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ANION EFFECTS IN THE EXTRACTION OF METAL IONS INTO ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

by

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ABSTRACT
ANION EFFECTS IN THE EXTRACTION OF METAL IONS INTO ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

by

Sarah Lynn Garvey

The University of Wisconsin-Milwaukee, 2013
Under the Supervision of Professor Mark L. Dietz, Ph.D.

As part of a broader program directed at the development of improved approaches to the removal of actinides and heat-producing fission products from spent nuclear fuel, the fundamental aspects of the partitioning of selected metal ions between aqueous solution and various room-temperature ionic liquids (ILs) containing a neutral extractant have been investigated.

Prior work has shown that in contrast to the partitioning of alkaline earth cations into conventional solvents in the presence of a crown ether, which is known to proceed *via* a single pathway (*i.e.*, neutral complex extraction), their extraction into an IL is often a complex, multi-path process in which the ionic liquid itself plays an active role. Specifically, in addition to the extraction of a neutral complex, ion exchange involving a protonated extractant molecule or the cationic constituent of the ionic liquid can also comprise important modes of ion transfer. In an effort to clarify the factors governing the balance among these various pathways, the influence of the aqueous phase and IL anions has been examined. In addition, the effect of the presence of an extractable anion (here, TcO_4^-) has been explored. The results indicate that the predominant mode of extraction of an alkaline earth cation by crown ethers is strongly influenced by both the aqueous phase anion (with low hydration energy favoring neutral complex extraction) and the IL anion (with hydrophilic anions also favoring extraction of a neutral species). The nature of the extracted species has also been determined to influence the preferred mode(s) of partitioning. That is, for an extractable anion, additional pathways are observed, with ion exchange involving either a cation-crown ether-nitrato ion-pair or the anionic constituent of the IL representing important routes for extraction.

In related work, the radiolysis of two families of ILs has been examined and the structural features of the IL cation and anion leading to satisfactory radiolytic stability have been identified. Taken together with the extraction studies, these results represent an important step in the development of viable, IL-based separation systems for the removal of fission products from nuclear waste streams and for their analytical-scale separation for subsequent determination.

DEDICATION

This is dedicated to my husband, Michael, whose love, support, and knowledge helped me get through this journey, and to my parents, who have always supported my decisions and encouraged my love for the sciences.

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CHAPTER 1:

INTRODUCTION

1.1 Overview and Scope

Rising global energy consumption, along with increasing concerns over the environmental impact of energy production, have led to growing interest in approaches to the large scale generation of electricity that do not produce greenhouse gases, among them nuclear energy [1]. For nuclear energy to truly represent a safe and viable alternative to fossil fuels, the issue of spent nuclear fuel and high-level waste must be addressed. Since 1977, when then-President Jimmy Carter suspended the commercial reprocessing of spent fuel and the recycling of plutonium, nuclear energy production in the United States has operated in a "once through" mode [2]. Recently, however, efforts have been undertaken to devise a "closed" nuclear fuel cycle, in which spent nuclear fuel would be reprocessed and recycled. Success in developing such a capability will require significant advances in separations chemistry, both because spent fuel is very complex and because of the extreme conditions under which the separations processes would need to operate.

The reprocessing of spent nuclear fuel (SNF) requires, among other things, the removal of heat-producing radionuclides, in particular radiostrontium (*i.e.,* ^{89}Sr and ^{90}Sr) and ^{137}Cs [3, 4]. This allows for a reduction in the overall volume of high-level wastes and facilitates subsurface or repository storage of the remaining waste. (Surprisingly, despite the significant amount of heat generated by ^{89}Sr, ^{90}Sr and ^{137}Cs, these isotopes make up only *ca.* 5% of the light products of uranium fission [5]). Although a variety of methods have been proposed for the separation of Sr from SNF, including precipitation and ion exchange, the most widely employed method remains solvent extraction [6], a result of its ease of operation, speed and continuous nature [4].

