Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Dietz, Mark L.(2006) 'Ionic Liquids as Extraction Solvents: Where do We Stand?', Separation Science and Technology, 41: 10, 2047 — 2063
To link to this Article: DOI: 10.1080/01496390600743144
URL: http://dx.doi.org/10.1080/01496390600743144

Separation Science and Technology, 41: 2047–2063, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600743144

Ionic Liquids as Extraction Solvents: Where do We Stand?

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Abstract: The unique physicochemical properties of ionic liquids (ILs) and the relative ease with which these properties can be fine-tuned by altering the cationic or anionic moieties comprising the IL have led to intense interest in their use as alternatives to conventional organic solvents in a wide range of synthetic, catalytic, and electrochemical applications. Recent work by a number of investigators has been directed at the application of ionic liquids in various separation processes, among them the liquid-liquid extraction of metal ions. Although certain IL-extractant combinations have been shown to yield metal ion extraction efficiencies far greater than those obtained with molecular organic solvents, other work suggests that the utility of ILs may be limited by solubilization losses and difficulty in recovering extracted metal ions. In this report, recent efforts to overcome these limitations are described, and progress both in achieving an improved understanding of the fundamental aspects of metal ion transfer into ILs and in devising viable IL-based systems for metal ion separation is detailed. In addition, areas upon which future research efforts might profitably be focused are identified.

Keywords: Ionic liquids, extraction solvents, metalion exchange

INTRODUCTION

Liquid-liquid (i.e., solvent) extraction continues to represent a separation technique of significance in both metal ion separations and trace organic

Received 18 November 2005, Accepted 16 February 2006

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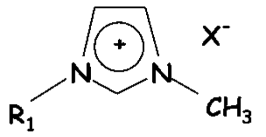
analysis, as well as in the commercial process-scale separation of a variety of materials (1). Solvent extraction offers a number of advantages over competing techniques, among them the ability to operate in a continuous mode, to employ only simple equipment and small quantities of extractant, and to achieve high sample throughout. These advantages, together with the flexibility of the chemistry employed in the extraction process (e.g., nature and concentration of extractant, aqueous phase composition) and the concomitant "tailorability" of separations, account for the ongoing popularity of the method. As traditionally practiced, however, liquid-liquid (l-l) extraction employs water-immiscible organic solvents, many of which are toxic, flammable, or volatile. Given the rising costs for their eventual disposal and the growing awareness of the environmental impact associated with their use, it is clear that the replacement of these solvents with less noxious alternatives is desirable (2). Recently there has been increasing emphasis on the development of environmentally benign separation processes, both as an end in itself and in conjunction with the design of "green" manufacturing processes. An important aspect of this effort to devise greener separations is, in fact, the identification, characterization, and application of novel solvents exhibiting few or none of the drawbacks of their traditional organic counterparts (3).

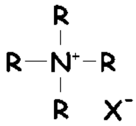
Of particular recent interest among alternative solvents have been ionic liquids (ILs), low melting ($\leq 100°C$) ionic salts typically comprising a bulky asymmetric organic cation in combination with any of a wide assortment of anions (Table 1). Ionic liquids exhibit several properties that make them attractive as a potential basis for improved extraction processes, among them a wide liquid range, good thermal stability, the ability to solubilize a wide range of solutes, a near-absence of vapor pressure (arising from the prevalence of high coulombic forces within the liquid), and an extraordinary degree of tunability (4). Although the existence of ionic salts that are liquid at modest (even ambient) temperatures has been known since 1914 (5), it was not until the early 1990s, when the work of Wilkes and Zaworotko (6) led to the first air- and water-stable ionic liquids, that the field blossomed. In 1998, Rogers and co-workers (3) suggested that ionic liquids may be suitable as the basis for novel liquid-liquid extraction systems, and demonstrated that a variety of ionizable and non-ionizable substituted aryl molecules will partition into $[C_4mim][PF_6]$ from water, with distribution ratios as high as 1000 or more in certain instances (e.g., 4,4′-dichlorobiphenyl). Significantly, solute partitioning in this system was found to parallel that observed for the same solutes in a conventional octanol/water system. In addition, for ionizable solutes, the distribution coefficient for the uncharged form of the solute was found to exceed that of the anionic (e.g., benzoic acid) or cationic (e.g., aniline) form, as is the case in conventional solvents.

