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Talanta 69 (2006) 527–531

Talanta

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Short communication

Fluorous ionic liquids as solvents for the liquid–liquid extraction of metal ions by macrocyclic polyethers

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Received 4 May 2005; received in revised form 6 September 2005; accepted 6 September 2005
Available online 28 November 2005

Abstract

The predominant mode of strontium ion transfer from aqueous nitrate media into a series of 1-fluoroalkyl-3-methylimidazolium *bis*[(trifluoromethylsulfonyl)]imides containing dicyclohexano-18-crown-6 (DCH18C6) is shown to shift from cation exchange to strontium nitrato-crown ether complex partitioning as the length of the fluoroalkyl substituent is increased. Fluoroalkyl substituents are shown to be only slightly more effective than their non-fluorous analogs at inducing this shift. At the same time, the fluorinated ionic liquids (ILs) yield strontium distribution ratios as much as an order of magnitude lower than the corresponding 1-alkyl-3-methylimidazolium ($C_n$mim$^+$) salts. Fluorous ILs thus appear to offer no compelling advantages over $C_n$mim$^+$ ionic liquids as extraction solvents.

Keywords: Ionic liquids; Strontium extraction; Crown ethers

1. Introduction

Ionic liquids (ILs) have recently attracted intense interest as possible "environmentally benign" alternatives to conventional organic solvents in a wide range of synthetic [1–4], catalytic [5–7], and electrochemical [8,9] applications. This interest has been prompted both by their unique and useful properties (e.g., negligible vapor pressure and wide electrochemical window) and by the relative ease with which these properties can be tailored by varying the anionic or cationic constituents of the ionic liquid [5,6,10]. To date, investigations of ionic liquids have frequently focused on systems employing *N*-alkylpyridinium or 1-alkyl-3-methylimidazolium cations (Fig. 1), in conjunction with any of a number of organic (e.g., triflate) or inorganic (e.g., thiocyanate) anions. Of particular interest and utility have been various fluorinated anions (e.g., *bis*[(trifluoromethylsulfonyl)]imide), whose weak basicity and poor hydrogen-bonding ability typically afford ionic liquids exhibiting a number of favorable properties, including comparatively low viscosity and good thermal stability [11]. In contrast, little attention has been directed at the properties and applications of ionic liquids comprising fluorinated cations ("fluorous" ionic liquids) (Fig. 1). In fact, despite the now voluminous literature on ionic liquids, only a handful of studies describing such compounds [12–16] have appeared since the initial report by Davis et al. [17] of an IL pairing a fluoroalkyl-functionalized miconazole with hexafluorophosphate anion.

Recent research in this laboratory has concerned the utility of ionic liquids in chemical separations, in particular, their suitability as replacements for the volatile organic solvents frequently employed as diluents in the liquid–liquid extraction of metal ions [18–22]. Reports by several investigators suggest that ionic liquids offer great promise in such an application. Dai et al. [23], for example, observed extraction coefficients far greater than those obtained with any conventional organic solvent for the extraction of Sr^{2+} from water into solutions of dicyclohexano-18-crown-6 (DCH18C6) in any of several imidazolium-based ILs. Similarly, subsequent work by Visser and Rogers [24] showed that the extraction of Pu^{4+}, Th^{4+} or UO_2^{2+} into 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]PF_6) by a mixture of octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and

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doi:10.1016/j.talanta.2005.09.046

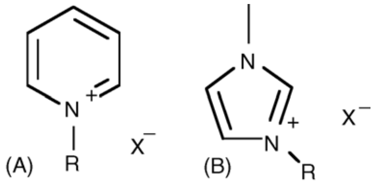

Fig. 1. Structures of *N*-alkylpyridinium (A), 1-alkyl-3-methylimidazolium (B, with R = CH_3–$(CH_2)_n$–), and 1-fluoroalkyl-3-methylimidazolium (B, with R = CF_3–$(CF_2)_n$–$(CH_2)_2$–) ionic liquids.

tri-*n*-butyl phosphate (TBP) is at least an order of magnitude higher than that obtained for the same extractant concentrations in dodecane. In addition, distribution ratios for Am^{3+}, which is weakly extracted from, for example, 1 M HNO_3 by the CMPO/TBP/dodecane system, were found to be at least two orders of magnitude higher when $[C_4mim]PF_6$ was substituted for dodecane.

