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Effect of aqueous phase anion on the mode of facilitated ion transfer into room-temperature ionic liquids

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ABSTRACT

Measurements of the partitioning of various alkali and alkaline earth cations between solutions of hydrochloric acid and a series of 1,3-dialkylimidazolium-based ionic liquids (ILs) to which a crown ether has been added have revealed substantial differences in extraction behavior *versus* both conventional molecular solvents (*e.g.*, 1-octanol) under the same conditions and the same ILs when nitric acid solutions are employed as the aqueous phase. These results can be rationalized by application of a three-path model for metal ion partitioning into ILs in the presence of a neutral extractant. Additionally, the results point to a significant role for anion hydration energy in determining the balance amongst the possible modes of partitioning and strongly suggest that ion exchange involving the cationic metal complex and the cationic constituent of the ionic liquid constitutes the “default” route for metal ion extraction in IL systems incorporating a neutral extractant.

1. Introduction

Liquid–liquid extraction (LLE) represents one of the most well established methods of separation, a result of its relative simplicity, ease of use, and versatility. As applied to metal ions, LLE has proven itself to be a flexible and powerful approach to achieving separations, both on the analytical and process scale [1]. Despite its many virtues, however, as ordinarily practiced the technique also suffers from a variety of limitations, most notably the frequent need for toxic (*e.g.*, chlorinated hydrocarbons) or volatile (*e.g.*, paraffinic hydrocarbons) organic solvents. This drawback has led to widespread interest in alternative approaches to extraction employing more environmentally benign solvents, including supercritical fluids [2] and, more recently, bio-based diluents [3] and ionic liquids (ILs) [4–6]. Work in this laboratory has concerned the application of the latter solvents, particularly those that are liquid at room temperature (RTILs), in the extraction of metal ions from the highly acidic aqueous phases encountered in such applications as nuclear fuel reprocessing [7] or analytical-scale radionuclide separation and preconcentration for subsequent determination [8]. In the course of these studies, it has become apparent that the process by which a metal ion is extracted into an ionic liquid can be significantly more complex than that observed with conventional (*i.e.*, molecular) organic solvents [9–12]. This is particularly true, it has been found, when neutral extractants are employed. Prior work indicates that in systems employing a crown ether as the extractant, for example, partitioning can follow any one or more of three distinct pathways: extraction of a neutral complex, in which the metal ion-crown ether complex initially formed is paired with an aqueous phase anion to yield a neutral species, which then partitions into the IL phase; formation of a cationic metal-crown ether complex, followed by its exchange for the cationic component of the IL; and formation of an acid-crown ether complex, followed by exchange of an aqueous phase metal ion for the complexed proton (or hydronium ion) [9–11]. Despite progress in elucidating the factors governing the balance among these pathways, these factors remain incompletely understood.

It is now well known that certain characteristics of an ionic liquid strongly influence the mode of metal ion partitioning into it. For example, the use of ILs incorporating a hydrophobic cation has been shown to favor the extraction of neutral complexes, while more hydrophilic cations favor ion-exchange processes [10]. Other recent results suggest that the nature of the IL anion is similarly influential in determining the preferred mode of extraction [13]. To date, the effect of aqueous phase composition on the “balance of pathways” has received scant attention, despite its obvious importance. That is, because of their utility in a wide variety of metal ion separations involving extraction into conventional organic solvents, nearly all studies of metal ion extraction into ILs have employed acidic nitrate-containing aqueous phases. Chloride-containing aqueous phases, however, are also of significance in numerous conventional metal ion extraction systems. For example, a chloride-based analog of the well-known TRUEX Process for nuclear waste treatment has been described [14]. Along these

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same lines, chloride-containing aqueous phases provide the basis of several analytical-scale actinide separation schemes employing extraction chromatography [15], a form of LLE in which the extractant solution is coated into an inert polymeric support [16]. For this reason, we have undertaken a systematic examination of the effect of aqueous phase anion on the partitioning of several alkali and alkaline earth cations into various 1,3-dialkylimidazolium-based ILs in the presence of a dicyclohexano-18-crown-6 (DCH18C6). The results obtained, in addition to providing new insights into the fundamental aspects of the behavior of neutral extractants in ionic liquids, may be of practical value in efforts to design improved metal ion separations employing these unique solvents.