Since this initial report, numerous studies have appeared describing the application of ionic liquids as solvents in the extraction of various simple

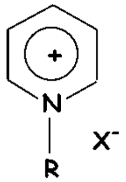
Table 1. Representative ionic liquids



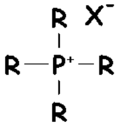
N, N′-dialkylimidazolium salts



quaternary ammonium salts



N-alkylpyridinium salts



alkylphosphonium salts

where X = Cl^-, Br^-, I^-, BF_4^-, PF_6^-, NTf_2^-, etc.

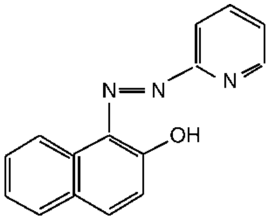
organic compounds (7–10), biomolecules (11, 12) (e.g., amino acids), and metal ions (13–33). Of particular interest in our laboratory has been metal ion extraction into these solvents (34–43), and in this paper, we summarize efforts in this area, with particular emphasis on those aspects of published work that have helped to define the strengths and limitations of ILs as extraction solvents. In addition, we suggest areas of investigation in which further work is required if these unique solvents are to achieve their full potential in this role.

DISCUSSION

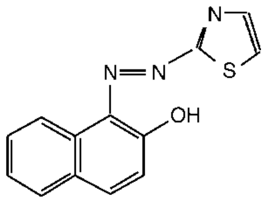
Groundwork

In 1999, a pair of publications appeared that laid the foundation for much of the work that followed concerning the application of ILs as diluents for the extraction of metal ions. That year, Rogers et al. (13) showed that two well known extractants, 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolyl)-2-napthol

(TAN), can extract various metal cations from aqueous solution into an ionic liquid phase (i.e, [C_6mim][PF_6]), with



PAN



TAN

distribution rations (D_M) exceeding 1 for Fe^{3+}, Co^{2+}, and Cd^{2+} at sufficiently high pH (≥ 12). In the absence of extractant, in contrast, no appreciable extraction of any of the ions was seen. In all cases, back extraction could be effected by a reduction in pH. Although the observed D_M values were modest at best and no data were presented to indicate how these values compared to those obtained with a conventional solvent under the same conditions, an important point was nonetheless made: that ionic liquids can function as solvents for metal ion separations. At around the same time, *Dai* et al. (14) examined the extraction of strontium nitrate from water into a series of dialkylimidazolium-based ionic liquids containing a crown ether, dicyclohexano-18-crown-6 (DCH18C6). In most instances, the values of the strontium distribution ratio obtained were enormous, exceeding 10^4 in one case. That these results were obtained using an aqueous phase containing only millimolar concentrations of nitrate was all the more remarkable, as under such conditions, most conventional solvents yield immeasurably low strontium extraction. Particularly interesting from the perspective of metal ion separations is that the strontium distribution rations were not merely large, but readily tunable by varying either the substituents on the imidazolium cation or the nature of the IL anion. These results thus demonstrated that the ready tunability of IL structure will translate to tunable performance as an extraction solvent, an important insight.

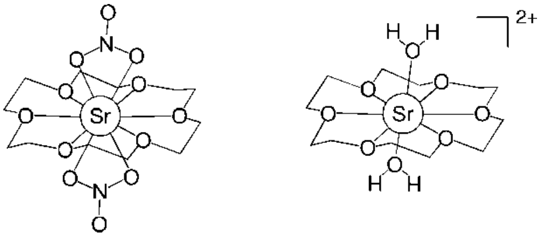
Since these reports, research concerning the performance of ionic liquids as solvents in the l-l extraction of metal ions has followed three paths: investigations of the use of extraction systems employing neutral extractants (e.g., crown ethers, calixarenes), acidic or anionic extractants (e.g., organophosphorus acids, pseudohalides), or “extractant-functionalized” (more commonly known as “task-specific”) ionic liquids (TSILs). Of the three, the use of neutral extractants has received the most attention to date, doubtless a result of the important role that these compounds, as represented by such reagents as tri-*n*-butyl phosphate (TBP), crown ethers, and calixarenes, have played in metal ion separation systems based on conventional solvents. The first two of these areas will now be considered in turn. The third, in which the ionic liquid serves as both solvent and extractant, has been the subject of a pair of recent reviews (44, 45), and thus, will not be considered further.