Various solvent extraction technologies are used worldwide, among them the PUREX (plutonium uranium extraction), SREX (strontium extraction) and TRUEX (transuranics extraction) processes [6]. The PUREX process, one of the most commonly used separation processes for SNF, uses a solution of tri(n-butyl)phosphate, TBP, as the extractant in kerosene to separate UO_2^{2+} and Pu^{4+} from fission products [7]. In this process, uranium fuel elements are dissolved in 6-8 M HNO_3 solution followed by a contact with the kerosene/TBP solution. The PUREX process allows for recovery of purified plutonium from uranium with decontamination factors greater than 10^7 from fission products [7]. In this process, both the solvent and aqueous reagent streams can be recycled for reuse, which will ultimately reduce the amount of process waste. Depending on the composition of the spent nuclear fuel, additional separation steps may need to be incorporated to obtain better separations of certain fission products. For example, additional processes such as ion-exchange can be used to remove long-lived isotopes (*e.g.,* ^{99}Tc) or highly radioactive fission products (*e.g.,* ^{137}Cs) and solvent extraction systems (*e.g.,* SREX process) to remove heat-producing materials (*e.g.,* ^{90}Sr) [7]. Obviously, ensuring that the removal of these materials is as efficient as possible (*i.e.,* reducing the number of separation stages and obtaining high selectivity) is crucial.

Work in this lab has explored the possibility of using ionic liquids as the extraction solvent with the notion that higher extraction efficiencies and greater selectivity for strontium versus other alkali and alkaline earth metals (present in high concentrations in SNF) could provide the needed level of performance. In addition, an examination of the extraction efficiency of metal anions has also been completed. ^{99}Tc, a long-lived β-emitting radionuclide with high mobility in the environment, is one of the main fission products of uranium (having a yield of 6.3%) [8]. Eliminating the possibility of the release of ^{99}Tc into the environment [8-11] represents an important step toward improving the safety of spent nuclear fuel processing and restoring public confidence in the sustainable nuclear power option [11]. The current baseline flowsheet for the processing of spent nuclear fuel in the U.S. involves coextraction of uranyl and technetium as one of the stages [8]. The U separation process (UREX) involves the extraction of uranyl nitrate from 1-3 M nitric acid with tri(*n*-butyl) phosphate (TBP) in *n*-dodecane. ^{99}Tc is coextracted by TBP as $UO_2(TCO_4)(NO_3)\cdot 2TBP$, $UO_2(TcO_4)_2\cdot TBP$, and $HTcO_4\cdot 3TBP$ complexes, hence its presence in the U stream designated for calcining to solid UO_x and further recycling. In the current implementation of the UREX process, ^{99}Tc is present in the U/Tc stream as ~0.6 mM pertechnetate (TcO_4^-) in the 0.34 M $UO_2(NO_3)_2$ solution generated by stripping the organic phase using 0.01 M HNO_3. TcO_4^- is removed from this aqueous stream using a column of the weakly basic poly(vinylpyridine) resin (Rellex HPQ) and subsequently eluted using 1 M NH_4OH [12-14]. The resulting solution is only ~10 times more concentrated in TcO_4^- than the initial feed. Although further processing steps have not been decided upon, one scheme currently under consideration involves precipitating TcO_4^- using tetrabuylammonium hydroxide, followed by calcination of NBu_4TcO_4 and steam reforming of TcO_2 to Tc(0) [13, 14]. Additionally, an examination of alternative approaches in which TcO_4^- is extracted from the Rellex HPQ column effluent (1 M NH_4OH) and concentrated in hydrophobic IL solvent comprising trihexyl(tetradecyl)phosphonium *bis*[(trifluoromethyl)sulfonyl]imide ($P_{666,14}{}^{+}Tf_2N^{-}$) has been completed [15].

In general terms then, the objective of the present studies is to explore the processes involved in metal ion extraction from aqueous solutions by crown ethers into imidazolium and phosphonium-based room-temperature ionic liquids, and eventually, to establish guidelines for the selection of an appropriate ionic liquid (IL) solvent for the selective extraction of strontium and technetium. In the interest of applying a systematic approach of the behavior to the study of ILs as extraction solvents, the focus of this work is the investigation of the effect of anions on extraction efficiency. The alteration of this component will be examined in multiple ways. That is, an examination of the effect of the aqueous phase anion and of the anionic component of the ionic liquid on the efficiency of extraction and the preferred mode of partitioning into an ionic liquid have been carried out. In addition, the partitioning of a metal anion between aqueous phases and various ionic liquids has been explored.

1.2 Ionic Liquids

Although ionic liquids were first described in 1800 (when Sir Humphry Davy investigated the electrolytic decomposition of simple molten salts under the influence of an applied DC electric field [16]) and were synthesized strictly for their ionic character as early as 1914 [17], it was not until the introduction of the first air- and water-stable ionic liquid in 1992 [18] that these materials attracted intense interest. Since this time, the number of publications in the field has increased dramatically, from a mere 120 in 1990 to nearly 5000 in 2010. Today, this high level of activity continues unabated.