2. Materials and methods

2.1. Materials

The ionic liquids employed (1-pentyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide and its 1-octyl- and 1-decyl-analogs, hereafter abbreviated as $C_n mim^+ Tf_2N^-$, where n = 5, 8, or 10) were prepared *via* either conventional or microwave synthesis, purified, and characterized according to published methods [17,18]. For partitioning studies, the DCH18C6 used was a commercial mixture of *cis-syn-cis* (A) and *cis-anti-cis* (B) isomers (Parish Chemical Company, Orem, UT). Aqueous acid solutions were prepared using Milli-Q2 water and Optima^{TM} nitric or hydrochloric acid (Aldrich, Milwaukee, WI) and standardized using certified sodium hydroxide solutions (Ricca, Arlington, TX) using phenolphthalein indicator (Ricca, Arlington, TX).

2.2. Methods

All strontium, barium, and sodium distributions were determined radiometrically using commercial Sr-85, Ba-133 and Na-22 radiotracers, respectively (Isotope Products Laboratories, Burbank, CA), assayed *via* gamma spectroscopy (Perkin Elmer 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.

3. Results and discussion

To understand the behavior of extraction systems comprising a chloride-based aqueous phase in contact with an ionic liquid containing a metal ion extractant, it is helpful to begin by considering analogous systems employing conventional (*i.e.*, molecular) organic solvents. For this reason, our efforts to understand the partitioning of alkali and alkaline earth cations between acidic chloride media and various $C_n mim^+ Tf_2N^-$ ionic liquids in the presence of dicyclohexano-18-crown-6 (DCH18C6) began with an examination of their extraction into a series of aliphatic alcohols under the same conditions. In such solvents, the extraction of a metal cation by a neutral extractant such as a crown ether requires co-extraction of aqueous phase anions to maintain electrical neutrality. Thus, extraction in these systems involves partitioning of a neutral complex, as shown here [19]:

$$M^{n+} + nX^- + E_{org} \rightarrow MX_n \cdot E_{org} \quad (1)$$

where M^{n+} designates a metal ion of charge *n*, X^- is a co-extracted anion, and E represents the extractant, here a crown ether such as DCH18C6. Accordingly, as shown in Fig. 1, which depicts the hydrochloric acid dependency of the distribution ratio, D_M (defined as $[M_{org}]/[M_{aq}]$ at equilibrium), obtained in the extraction of three representative alkali and alkaline earth cations (Sr^{2+}, Ba^{2+}, and Na^+) by DCH18C6 in 1-pentanol, 1-hexanol, 1-octanol, and 1-decanol, increasing chloride (*i.e.*, hydrochloric acid) concentration is generally accompanied by an increase in the extraction efficiency (as reflected in the rising value of D_M). Comparison of these results to those obtained in nitric acid (Fig. 2) shows that the same general trends are observed. That is, D_M values for Sr^{2+} and Ba^{2+} typically exceed those of Na^+, consistent with the larger metal ion-DCH18C6 formation constants for the former ions [20]. In addition, all else being equal, the values of D_M decrease as the hydrophobicity of the alcohol rises, a result of the decrease in organic phase water content that accompanies increasing alkyl chain length and the importance of this water content in facilitating anion co-extraction [19,21]. As would be expected from its higher hydration energy and the