Unfortunately, work in this and other laboratories has shown that 1-alkyl-3-methylimidazolium salts exhibit certain characteristics that could adversely impact their utility as solvents in metal ion separations. For example, as has been noted previously, the determination of various metal ions in many "real-world" biological and environmental samples frequently requires their preliminary separation and/or preconcentration from solutions containing high concentrations of nitric acid [25]. The use of dialkylimidazolium-based ionic liquids, however, appears limited to systems in which the aqueous phase nitric acid concentration is relatively low ($\leq$1 M), a result of increased solubilization of the IL and the concomitant degradation of the biphasic system upon repeated contact of the IL with highly acidic solutions [18,26,27]. In addition, a precipitous decline in the efficiency of metal ion extraction into these ILs with increasing aqueous acidity is often observed [18,21,26]. Such a decline clearly poses a problem if extraction (or sorption) of a metal ion from acidic solution and its recovery in water or dilute acid is required. These drawbacks represent significant obstacles to the development of viable metal ion separation processes based on these ionic liquids and underscore the need to investigate the suitability of other IL families as extraction solvents. Studies of metal ion extraction into a range of ionic liquids are important from a fundamental perspective as well. That is, the rational design of ionic liquid-based separation systems for metal ions would be greatly facilitated by an improved understanding of the fundamental aspects of ion transfer into these solvents, an understanding which can only be obtained by systematic study of a number of types of ionic liquids. With these considerations in mind, we have undertaken a preliminary evaluation of imidazolium-based ionic liquids bearing fluoroalkyl substituents (i.e., fluorous ILs) as diluents in the extraction of strontium by DCH18C6. Our choice of this system was prompted both by the ongoing interest in the extraction of alkali and alkaline earth cations into ionic liquids by various macrocycles [18,22,23,27,28–30] and by the absence of published information concerning the behavior of fluorous ILs as extraction solvents.