Neutral Extractants

Shortly after the report by Dai et al. of extraordinarily efficient extraction of strontium by DCH18C6 into various ILs (14), Visser et al. (16) described results for the extraction of Sr^{2+} and two other cations (Na^+ and Cs^+) by three different crown ethers (18C6 and its dicyclohexano- and di-*tert*-butylcyclohexano- analogs) into a series of 1-alkyl-3-methylimidazolium hexafluorophosphates, $[C_n\text{mim}][PF_6]$, of increasing alkyl chain length (n = 4, 6, 8) from aqueous phases containing various mineral acids or metal salts. Certain of the results obtained were precisely those expected from the extraction behavior of these metal ions with the same extractants in conventional molecular solvents. For example, the relative efficiency of the three extractants (DtBuCH18C6 > DCH18C6 > 18C6) was found to be consistent with results obtained in, for example, 1-octanol. In addition, for a given extractant and $[HNO_3]_{aq}$, D_M values (for Sr^{2+} and Cs^+) were found to decrease with an increase in the chain length of the 1-alkyl-3-methyl imidazolium salt ($C_4\text{mim}^+ > C_6\text{mim}^+ > C_8\text{mim}^+$), much as they do for a given class of conventional molecular solvents (e.g., D_{Sr} is lower for 1-decanol than for 1-octanol (46)). Finally, when $Al(NO_3)_3$ solutions were employed as the aqueous phase, metal ion distribution ratios were found to increase with increasing $[Al(NO_3)_3]_{aq}$, as would be expected from results in traditional solvents. In certain other respects, however, the results were entirely unexpected. For example, under many conditions, the extraction of strontium and cesium was remarkably similar. The nitric acid dependencies of D_M for the two ions using DtBuCH18C6 in $[C_8\text{mim}][PF_6]$, in fact, are nearly identical. Also, and perhaps more importantly, for extraction from HNO_3 solutions by DtBuCH18C6 in $[C_4\text{mim}][PF_6]$, the distribution ratios for all three ions (Sr^{2+}, Cs^+, and Na^+) were found to fall to a minimum at *ca.* 1M HNO_3 then rise again. Such a dependency is unlike that seen in any conventional solvent. These results were attributed primarily to changes in the water content of the IL phase, which for $[C_4\text{mim}][PF_6]$, was found to track the metal ion distribution ratios, falling with increasing $[HNO_3]_{aq}$ to a minimum at 1 M HNO_3, then rising again. On the basis of results obtained with many conventional solvents (e.g., oxygenated aliphatic diluents), increased water content would be expected to facilitate transfer of hydrated metal ions and their accompanying counter anion(s) (46, 47), so this is a reasonable explanation. It is important to note, however, that the enormous D_{Sr} values reported by Dai et al. (14) were not accompanied by high IL water contents. Rather, immeasurably low water contents were reported.

In an examination of the competitive extraction of various alkali metal chlorides by DCH18C6 into the same 1-alkyl-3-methylimidazolium hexafluorophosphates, Bartsch et al. (17), observed yet another peculiar aspect of their behavior as diluents for solvent extraction. That is, a change in the aqueous phase anion was found to have essentially no effect on the extraction of a series of alkali metal salts into $[C_8mim][PF_6]$, a result markedly different than that seen in molecular diluents such as chloroform or 1-octanol, for which a change in anion can yield significant changes in extraction efficiency (46).