Ionic liquids are defined as salts that melt below 100°C, and thus, they can be thought of as low-melting, (usually) organic analogs of classical molten salts. Ionic liquids exhibit several properties that make them attractive as alternative solvents in many processes, among them a wide liquid range, good thermal stability (*e.g.,* decomposition temperatures ≥200°C), low melting points or glass transitions (≥ -90°C), a near-absence of vapor pressure, and a high degree of tunability [19-21]. As can be seen from Figure 1.1, the cationic constituent of an ionic liquid tends to be a bulky, typically asymmetric, charge-delocalized organic species. By appropriate choice of substituents on the cation and of the IL anion, the solubility of the IL can be varied from water-miscible to hydrocarbon-soluble. For example, 1,3-dialkyl-imidazolium ionic liquids can be made progressively more water soluble by shortening the alkyl moieties appended to the imidazolium cation [19]. Similarly, incorporation of a sufficiently hydrophilic anion (*e.g.,* Cl^-) into these same ionic liquids can render them completely water-miscible [22]. Incorporation of a highly fluorinated IL anion, such as the *bis*[(trifluoromethyl) sulfonyl]imide (Tf_2N) anion developed by Grätzel *et al.* [23], has the opposite effect. The precise nature of the cationic and anionic constituents of the ionic liquid determines not only its water solubility, but also such properties as density [24], water content [25, 26], thermal [25, 27] and radiolytic [28] stability, lubricity [29], toxicity [30] and conductivity [31], 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 [32], synthesis [33] and catalysis [34]. Work in this lab, including that described in this thesis, has focused on the effect of altering both the cationic [26, 35, 36] and anionic [37] constituents of the ionic liquid on the suitability of the solvent in metal ion separations by liquid-liquid extraction (LLE).