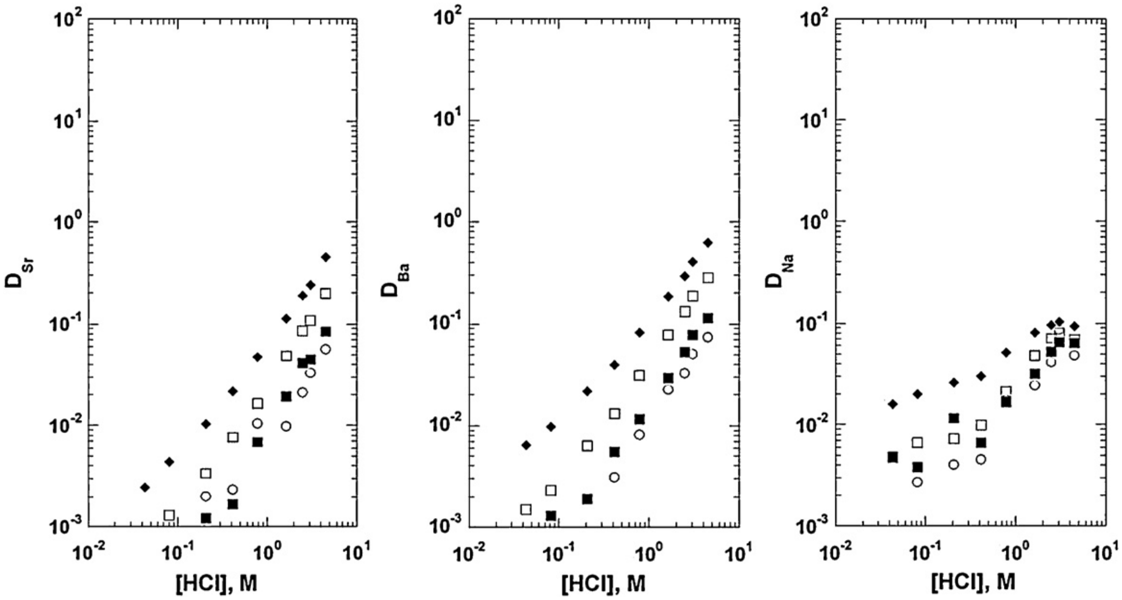

Fig. 1. Effect of hydrochloric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in *n*-alcohol (♦ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

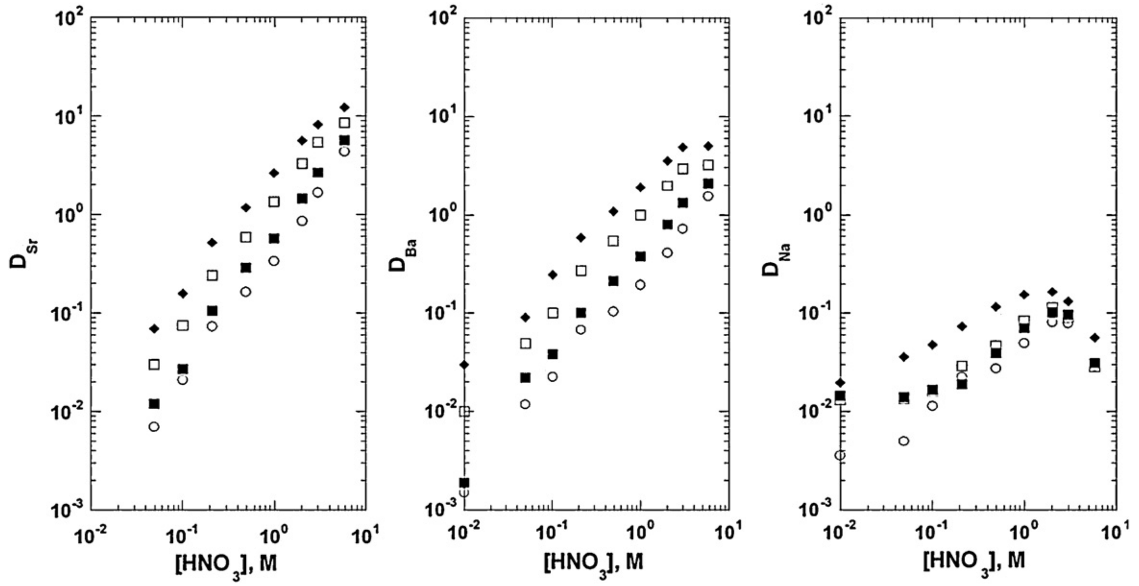

Fig. 2. Effect of nitric acid concentration on the extraction of Sr^{2+} (left panel), Ba (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in *n*-alcohol (♦ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).
Adapted from Ref. [24].

accompanying greater difficulty in dehydrating the co-extracted anion [19], however, the values of D_M tend to be lower under a given set of conditions for chloride-containing aqueous phases than for the corresponding nitrate-based systems.