Clearly, if these peculiarities are to be understood (and perhaps, exploited for improved metal ion separations), an understanding of the fundamental chemistry of these systems (in particular, a detailed description of the extraction process and the nature of the extracted species) is required. With this in mind, we undertook a systematic comparison of the extraction of strontium by DCH18C6 into a series of 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imides, $[C_nmim][NTf_2]$, and a representative molecular solvent, 1-octanol (34). Interestingly, these solvents were found to differ in nearly every aspect considered. For example, for 1-octanol, an increase in organic phase water content (which accompanies rising aqueous acidity) was found to yield an increase in the extraction of strontium. For $[C_2mim][NTf_2]$, however, rising organic phase water content was accompanied by falling D_{Sr} values. Also, while D_{Sr} rose with $[HNO_3]_{aq}$ (and therefore $[NO_3^-]_{aq}$) for 1-octanol, as would be expected for extraction of the strontium-crown ether-nitrato complex, it declined with $[HNO_3]_{aq}$ for the IL. (Such an acid dependency, in which metal ion partitioning decreases with acidity, poses a problem in practical separation applications, as "real world" separation processes frequently require extraction from acidic media and recovery in water or dilute acid.) In addition, while the difference between extraction of strontium from HNO_3 and HCl into 1-octanol is typically *ca.* two orders of magnitude (46), for the IL, the acid dependencies differed little. Finally, in contrast to 1-octanol, increased strontium loading of the extractant (DCH18C6) in the ionic liquid was found to be accompanied by increased aqueous solubilization of the organic phase. Taken together, these observations strongly indicate that strontium partitioning into the ILs involves a process other than the extraction of a neutral strontium-crown ether-nitrato complex, as is observed for 1-octanol and other molecular solvents. Rather, a cation-exchange process in which the 1:1 $Sr\text{-}DCH18C6^{2+}$ complex is exchanged for the cationic component of the IL provides the means by which strontium ion partitioning occurs. Further support for this idea was obtained in subsequent EXAFS studies of the extracted species (35). Briefly, strontium-EXAFS revealed a fundamental difference between the nature of the complex extracted into 1-octanol and a representative IL, $[C_5mim][NTf_2]$. That is, while a neutral complex bearing axial nitrate anions is extracted into the alcohol, data for the complex extracted into $[C_5mim][NTf_2]$ were consistent with partitioning of a cationic species (i.e, [Sr-DCH18C6]$^{2+}$) in which the axial positions are occupied by water molecules.



That nitrate ions are not instead present in the *outer* coordination sphere of strontium (and are thus able to accompany extracted strontium without appearing in the EXAFS) was demonstrated by both NMR and ion chromatographic determinations of the extent of nitrate co-extraction, which indicated that only a few percent of the amount of nitrate required to maintain change balance (i.e, to form a neutral complex) accompanies the strontium. Thus, the prevalence of ion exchange in this system apparently has its origins in differences in the nature of the species extracted into ionic liquids vs. conventional solvents.

Since these initial reports demonstrating the possibility of ion exchange as a mode of metal ion transfer into ILs, nearly a dozen other studies involving cation extraction by various neutral extractants have appeared (Table 2). Almost without exception, a cation-exchange mechanism has been found to be prevalent. Moreover, in the few instances in which information has been

Table 2. Metal ion extraction systems combining neutral extractants and ionic liquids

Metal ion(s)	Extractant(s)	Ionic liquid(s)	Reference
Sr^{2+}	DCH18C6	$[C_nmim][PF_6]$ or NTf_2	(14)
Na^+, Cs^+, Sr^{2+}	18C6 DCH18C6 DtBuCH18C6	$C_nmim][PF_6]$	(16)
Alkali metal chlorides	DCH18C6	$[C_nmim][PF_6]$	(17)
Sr^{2+}	DCH18C6	$[C_nmim][NTf_2]$	(34, 39)
Ln^{3+}	CMPO	$[C_4mim][PF_6]$	(21)
UO_2^{2+}	CMPO-TBP	$[C_nmim][PF_6]$ or NTf_2	(22)
Ag^+	Calixarenes	$[C_nmim][PF_6]$	(27)
Cs^+, Sr^{2+}	N-alkyl aza-18-crown-6's	$[C_nmim][NTf_2]$	(28)
Cs^+	BOBCalixC6	$[C_nmim][NTf_2]$	(29)
UO_2^{2+}	TBP	$[C_nmim][PF_6]$	(30)
Ln^{3+}	CMPO	$[C_4mim][PF_6]$ or NTf_2	(31)
Na^+, Ca^{2+}, Sr^{2+}	DCH18C6-TBP	$[C_nmim][NTf_2]$	(41)
UO_2^{2+}	TBP	$[C_4mim][PF_6]$	(32)

presented concerning the extracted species, its form in the IL has proven to differ from that seen in the conventional solvent. Work by Visser et al. (23), for example, has shown that uranyl nitrate extraction by CMPO in TBP-modified ionic liquids ($[C_4mim][PF_6]$ and $[C_8mim][NTf_2]$) involves partitioning of the cationic complex $UO_2(NO_3)(CMPO)^+$, specifically, its exchange for the cationic constituent of the ionic liquids. In contrast, a neutral (i.e, 1:2:2) $UO_2(NO_3)_2(CMPO)_2$ complex is extracted into dodecane. Dai et al. (14) have noted that from a thermodynamic perspective, the solvation of ionic species should be more favorable in an ionic liquid than in a conventional solvent, so the apparent prevalence of cationic complexes in these systems is not entirely unexpected.