2. Experimental

2.1. Materials

The 1-alkyl-3-methylimidazolium ionic liquids were prepared and purified according to published methods [31]. The fluorous ILs were prepared via a minor modification of a previously published procedure [12]. Typically, an appropriate fluorinated alkyl iodide (1,1,1,2,2,3,3-heptafluoro-5-iodopentane (9.5 g); 1H, 1H,2H,2H-perfluorooctyl iodide (4.3 g); or 1H,1H,2H,2H-perfluorodecyl iodide (17.5 g) Oakwood Products, Inc., West Columbia, SC) was refluxed at 80 °C under nitrogen (to inhibit oxidation of iodide) with a 10% molar excess of 1-methylimidazole (redistilled, >99%, Aldrich, Milwaukee, WI) in toluene for 1–3 days. (In each case, traces of dark, brown oil became evident at the bottom of the flask soon after the start of the reaction.) After cooling, the solvent remaining was removed by decantation and vacuum drying at 50 °C. Fresh toluene was added and the process of refluxing (30 min) and solvent removal in vacuo repeated three additional times to yield the $[F\text{-}C_nmim]I$ salt as either a viscous, brown liquid ($[F\text{-}C_5mim]I$ and $[F\text{-}C_8mim]I$) or cream-colored crystals ($[F\text{-}C_{10}mim]I$). Conversion of the iodide salts to the corresponding *bis*[(trifluoromethylsulfonyl)imides] was accomplished by combining under nitrogen a solution of the salt (typically ca. 7.3 g) in a minimum volume of acetone with an equal number of moles of *N*-lithiotrifluoromethanesulfonimide ($LiNTf_2$; 97%, Aldrich) in deionized water (20 mL). After 24 h of stirring, the second (denser) layer (which had begun to form immediately upon mixing) was isolated, dissolved in methylene chloride, washed four times with an equal volume (20 mL) of deionized water, and finally, following removal of the bulk of the solvent by rotary evaporation, dried in a vacuum oven overnight at 50 °C. The purity of all products was established by ^1H NMR spectroscopy, elemental analysis, and FAB-mass spectrometry. $[F\text{-}C_5mim]NTf_2$: ^1H NMR: 3.05 (2H, m), 4.06 (3H, s), 4.80 (2H, t, $J = 7.2$ Hz), 7.72 (1H, t, $J = 1.8$ Hz), 7.89 (1H, t, $J = 1.8$ Hz), 9.14 (1H, s). HR-FAB, positive: 279.0720. Elemental analysis found: C, 23.49; H, 1.81. Calcd. for $C_{11}H_{10}O_4F_{13}N_3S_2$: C, 23.62; H, 1.80. $[F\text{-}C_8mim]NTf_2$: ^1H NMR: 3.09 (2H, m), 4.06 (3H, s), 4.82 (2H, t, $J = 7.2$ Hz), 7.74 (1H, t, $J = 1.8$ Hz), 7.91 (1H, t, $J = 1.8$ Hz), 9.17 (1H, s). HR-FAB, positive: 429.0639. Elemental analysis found: C, 23.77; H, 1.49. Calcd. for $C_{14}H_{10}O_4F_{19}N_3S_2$: C, 23.71; H, 1.42. $[F\text{-}C_{10}mim]NTf_2$: ^1H NMR: 3.10 (2H, m), 4.07 (3H, s), 4.82 (2H, t, $J = 7.2$ Hz), 7.74 (1H, t, $J = 1.8$ Hz), 7.91 (1H, t, $J = 1.8$ Hz), 9.16 (1H, s). HR-FAB, positive: 529.0573. Elemental analysis found: C, 23.76; H, 1.23. Calcd. for $C_{16}H_{10}O_4F_{23}N_3S_2$: C, 23.74; H, 1.25.

Unless otherwise noted, for partitioning studies, the DCH18C6 (Aldrich, Milwaukee, WI) was a mixture of the *cis-syn-cis* and *cis-anti-cis* isomers, consistent with prior work [18,23]. Aqueous acid solutions were prepared from Milli-Q2 water and Ultrex nitric acid (J.T. Baker Chemical Co.).

2.2. Methods

All strontium distribution ratios were determined radiometrically using a commercial Sr-85 radiotracer (Isotope Products Laboratories, Burbank, CA), assayed by gamma spectroscopy using standard procedures. Preconditioning of the organic phases prior to distribution ratio determinations was accomplished via a single contact with twice the volume of water or an appropriate nitric acid solution. All measurements were carried out at room temperature (23 ± 2 °C). (Note that [F-C_{10}mim]NTf_2 slowly solidifies upon standing. Measurements were therefore made following gentle warming of the material to ca. 30 °C and a brief period of standing at room temperature.)

The water solubility of the ionic liquids was determined by ^{1}H NMR. Specifically, a 0.1 M solution of DCH18C6 in the ionic liquid of interest (0.25 mL) was equilibrated for 1–2 h with 2 mL of deionized water. A measured aliquot of the aqueous phase was then removed and evaporated to dryness. The remaining residue was dissolved in chloroform and the concentration of the imidazolium cation present determined by ^{1}H NMR using toluene-d_8 as an internal standard.