The dependency of the extraction of the three cations from acidic chloride media upon the crown ether concentration (Fig. 3) is also consistent with the partitioning of a neutral complex. That is, for Na^+, a log–log plot of D_M *versus* [DCH18C6] yields a line of near-unit slope (0.9), as expected from Eq. (1). In contrast, for the divalent cations, the extractant dependency is nearly flat over the range of concentrations examined. Prior work considering the extraction of potassium and strontium ions from acidic nitrate media into 1-octanol [22] found much the same results, which were attributed to differences in the propensity of monovalent and divalent ions to form an aqueous phase complex with DCH18C6. (The greater tendency to do so for Sr^{2+} was accompanied by a much more pronounced curvature in its extractant dependency. In fact, this dependency was found to be essentially flat at all but very low extractant concentrations.) For ease of comparison, these previous results for Sr^{2+} have been reproduced in Fig. 4, along with data for Na^+ and Ba^{2+}, also for an acidic nitrate-containing aqueous phase. The higher values of D_M for a given cation under a particular set of conditions for the nitrate-containing aqueous phases are, again, consistent with the greater ease of hydration of this anion and the accompanying ease of its co-extraction [19]. Taken together, the results presented for aliphatic alcohols show that regardless of conditions, alkali and alkaline earth cation partitioning from acidic chloride media into these solvents in the presence of DCH18C6 involves extraction of a neutral metal-chloro-crown ether complex, in analogy to extraction of

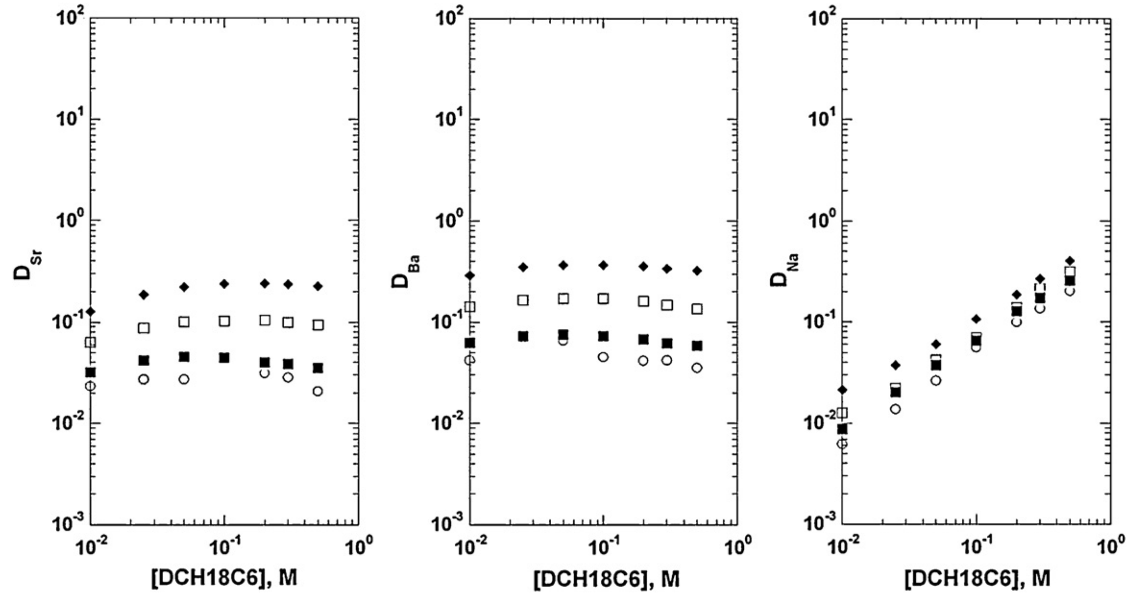

Fig. 3. Effect of crown ether concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by HCl (3.070 M for Sr^{2+} and Ba^{2+} and 3.286 M for Na+) in *n*-alcohol (♦ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