Obviously, a partitioning mechanism in which metal ion transfer is accompanied by loss of the IL cation to the aqueous phase poses a significant problem in potential applications of ionic liquids in L-L extraction, both from a cost and environmental impact perspective. For this reason, there has been considerable interest in the identification of means by which ion exchange (IX) can be suppressed, ideally without sacrificing other, positive aspects of the performance of ILs as extraction solvents. To date, three approaches have been described by which the significance of IX as a pathway for cation extraction by neutral ligand can be diminished: increasing the length of the alkyl chain of the 1-alkyl-3-methylimidazolium salt, fluorination of this alkyl chain, and use of a sacrificial cation exchanger. Each of these approaches exhibits varying degrees of effectiveness.

Table 3 summarizes the results of studies carried out in this laboratory (39) concerning the effect of increasing the alkyl chain length of the cationic constituent of the IL on the “balance of pathways” (i.e, nitrato complex extraction vs. IX) observed in the extraction of Sr^{2+} by DCH18C6 into $[C_nmim][NTf_2]$ ILs. Since IX requires transfer of the cationic portion of the IL into an aqueous phase, increasing alkyl chain length should make this process more difficult, eventually tipping the balance in favor of neutral complex extraction. Shown are the percent strontium extracted under the experimental conditions, determined radiometrically, and the corresponding percent nitrate extracted (determined by ion chromatography) under identical conditions. As can be seen, for $[C_5mim][NTf_2]$, the amount of nitrate extracted is far less that the amount of Sr^{2+} transferred, and thus, is not sufficient to produce a neutral strontium-crown ether-nitrato complex. As the alkyl chain is lengthened, however, nitrate co-extraction becomes increasingly significant, consistent with a shift from ion exchange to neutral complex extraction. Eventually, for $[C_{10}mim][NTf_2]$, the amount of nitrate extracted is that expected if partitioning occurs solely by extraction of the neutral complex.

Additional evidence of a shift in the mode of partitioning is found in the nitric acid dependencies of D_{Sr} for solutions of DCH18C6 in 1-octanol, $[C_5mim][NTf_2]$ and $[C_{10}mim][NTf_2]$ (39). For the C_5-IL, increasing acidity is accompanied by falling D_{Sr} values, which as noted earlier for the C_2

Table 3. Strontium[a] and nitrate[b] ion partitioning between water[c] and solutions of DCH18C6[d] in $[C_n mim][NTf_2]$

Organic phase	$\%E_{Sr}$	$\%E^{e}_{NO3-}$	Partitioning mode indicated
$[C_5mim][NTf_2]$	96.5	9 ± 7^{f}, $16^{f,g}$	Cation exchange
$[C_6mim][NTf_2]$	82.6	16.1 ± 0.8	Cation exchange
$[C_8mim][NTf_2]$	39.0	20.9 ± 1.0	Mixed
$[C_{10}mim][NTf_2]$	20.2	20.0 ± 1.0	Extraction of neutral complex

[a] Determined radiometrically.

[b] Determined by ion chromatography, unless otherwise noted.

[c] Containing 0.0310 M $Sr(NO_3)_2$.

[d] 0.202 M *cis-syn-cis* DCH18C6 in the indicated ionic liquid.

[e] For partitioning *via* extraction of the neutral strontium nitrato-crown ether complex only, the percentage extraction of nitrate ion should correspond to $\%E_{Sr}$. For partitioning *via* cation exchange, no nitrate co-extraction ($\%E_{NO3-} = 0$) is expected.

[f] As reported in reference 35.

[g] Determined by ^{15}N-NMR.

analog, is not consistent with neutral complex partitioning. In contrast, for the C_{10}-IL, increasing acidity (and therefore, $[NO_3^-]_{aq}$) yields an increase in D_{Sr}, just as in 1-octanol and other conventional molecular solvents. Although these results would seem to settle the issue of how ion exchange can be suppressed, other, more recent studies have demonstrated that the increase in IL cation hydrophobicity that accompanies the change from C_5 to C_{10} is not sufficient to eliminate the possibility of IX for all metal ion/extractant combinations (42), thus making it necessary to consider alternatives.