3. Results and discussion

In earlier reports, we demonstrated that in contrast to its extraction into conventional (i.e., molecular) solvents, the extraction of strontium ion from aqueous nitrate media by DCH18C6 into various "short-chain" 1-alkyl-3-methylimidazolium bis[(trifluoromethylsulfonyl)]imides ([$C_n$mim]NTf_2, with $n < \sim 8$) does not involve co-extraction of a nitrate ion [18–21]. Rather, an ion-exchange process in which strontium is exchanged for the cationic component of the ionic liquid is found to occur. In practical terms, this difference manifests itself as a difference in the shape of the nitric acid dependency of the strontium distribution ratio, D_{Sr} (defined as $[Sr]_{total, org}/[Sr]_{total, aq}$ at equilibrium). Specifically, strontium partitioning into molecular solvents (e.g., 1-octanol) increases with rising aqueous nitric acid (and therefore, nitrate) concentration, as expected for extraction of a strontium nitrato-crown ether complex. Increasing acidity is accompanied by a significant *decrease* in strontium extraction into the ILs (e.g., [C_2mim]NTf_2 [18] or [C_5mim]NTf_2 [21]), however, a result clearly inconsistent with nitrato complex extraction. Given that a number of procedures for the determination of various metal ions (e.g., radiostrontium) in environmental and biological samples involve a preliminary digestion or leaching of the sample with nitric acid (thereby yielding a highly acidic sample solution) [25], this decrease in D_{Sr} would obviously complicate the application of these ILs in the analytical-scale separation and preconcentration of strontium (and other metal ions whose extraction exhibits the same dependency on aqueous acidity).

Increasing the hydrophobicity of the IL cation to inhibit ion exchange (thus altering the slope of the acid dependency) represents an obvious means of addressing this problem, and in fact, prior studies of the extraction of $Sr(NO_3)_2$ from water into [$C_n$mim]NTf_2 ILs in the presence of DCH18C6 have shown that increasing the length of the alkyl group (from $n = 5$ to 8 and finally, to $n = 10$) leads to a gradual shift in the mechanism of partitioning from ion exchange to nitrato complex partitioning [21]. As a result, the acid dependency of D_{Sr} for [C_{10}mim]NTf_2 exhibits an *increase* in strontium partitioning with rising acidity. This change in the slope of the acid dependency, however, is accompanied by an often-substantial decrease in the value of D_{Sr} at a given acidity versus that observed for [C_5mim]NTf_2. The magnitude of this decrease, in fact, is such that the [C_{10}mim]NTf_2 IL offers no appreciable advantage over many conventional molecular solvents in terms of extraction efficiency from strongly acidic media [32].

Table 1
Strontium[a] and nitrate[b] ion partitioning between water[c] and solutions of DCH18C6[d] in [$C_n$mim]NTf_2[e] or fluorous ionic liquids

Organic phase	$\%E_{Sr}$	$\%E_{NO_3^-}$		Predominant partitioning mode
		Observed	Expected[f]	
[C_5mim]NTf_2	96.5	9	96.5	Cation exchange
[C_8mim]NTf_2	39.0	20.9	39.0	Mixed
[C_{10}mim]NTf_2	20.2	20.0	20.2	Neutral complex extraction
[F-C_5mim]NTf_2	97.4	1.6	97.4	Cation exchange
[F-C_8mim]NTf_2	6.9	5.5	6.9	Neutral complex extraction
[F-C_{10}mim]NTf_2	0.5	1.0	0.5	Neutral complex extraction

[a] Determined radiometrically.

[b] Determined by ion chromatography.

[c] Containing 0.0310 or 0.0155 M $Sr(NO_3)_2$ for [$C_n$mim]NTf_2 and [F-$C_n$mim]NTf_2, respectively.

[d] 0.202 or 0.100 M *cis-syn-cis*-DCH18C6 in the [$C_n$mim]NTf_2 and [F-$C_n$mim]NTf_2 ionic liquids, respectively.

[e] Results from reference 21.

[f] Assuming extraction of the neutral strontium nitrato-crown ether complex. For partitioning *via* cation exchange, no nitrate co-extraction ($\%E_{NO_3^-} = 0$) is expected.