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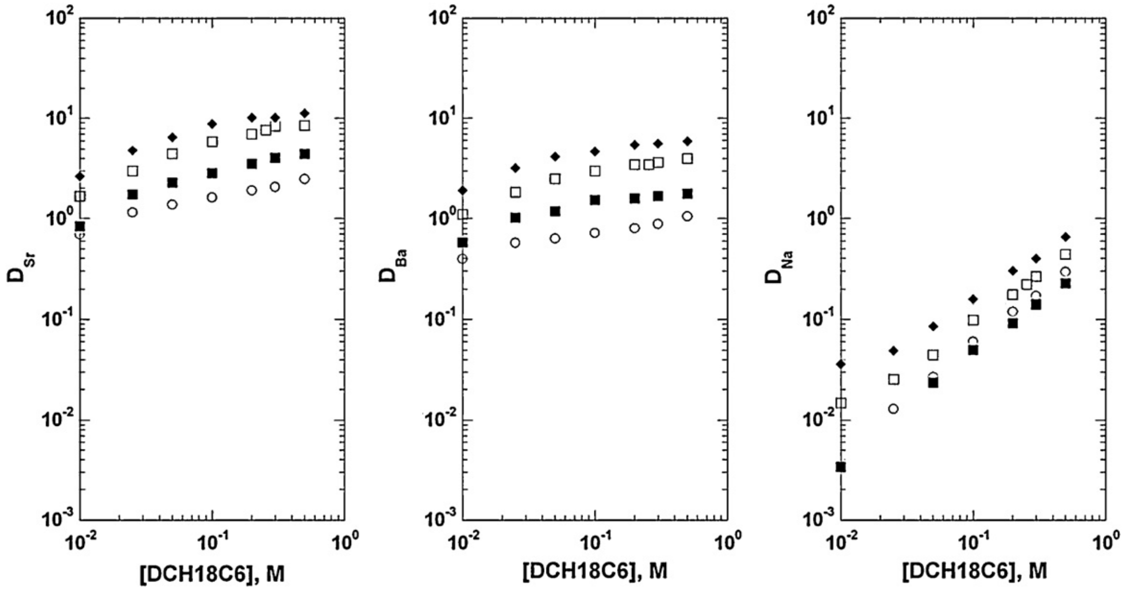

Fig. 4. Effect of crown ether concentration on the extraction of Sr^{2+} (left panel), Ba (middle panel) and Na^+ (right panel) by HNO_3 (3.000 M for Sr^{2+}, 3.008 M for Ba^{2+} and 3.000 M for Na+) in *n*-alcohol (♦ = 1-pentanol, ☐ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

a neutral metal nitrato-crown ether complex from acidic nitrate media.

It is immediately apparent that this is not the case for the ionic liquids upon examination of the hydrochloric acid dependency of D_M for the same three metal ions for extraction into $C_5mim^+Tf_2N^-$, $C_8mim^+Tf_2N^-$, and $C_{10}mim^+Tf_2N^-$ (Fig. 5). As can be seen (left panel), the extraction of strontium exhibits a significant decline as the acidity rises until *ca.* 2 M HCl, above which an increase is observed. As noted previously [9], a decline in D_{Sr} with aqueous acidity (*i.e.*, increasing aqueous phase anion concentration) is inconsistent with the partitioning of a neutral metal complex. Rather, on the basis of prior results in the extraction of strontium and sodium ion from acidic nitrate media by the same crown ether into these ILs, the decline can be attributed to a combination of two ion-exchange processes. That is, at low acidity, the cationic strontium-crown ether complex, $Sr{\cdot}DCH18C6^{2+}$, is exchanged for the cationic constituent of the ionic liquid, C_nmim^+, according to the following equation [9,10]:

$$\mathrm{Sr}\cdot(\mathrm{DCH18C6})^{2+} + 2\mathrm{C}_n\mathrm{mim_{org}}^{+} \rightarrow \mathrm{Sr(DCH18C6)_{org}}^{2+} + 2\mathrm{C}_n\mathrm{mim}^{+} \qquad (2)$$

That D_{Sr} falls at a given acidity as the IL cation chain length is raised from $n = 5$ to $n = 8$ to $n = 10$ is consistent with the greater difficulty expected in transferring the increasingly hydrophobic IL cation to the aqueous phase. As the hydrochloric acid concentration is increased, a second ion-exchange process, in which the strontium ion is exchanged for hydronium ions complexed by the crown ether, apparently becomes increasingly prominent, in analogy to results described previously for the extraction of Na^+ into these