With this in mind, the effect of fluorination of the IL cation on the mode of strontium partitioning in the presence of DCH18C6 for partially fluorinated analogs of C_5-, C_8-, and $[C_{10}mim][NTf_2]$ has been investigated (43). As can be seen from Fig. 1, fluorination of the IL cation is not significantly more effective at inhibiting IX than a simple lengthening of the alkyl chain. Moreover, it is accompanied by an often- appreciable reduction in D_{Sr} under a given set of conditions. The magnitude of this reduction, in fact, is such that under the conditions normally employed for strontium extraction (i.e, high $[HNO_3]_{aq}$), the extraction efficiency is actually poorer than that obtained with 1-octanol. Thus, suppression of IX by this approach comes at the price of diminished extraction efficiency.

Luo and co-workers (29) have pursued an alternative approach to reducing the significance of ion exchange in metal ion extraction into ILs, one which does not involve modification of the structure of the ionic liquid, but rather addition of a "sacrificial" cationic species to the ionic liquid phase. Ideally, this species transfers to the aqueous phase in preference to the IL cation upon metal ion extraction, thus reducing the loss of imidazolium cations that can accompany metal ion partitioning. The key

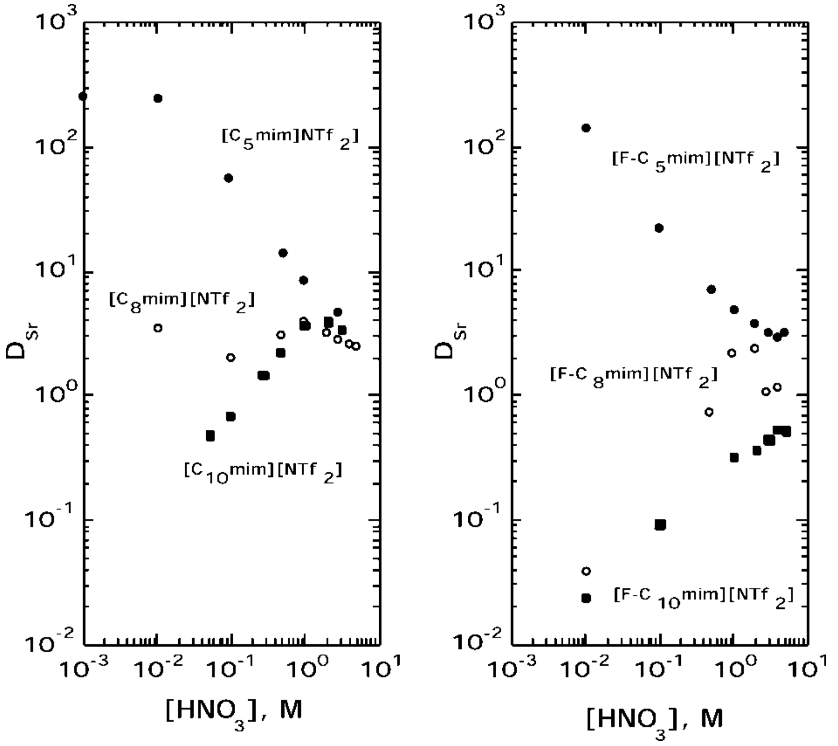


Figure 1. Nitric acid dependency of D_{Sr} for extraction by DCH18C6 (0.1 M) into (left panel) $[C_5mim][NTf_2]$, $[C_8mim][NTf_2]$, and $[C_{10}mim][NTf_2]$; and (right panel) $[F\text{-}C_5mim][NTf_2]$, $[F\text{-}C_8mim][NTf_2]$, and $[F\text{-}C_{10}mim][NTf_2]$.

to satisfactory performance in this role is that the sacrificial species have no affinity for the extractant and that it be more hydrophilic than the IL cation. In Luo's experiments, sodium tetraphenylborate ($Na^+BPh_4^-$) was shown to reduce (by 24%, on average) the release of C_4mim^+ to the aqueous phase upon extraction of Cs^+ into $[C_4mim][NTf_2]$ by "BOB-CalixC6" without any adverse effect on D_{Cs} values. These results, while preliminary (and reducing, rather than eliminating IX) suggest that this is an approach that warrants further investigation.