Incorporation of fluorine atoms into the IL cation has been proposed [26] (but not demonstrated) as an alternative approach to increasing the hydrophobicity of the IL cation and thus, diminishing the prevalence of ion exchange. Consideration of the influence of fluorine substitution in these ionic liquids on their water solubility (i.e., $[\text{F-C}_n\text{mim}^+]_{aq, equil} = 1.3 \times 10^{-3}, 2 \times 10^{-4}$ and $\leq 9 \times 10^{-5}$ M (the estimated limit of detection for our solubility measurements) versus $[\text{C}_n\text{mim}^+]_{aq, equil} = 8.8 \times 10^{-3}$, 1.6×10^{-3} and 3×10^{-4} M, for $n = 5$, 8, and 10, respectively), in fact, suggests that such substitution should be effective in this regard. Table 1 summarizes the results of measurements of the partitioning of strontium and nitrate ions between a series of [F-$C_n$mim]NTf_2 ionic liquids and water in the presence of DCH18C6. Also shown, for purposes of comparison, are the results of identical measurements (detailed previously [21]) for the corresponding non-fluorinated ILs. As can be seen, for [F-C_5mim]NTf_2, the amount of nitrate extracted is clearly insufficient to yield a neutral strontium nitrato-crown ether complex, just as is the case for its non-fluorinated analog.

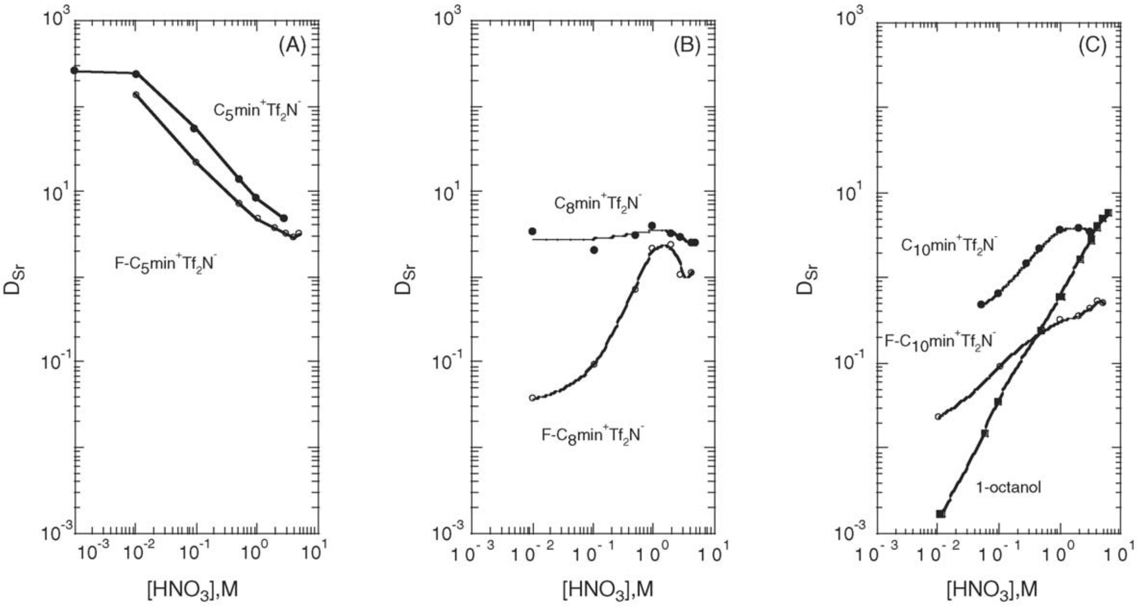

Fig. 2. Nitric acid dependency of D_{Sr} for extraction by DCH18C6 (0.1 M) into (A) [F-C_5mim]NTf$_2$ and [C_5mim]NTf$_2$; (B) [F-C_8mim]NTf$_2$ and [C_8mim]NTf$_2$; (C) [F-C_{10}mim]NTf$_2$, [C_{10}mim]NTf$_2$, and 1-octanol.