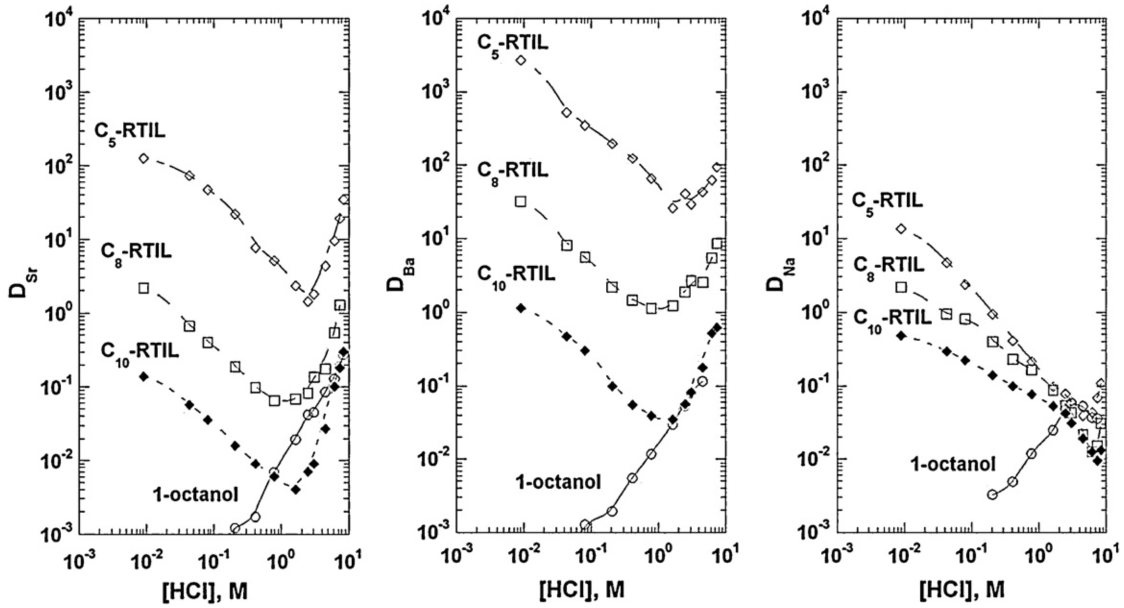

Fig. 5. Effect of hydrochloric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in C_nmimTf_2N (C_n-RTIL). Data for 1-octanol are provided for purposes of comparison.

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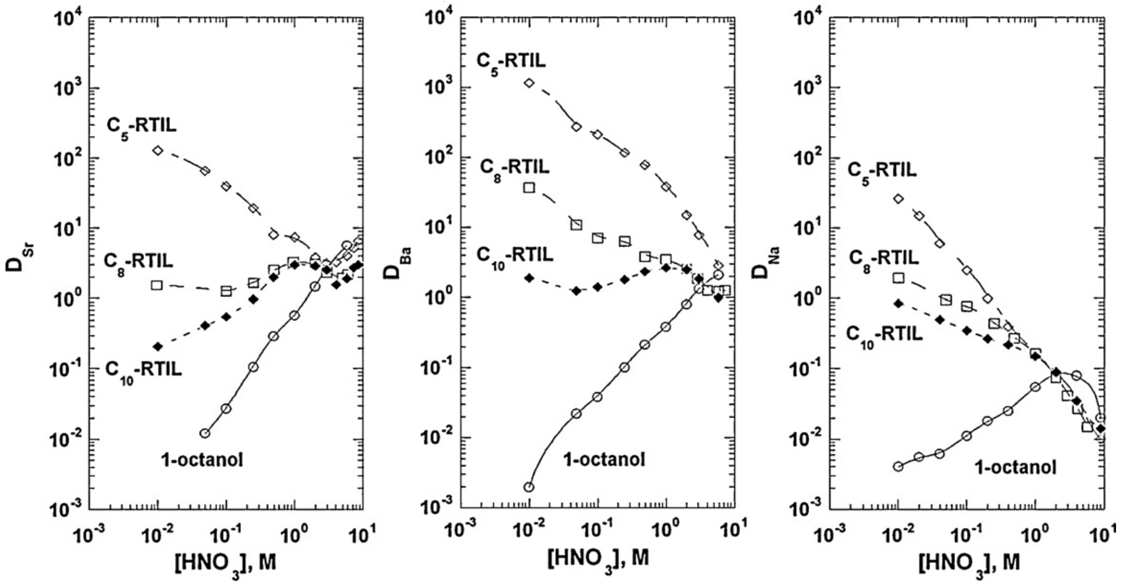