Acidic or Anionic Extractants

As already noted, research into the applications of ILs as extraction solvents for metal ions has involved not only an evaluation of neutral extractants, but of acidic and anionic extractants as well. Although the publications in this area, summarized in Table 4, are not yet especially numerous, they have

Table 4. Metal ion extraction systems combining acidic or anionic extractants and ionic liquids

Metal ion(s)	Extractant(s)	Ionic liquid(s)	Reference
Transition metal ions	PAN, TAN	$[C_nmim][PF_6]$	(18)
Hg^{2+}	halides pseudohalides		
Cu^{2+}	Dithizone 8-hydroxyquinoline PAN	$[C_4mim][PF_6]$	(24)
Cd^{2+}, Hg^{2+}, Ag^+, Pb^{2+}	Dithizone	$[C_4mim][PF_6]$	(25)
Ln^{3+}	2-thenoyltrifluoroacetone	$[C_4mim][NTf_2]$	(37)
UO_2^{2+}, Ln^{3+}, An^{3+}	HDEHP Cyanex 272	$[C_nmim][NTf_2]$	(48)
Pb^{2+} transition metal ions	2-Thenoyltrifluoroacetone	$[C_nmim][PF_6]$	(33)

already yielded important insights regarding the utility of IL/acidic or anionic extractant combinations. In 2001, Visser et al. (18), in a follow-up to an earlier paper involving the extraction of various metal ions (e.g., Fe^{3+}) with PAN and TAN (13), examined the extraction of these same (and other) metal ions by several inorganic anions (CN^-, OCN^-, SCN^-, and halide ions) into a pair of dialkylimidazolium salts (i.e, $[C_4mim][PF_6]$ or $[C_6mim][PF_6]$). The results obtained indicate that in terms of the D_M values obtained, inorganic extractants (i.e, halides and pseudohalides) represent a viable alternative to organic extractants in certain instances. For example, significant distribution ratios (exceeding 10, and in some cases 100) were observed for Hg^{2+} in the presence of I^- or Br^-, even with 2 M H_2SO_4 as the aqueous phase. (Such an aqueous phase is of interest, it should be noted, in hydrometallurgical processes for Hg^{2+} recovery). The extraction of Hg^{2+} and Co^{2+} in the presence of SCN^- was nearly as efficient. Although these results are clearly of potential practical significance, they are important from a more fundamental perspective as well. That is, from the complicated response of metal ion partitioning to the nature and concentration of the inorganic anion, it is clear that metal ion distribution ratios in these systems are determined by a combination of several competing factors, including speciation, hydration of metal ions, the hydrophobicity of the resultant metal complexes, and the chemistry of the ionic liquid itself. Thus, interpretation of partitioning data in these systems may, in some instances, be far from straightforward. Just as important is that given the anionic nature of the complexes expected, the possibility that ion transfer occurs *via* anion exchange cannot, as the authors noted, be ruled out.

Not long after this work, it was demonstrated (37) that, in fact, anion exchange does represent a possible mechanism for metal ion transfer into an ionic liquid, not in a system involving an inorganic ion as an extractant, but rather in the extraction of lanthanides (e.g., Eu^{3+}) by the well known organic extractant 2-thenoyltrifluoroacetone (Htta). In conventional solvents extraction systems, a variety of Eu-tta complexes can be formed. Depending on the experimental conditions, the extracted complex may be neutral ($Eu(tta)_3(H_2O)_n$; n = 2 or 3), cationic (e.g., $Eu(tta)_2(CE)(H_2O)_x^+ClO_4^-$, where CE = a crown ether), or even anionic (e.g., $Q^+Ln(tta)_4^-$, where Q is a quaternary or protonated tertiary amine). Given the not insignificant concentration of water present (*ca.* 1 M) in the IL phase used ($[C_4mim][NTf_2]$), it might be anticipated that extraction of the hydrated neutral complex would be favored, but in fact, extraction of an anionic complex is observed. Specifically, the slopes of the extractant and acid dependencies of D_{Eu} at constant $HClO_4$ (0.001 M) and Htta (0.5 M) concentration, respectively, indicate that 4 molecules of Htta participate in the extraction process and that 4 protons are released to the aqueous phase for each Eu^{3+} extracted, consistent with the partitioning of $Eu(tta)_4^-$. UV-visible spectroscopy and EXAFS measurements support this conclusion. In addition, the absence of Na^+ or H^+ co-extraction indicates that the europium-tta complex is exchanged for the anionic constituent of the IL (i.e, the NTf_2^-), an observation of obvious importance both from a fundamental and practical (i.e, "green") point of view.