For [F-C_8mim]NTf$_2$, however, the amount of extracted nitrate corresponds to nearly 80% of that required to afford the neutral complex, indicating that the strontium partitioning proceeds via a combination of ion exchange and neutral complex formation, with the latter predominating. Although this "mixed" partitioning is also observed for [C_8mim]NTf$_2$, for this IL, neither mode can be described as predominant, thus suggesting that fluoroalkyl substituents are somewhat more effective than their alkyl counterparts at inducing a change in the mode of partitioning. For [F-C_{10}mim]NTf$_2$, as for its non-fluorinated analog, the amount of nitrate extracted closely corresponds to that expected if strontium partitioning occurs solely via extraction of the neutral complex. Taken together, these results indicate that as is the case for alkyl substituents [21], increasing the length of a fluoroalkyl substituent on an imidazolium cation leads to a shift in the predominant mode of strontium partitioning into the ILs from ion exchange to neutral complex extraction.

Additional evidence for such a shift is presented in Fig. 2 (panels A–C), which depicts the dependency of D_{Sr} on nitric acid concentration for solutions of DCH18C6 in the various ionic liquids. As can be seen, the dependency for [F-C_{10}mim]NTf$_2$ is characterized by increasing strontium partitioning with rising acidity, consistent with partitioning of a neutral strontium nitrato-crown ether complex. A similar dependency is observed for the [F-C_8mim]NTf$_2$, again consistent with an extraction mechanism in which neutral complex partitioning predominates. In contrast, the dependency for [F-C_5mim]NTf$_2$, like that of the corresponding non-fluorinated IL, exhibits a decrease in strontium extraction with acidity.

Several aspects of these results are noteworthy. First, the replacement of three methylene groups with –CF$_2$– units in the *n*-pentyl side chain of [C_5mim]NTf$_2$ to yield [F-C_5mim]NTf$_2$ results in an increase in molecular weight greater than that obtained by changing the *n*-pentyl side chain to an *n*-decyl group. Nonetheless, ion exchange apparently remains the predominant mode of strontium ion transfer into [F-C_5mim]NTf$_2$. This suggests that factors other than simply IL cation molecular weight also contribute to determining the "balance of pathways" in the extraction of strontium (and by analogy, other cations) into these ionic liquids. Next, the results for the C-8 ionic liquids demonstrate that the shape of the nitric acid dependency is very sensitive to the relative contributions of ion exchange and neutral complex extraction. That is, for [C_8mim]NTf$_2$, for which roughly equal contributions of the two paths are observed in extraction from water (Table 1), a nearly flat acid dependency is obtained, an apparent compromise between the expected decline in D_{Sr} with acidity for ion exchange and the anticipated increase over the same range for neutral complex extraction. For the fluorinated analog, however, for which the vast majority of the extraction occurs via nitrato complex partitioning, the shape of the dependency is essentially that expected for neutral complex extraction alone. Finally, although interesting from a fundamental perspective, the results of these extraction studies are disappointing from a practical point of view. That is, without exception, the introduction of fluorinated substituents into the IL results in a decrease in the extraction of strontium at a given nitric acid concentration. Of particular note is the significant decrease (ca. a factor of 5–6) observed at high nitric acid concentrations for the C-10 ionic liquid. As already noted, strontium extraction into [C_{10}mim]NTf$_2$ from strongly acidic nitrate media is roughly comparable to that observed for such molecular solvents as 1-octanol [21,32]. Thus, [F-C_{10}mim]NTf$_2$ is actually less effective than many conventional diluents as an extraction solvent.

4. Conclusions

The development of viable, ionic liquid-based systems for metal ion separations requires, among other things, an improved understanding of the fundamental aspects of ion transfer into these unique solvents. The results presented here, by elucidating the factors governing the nature of the transfer process, represent a step in this direction. At the same time, the results suggest that fluorous ILs are unlikely to provide improved metal ion extraction efficiency versus their non-fluorinated counterparts when neutral extractants such as crown ethers are employed. It is unclear at present if modest extraction efficiency represents a general characteristic of extraction systems employing fluorous ILs as diluents. Work addressing this question is now underway in this laboratory.

Acknowledgment

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, United States Department of Energy under contract number W-31-109-ENG-38. Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954).

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