Fig. 6. Effect of nitric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in CnmimTf$_2$N (C$_n$-RTIL). Data for 1-octanol are provided for purposes of comparison.
Adapted from Ref. [24].

same solvents, again by DCH18C6, into nitric acid [11]:

$$Sr^{2+} + 2H_3O \cdot DCH18C6_{org}{}^{+} \rightarrow Sr \cdot DCH18C6_{org}{}^{2+} + 2H_3O^+ + DCH18C6_{org} \quad (3)$$

At still higher acidities (*i.e.*, ≥2 M HCl), the acid dependency of D_{Sr} is seen to turn upward, suggesting that eventually the amount of chloride ion present is sufficient to favor extraction of the neutral complex. A comparison of these dependencies to those seen under essentially the same conditions but employing nitric acid solutions as the aqueous phase (Fig. 6, left panel) indicates that the aqueous phase cation has a pronounced effect on the nature of the observed dependencies. Perhaps most striking is the fact that in contrast to the results obtained in nitric acid, for HCl, an increase in the hydrophobicity (*i.e.*, alkyl chain length) of the imidazolium cation does not result in a systematic shift in the predominant mode of strontium ion partitioning (from ion-exchange to neutral complex extraction). This is especially significant given prior reports that ILs can be rendered "greener" as extraction solvents simply by increasing the IL cation hydrophobicity sufficiently to suppress cation exchange (Eq. (2)) [10]. Also noteworthy is that at sufficiently high aqueous phase anion concentrations, both the HCl and HNO_3 dependencies show an increase in D_{Sr}, regardless of the IL cation, consistent with extraction of a neutral complex. That this up trend generally begins at lower aqueous acidity (*i.e.*, anion concentration) for nitric acid suggests that, as is the case for conventional organic solvents, the hydration energy of the co-extracted anion (*i.e.*, the relative ease of dehydration) is an important factor in governing metal ion partitioning behavior in IL-based extraction systems.

In an effort to confirm this, the acid dependency of D_{Sr} was determined for two additional acids, HI and HBr, whose anions are more readily dehydrated than chloride [23], which in extraction systems employing conventional solvents, leads to higher extraction efficiency. As shown in Fig. 7, for extraction by 0.1 M DCH18C6 in $C_{10}mim^+Tf_2N^-$, at any given acidity, D_{Sr} (HI) > D_{Sr} (HBr) > D_{Sr} (HCl). Just as important is that for all three acids, increasing the aqueous acidity (hence, the aqueous anion concentration) eventually leads to replacement of ion-exchange with neutral complex extraction as the dominant mode of strontium ion partitioning. The concentration at which this change becomes evident varies with the acid, however, being lowest for HI (0.8 M), higher for HBr (1.0 M), and higher still for HCl (1.6 M). These trends can be explained by considering the hydration enthalpies of the aqueous anions. That is, the higher the hydration enthalpy (*i.e.*, the more difficult is anion dehydration), the higher the concentration at which ion exchange is no longer the dominant mode of partitioning.

Measurements of the hydrochloric acid dependencies of barium ion extraction into the $C_nmim^+Tf_2N^-$ ILs in the presence of DCH18C6 (Fig. 5, middle panel) yield results consistent with

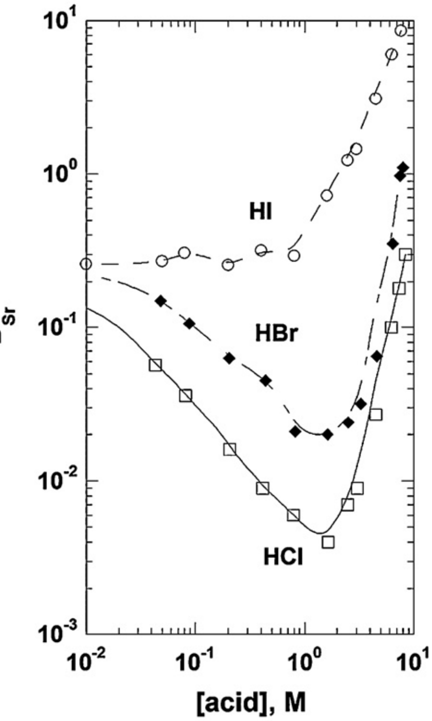

Fig. 7. Effect of acid (hydroiodic, hydrobromic, and hydrochloric) concentration on the extraction of Sr^{2+} by DCH18C6 (0.10 M) in C_{10}mimTf$_2$N.