That anion exchange is not a "universal" mechanism for metal ion extraction by β-diketones in ILs, however, is demonstrated by the results of a more recent study by Hirayama (33), in which the extraction of several other metal ions (Ni, Cu, or Pb) was found to proceed *via* partitioning of a neutral hydrated complex ($M(TTA)_2(H_2O)_n$; n = 1 or 2), as is the case in nitrobenzene chloroform, and toluene. Such results point up the difficulty in making generalizations as to the exact nature of the extracted species expected in ionic liquid systems given our current state of knowledge. Despite this, several recent studies do seem to suggest that extraction systems comprising an acidic (anionic) extractant in an IL will show behavior very similar to (and thus, predictable from) that seen with a traditional organic solvent. Wei et al., for example, have shown that the extraction of copper by dithizone or 8-hydroxyquinoline (24) and of lead by dithizone (25), both into $[C_4mim][PF_6]$, differs from extraction into dichloromethane only in $pH_{1/2}$ value (the pH at which 50% extraction occurs). Along these same lines, Cocalia et al. (48), employing a combination of radiotracer partitioning studies, UV-visible spectroscopy, and EXAFS measurements, have recently shown that both the general extraction behavior and metal ion coordination environment of uranyl ion and trivalent lanthanide and actinide ions are the same in their extraction into either $[C_{10}mim][NTf_2]$ or dodecane by HDEHP or Cyanex 272. In either solvent, for example, uranyl ion is extracted by a pair of H-bonded extractant dimers, while Am extraction requires three such monodeprotonated dimers. This result demonstrates that despite obvious and significant structural differences between dodecane and $[C_{10}mim][NTf_2]$, in this instance, the two compounds behave nearly identically as extraction solvents. Curiously, metal ion distribution ratios were actually higher in dodecane than in the ionic liquids, in the case of Am^{3+} extraction by Cyanex 272 from dilute HNO_3, by nearly an order of magnitude. Clearly then, it should not be assumed that the unique solvation environment provided by ILs necessarily translates to extraction efficiency superior to that of a conventional solvent.

CONCLUSIONS

Where then do ionic liquids stand as solvents for liquid-liquid extraction? Obviously, the work carried out to date does demonstrate that ionic liquids can be substituted for conventional organic diluents in the solvent extraction of a variety of metal ions. It is equally apparent, however, that such substitution can, and frequently does, substantially increase the complexity of the system chemistry. Of particular concern in this regard are systems employing neutral extractants. As illustrated by the results described both for alkali and alkaline earth cation extraction by crown ethers and for uranyl ion extraction by CMPO, the use of ILs in combination with a neutral extractant can lead to unanticipated (and undesirable) changes in extraction mechanism, complicating process design and compromising the putative “greenness” of ILs through solubilization losses. This is especially unfortunate given that the largest reported increases in extraction efficiency relative to conventional solvents have been typically observed in systems employing neutral extractants.

The problems of mechanistic complexity and the emergence of unexpected extraction pathways are not, as illustrated by the results presented for lanthanide extraction by the acidic extractant Htta, confined to neutral extractants. Nonetheless, the limited data now available seem to suggest that the behavior of IL/acidic extractant combinations may be more readily predictable from the behavior of conventional analogs. Unfortunately, it may also be the case that the generation of a neutral (rather than a charged) extractable species precludes taking full advantage of the unique solvent environment afforded by ILs.

Does all of this imply that ionic liquids have nothing to offer as extraction solvents? It does not; rather, it indicates that a great deal of additional work will be required before the potential of ILs in this role can be fully evaluated. Of obvious importance in this context are further studies relating IL composition and extractant structure to the mechanism of metal ion transfer, but this is only one of a number of issues that must be considered in such an evaluation, particularly for process-scale applications. For example, although progress is being made in the area (49, 50), the toxicity and environmental impact of ILs and their breakdown products are not yet well understood. Also unclear is the long-term stability/recyclability of ILs under "process relevant" conditions. Basic physicochemical data relevant to their application in metal ion extraction processes are also needed for many ILs and their mixtures, among them viscosity, solubility, and interfacial tension data. Closely related to this is the need to develop the means to model and predict these and other properties of ILs. Only when these issues (and others such as cost, which lie outside the scope of this review) have been addressed can one reasonably expect ionic liquids to assume a place of significance among the tools of the practitioners of liquid-liquid extraction.

ACKNOWLEDGEMENT

Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, United States Department of Energy, under Contract No. W-31-109-ENG-38.

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

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