutral extractants (e.g., crown ethers). In contrast to extraction into conventional (i.e., molecular) organic solvents, metal ion partitioning into ILs in the presence of a neutral extractant is a complex process comprising multiple pathways, the balance among which is determined by the characteristics of the metal ion (e.g., charge density) [14], the extractant [15], and the ionic liquid itself [16,17]. It has been shown for 1,3-dialkylimidazolium ILs, for example, that increasing the hydrophobicity of the IL cation can induce a change in the mode of partitioning of alkaline earth cations in the presence of crown ethers from one in which ion-exchange processes are favored to one in which neutral complex/ion-pair extraction is the predominant mode of metal ion partitioning [18]. As has recently been shown, such changes can have a significant influence on metal ion extraction efficiency and selectivity [14].

In contrast to IL cation effects on metal ion partitioning, which have been the subject of a number of investigations, the influence of IL anions has remained incompletely explored. Domańska and Rękawek [19], for example, examined the extraction of $\mathrm{Ag^+}$ by dithizone into 1-butyl-3-methylimidazolium hexafluorophosphate ($\mathrm{PF_6^-}$) and its bis[(trifluoromethyl)sulfonyl] imide ($\mathrm{Tf_2N^-}$) analog, noting only that the latter yields slightly higher (99.3% *vs.* 98.6%) extraction efficiency under the experimental conditions. Similarly, in a pair of papers by Giridhar et al. [20,21], the suitability of 1-butyl-3-methylimidazolium-based ILs incorporating either $\mathrm{PF_6^-}$ or $\mathrm{Tf_2N^-}$ as solvents for the extraction of uranium by TBP was evaluated. No attempt was made to examine the influence of IL anion on anything other than the extraction efficiency, however. More recently, the possible effect of IL anion on the nature of the

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partitioning species in the extraction of lanthanides (i.e., Nd^{3+} and Eu^{3+}) by thenoyltrifluoroacetone (HTTA) into 1,3-dialkylimidazolium-based ILs incorporating Tf_2N^- [16] or nonaflate (NfO^-) [17] has been considered by Jensen et al. The observed effects, in particular the greater propensity toward the extraction of various cationic lanthanide complexes when the latter solvents are employed, were attributed to the far higher concentrations of dissolved water present in the NfO^- IL following equilibration with aqueous buffer solutions. Along these same lines, work by Luo et al. [22] has explored IL anion (PF_6^- vs. Tf_2N^- vs. $BETI^-$, where $BETI^-$ represents the bis[(perfluoroethyl)sulfonyl]imide anion) effects in the extraction of Sr^{2+} and Cs^+ by crown ethers in several 1,3-dialkylimidazolium-based ILs. An important aspect of this work too was exploring the impact of a change in anion on the efficiency of metal ion extraction, with increasing IL anion hydrophobicity typically being accompanied by higher values of the strontium and cesium distribution ratios. Extraction selectivity for Sr^{2+} over several monovalent cations (e.g., Na^+) was also found to improve with increasing anion hydrophobicity. The practical utility of these results was limited, however, as all extraction studies were carried out using only water as the aqueous phase.

In the present study, we present a detailed examination of the effect of IL anion on the extraction of several alkali (e.g., Na^+) and alkaline earth (e.g., Sr^{2+}) cations by dicyclohexano-18-crown-6 (DCH18C6) into a series of 1,3-dialkylimidazolium-based ILs from acidic nitrate and chloride media, with emphasis on the effect of IL anion hydrophobicity on the predominate mode(s) of metal ion partitioning observed.

2. Experimental

2.1. Materials

For this study, three 1-alkyl-3-methylimidzolium hexafluorophosphate ionic liquids (abbreviated as $C_n mim^+PF_6^-$ where $n = 5$, 8, or 10), along with the corresponding bis[(trifluoromethyl)sulfonyl]imide and bis[(perfluoroethyl)sulfonyl]imide ILs (designated as $C_n mim^+Tf_2N^-$, and $C_n mim^+BETI^-$, respectively) were employed. The Tf_2N^- and $BETI^-$ ILs were prepared *via* either conventional or microwave synthesis, purified, and characterized according to published methods [23,24], while the PF_6^- ILs were purchased (IoLiTec, Tuscsaloosa, AL) and used without further purification. For partitioning studies, the dicyclohexano-18-crown-6 (DCH18C6) used was a commercial mixture of the cis-syn-cis (A) and cis-anti-cis (B) isomers (Parish Chemical Company, Orem, UT). Aqueous acid solutions were prepared from Milli-Q2 water and Optima™ nitric or hydrochloric acid (Aldrich Chemical Company, Milwaukee, WI) and standardized using certified sodium hydroxide solutions (Ricca, Arlington, TX) and phenolphthalein indicator (Ricca, Arlington, TX).