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those obtained for strontium. Specifically, D_{Ba} is seen to fall with increasing acidity until *ca.* 2 M HCl, at which point an upturn in extraction is observed, again suggesting a shifting balance between ion exchange and neutral complex extraction with changing aqueous acidity (*i.e.*, aqueous anion concentration).

Also shown in Fig. 5 (right panel) is the hydrochloric acid dependency of sodium ion extraction into the same series of ILs. As can be seen, in each instance, a significant decline in sodium partitioning (*i.e.*, the distribution ratio) occurs as the acidity increases. In contrast to strontium and barium ion extraction, for which a shift to neutral complex extraction is seen by *ca.* 2 M HCl, an upturn in sodium partitioning is barely discernible, even at 7 M HCl. This observation is consistent with the lower charge density of the monovalent sodium cation *vis-à-vis* Sr^{2+} and Ba^{2+} and the accompanying diminished electrostatic attraction between the cation and chloride ion, whose co-extraction is a necessary part of neutral complex extraction. Consistent with prior reports for nitrate [24], the D_{Na} values for the three ILs observed at low acidity vary considerably, falling as the IL cation hydrophobicity rises. That this difference diminishes with rising aqueous acidity is also consistent with prior reports for acidic nitrate media [11] suggesting a gradual shift from ion exchange involving the IL cation to a reaction of the type depicted in Eq. (4), which involves exchange of Na^+ for hydronium ion extracted by the crown ether:

$$Na^+ + H_3O \cdot DCH18C6_{org}{}^+ \rightarrow Na \cdot DCH18C6_{org}{}^+ + H_3O^+ \tag{4}$$

Not unexpectedly, the distribution ratios for sodium are considerably lower than those observed for strontium and barium under a given set of conditions.

4. Conclusions

The results of this study clearly demonstrate that the extraction of alkali and alkaline earth cations from acid chloride media into 1,3-dialkylimidazolium ionic liquids by a crown ether differs markedly from their extraction into conventional molecular solvents under the same conditions. While the latter simply involves the partitioning of a neutral metal-chloro-crown ether complex, extraction into the ILs is seen to involve a complicated combination of three distinct modes of partitioning, their relative contribution determined by the hydrophobicity of the IL cation, the aqueous phase acid and anion concentrations, and the nature of the metal ion (*i.e.*, charge density). In this respect, extraction from hydrochloric acid is thus similar to the extraction of the same ions from nitric acid. As we have shown, however, there are distinct differences between the two systems. Most notable is the greater propensity toward ion exchange in the chloride-based system, which is the apparent result of the greater hydration enthalpy of the chloride ion and the accompanying diminished anion co-extraction. In that ion exchange inevitably results in the loss of ionic liquid to the aqueous phase [9–12], this greater propensity has significant practical implications for the application of these solvents in “real-world” extraction processes.

Looked at more broadly, the results obtained here represent yet another step toward the full elucidation of the factors governing the “balance of pathways” observed in the extraction of metal ions into ionic liquids. In particular, these results make apparent that anion hydration plays a significant role in determining this balance. In addition, when considered in conjunction with prior studies of extraction from nitric acid solution [9–11,24], they strongly suggest that ion exchange involving the IL cation represents a “default” pathway for partitioning in these systems. When sufficient acid is present, this process may be supplanted by a second ion-exchange process involving the replacement of a hydronium ion in the protonated extractant with the metal ion or (if the energetics of anion co-extraction are favorable) by partitioning of a neutral complex. It remains to be seen if, as we expect, this model represents an all-encompassing description of metal ion extraction into ILs by neutral extractants. Work addressing this issue is now underway in this laboratory.

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