2.2. Methods

All strontium, barium and sodium distribution ratios (D_M, defined as $[M]_{org}/[M]_{aq}$ at equilibrium) were determined radiometrically using commercial Sr-85, Ba-133 and Na-22 radiotracers (Isotope Products Laboratories, Burbank, CA), respectively, assayed via gamma spectroscopy (Perkin Elmer Model 2480 Automatic Gamma Counter) using standard procedures. A 1:1 phase ratio was employed for all measurements and all determinations were carried out at ambient temperature (23 ± 2 °C). Preconditioning of the organic phase prior to distribution ratio measurements was accomplished *via* two contacts with twice the volume of an appropriate aqueous acid solution. To minimize the possible decomposition of the hexafluorophosphate-based ILs upon contact with acidic solutions, contact/equilibration times consistent with those described previously by Visser et al. [25] were employed. Under these conditions, no decrease in IL phase volume upon acid contact, reported to be symptomatic of IL decomposition [26], was observed. Aqueous nitrate concentrations were determined using a Dionex ICS-1000 ion chromatograph equipped with a conductivity detector, Dionex AS18/AG18 analytical and guard columns (4×250 and 4×50 mm respectively), a Dionex ASRS 300 (4 mm) conductivity suppressor, and 37 mM NaOH eluent. IC eluent flow rates were 1.00 mL/min and the column temperature was maintained at 30 °C.

The density of each IL was determined by weighing a known volume of it in either a volumetric flask or a volumetric pipet. The water content of the ILs was measured using a Metrohm 870 KF Titrino Plus coulometer. The solubility of the IL in water was measured by UV–visible absorption using a Shimadzu UV-2450 spectrophotometer. For these solubility measurements, a 1 mL aliquot of the IL was contacted with a 10 mL portion of deionized (18 MΩ) water, vortexed for 10 min, and allowed to stand undisturbed to equilibrate for 1 h. Following centrifugation, the aqueous phase was taken and diluted as needed for solubility measurements, while the organic phase was used for water content measurements. The characterization data collected for the ionic liquids of interest are summarized in Table 1.

3. Results and discussion

To fully understand metal ion partitioning behavior in extraction systems using ionic liquids as replacements for the conventional organic solvents ordinarily employed, the effect of each constituent of the ionic liquid on the extraction process must be considered. As noted above, although considerable effect has been expended to determine the effect of the ionic liquid cation on this process, must less attention has been directed at the ionic liquid anion. In an earlier report, Luo et al. [22] examined the effect of IL anion on the extraction of a monovalent and divalent metal ion from chloride-containing aqueous phases. This study, by focusing on systems employing short-chain (i.e., relatively hydrophilic) imidazolium cations ($C_n mim^+$, with $n = 2$–8) and aqueous chloride solutions, chose conditions subsequently determined to strongly favor extraction *via* ion-exchange [27], a process known to be undesirable [26]. Moreover, this study focused upon extraction efficiency, rather than considering the effect of IL anion on the preferred mode of extraction. In contrast, the present work focuses more on conditions expected to favor neutral complex (ion-pair) extraction as the primary mode of partitioning, in particular less hydrophilic IL cations and nitrate-containing aqueous phases. In an effort to build on prior work, however, several of the same IL cations are also examined, as are the same IL anions, with the objective of understanding the interplay of all of these factors in governing the nature of the extraction process.

3.1. Effect of IL anion on the mutual solubility of ILs and water

Table 1 summarizes the results of measurements of water solubility and water content of the ILs considered, properties indicative of the relatively hydrophobicity of the solvents. As can be seen, for a given $C_n mim^+$ cation, a change from PF_6^- to Tf_2N^- to $BETI^-$ typically results in a decrease in solvent water content and a decline in the water solubility of the IL. Such observations are consistent with the order of anion hydrophobicity proposed by Luo et al. [22], specifically $PF_6^- < Tf_2N^- < BETI^-$, and are indicative of significant differences among the three anions.