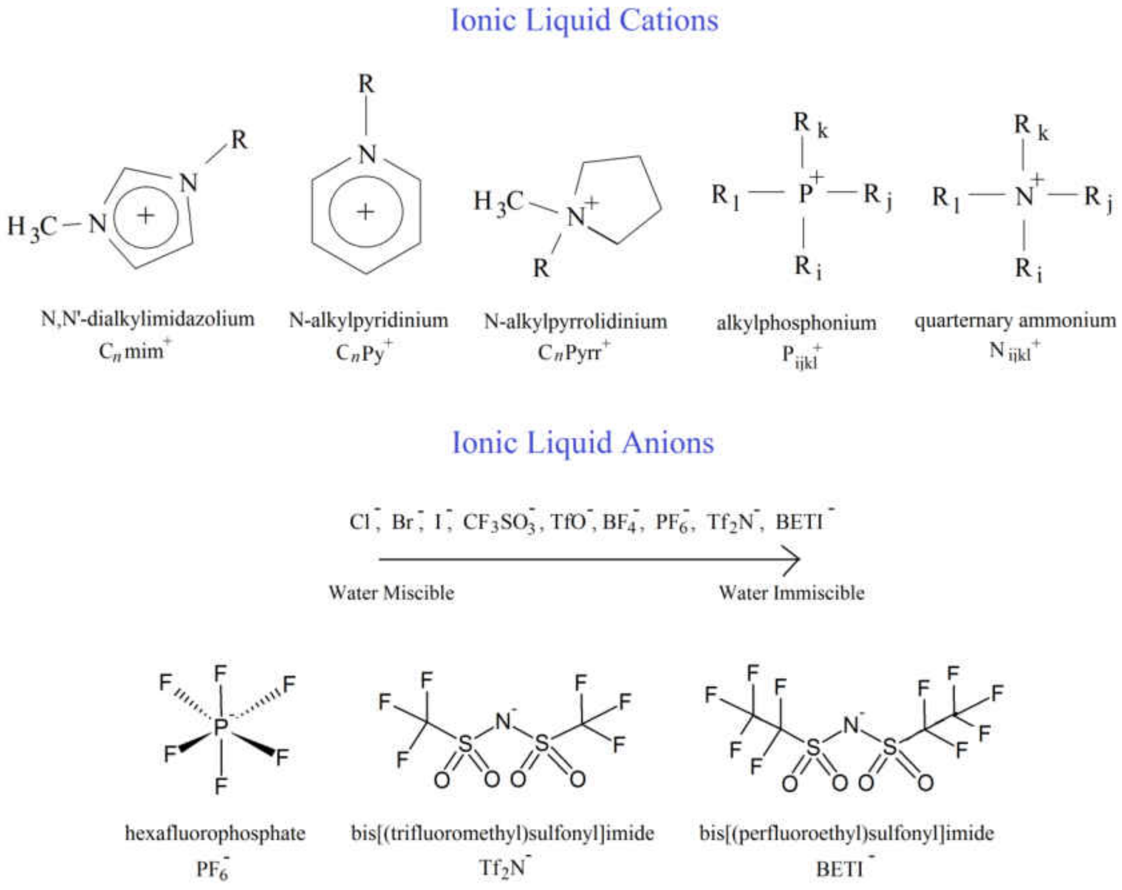

Figure 1.1: Structures of common ionic liquid cations and anions.

1.3 Solvent Extraction of Metal Ions into Conventional Organic Solvents and Ionic Liquids

Liquid-liquid extraction represents one of the most well-established methods of separation, due to 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 scales [5]. Despite its many virtues, however, as ordinarily practiced, the technique also suffers from a variety of limitations, most importantly 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 [38] and, more recently, bio-based diluents [39] and ionic liquids [20, 40, 41].

Since the first publication proposing ILs as replacements for conventional solvents for metal ion extraction [42], publications describing a wide variety of extraction systems have appeared. Early studies by Dai *et al.* [42] investigating the utility of ionic liquids as solvents in the extraction of strontium ion showed remarkably efficient extraction of the ion from water into a series of *N,N'*-dialkylimidazolium-based ILs containing DCH18C6. Several of the ionic liquids, in fact, yielded strontium distribution ratios (D_{Sr}) that exceeded those obtained with conventional molecular solvents (*e.g.,* chloroform) under the same conditions by a factor of 1,000 or more. Since this time, it has been shown that a variety of other metal ions can be efficiently extracted into a room-temperature ionic liquid from aqueous solution using an appropriate complexing agent [43]. For example, several transition metal ions (*e.g.,* Ag^+, Cu^{2+}, Zn^{2+}, Co^{2+}, or Ni^{2+})

have been extracted from aqueous solution using a calixarene (*e.g.,* pyridinocalix-[4]arene) [44]. Similarly, various crown ethers, such as 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DCH18C6) and 4,4'-(5')-di-(*tert*butylcyclohexano)-18-crown-6 (Dtb18C6), have been evaluated for the extraction of alkali and alkaline earth metals [45]. The use of chelating task-specific ionic liquids has also been reported for the removal of metal ions, particularly Cu(II), Ni(II) and Co(II) [46].

What is clear from many of these reports is that the ionic nature of ILs can lead to extracted species not observed in molecular solvents and partitioning mechanisms more complex than those seen in conventional extraction systems. In the case of strontium extraction by a crown ether, for example, neutral complex formation (ion-pair extraction), ion exchange or a combination of the two can be observed, depending on the precise system conditions [35, 47, 48]. Obtaining a complete understanding of the conditions under which each of these pathways predominates is not straightforward, a result of the numerous cation and anion combinations (estimated to be 10^6 or more [49]) possible for ILs. Work in this laboratory has nonetheless sought to clarify the factors that determine the balance of pathways in the extraction of a given metal ion into an ionic liquid in the presence of various extractants (*e.g.,* a crown ether). As part of these ongoing efforts, the work described here explores the extraction of strontium and sodium ions (as representative alkaline earth and alkali metal ions, respectively) and pertechnetate, a representative metal anion, by DCH18C6 into a variety of ionic liquids.

1.4 Overview of the Chapters

Chapter 2 describes the investigation of the various pathways involved in the partitioning of alkali and alkaline earth metal ions between aqueous mineral acids and various conventional solvents and ionic liquids containing a crown ether. In particular, this study examines the effect of the aqueous phase anion on the extraction pathways observed. The results, particularly those utilizing acidic nitrate media, provide the framework for a generalized model of the equilibria involved in these systems.

Chapter 3 examines the effect of the ionic liquid anion on the pathways by which alkali and alkaline earth metal ions are extracted, again by a crown ether. In this study, the hydrophobicity of both the IL cation and anion are altered to determine criteria that allow extraction to proceed *via* the preferred pathway, neutral complex formation.

Chapter 4 describes an extraction system in which the partitioning species is a metal anion, pertechnetate. In this study, extraction of TcO_4^- is examined in alkaline and salt solutions utilizing both conventional solvents and imidazolium and phosphonium ionic liquids.

In Chapter 5, the radiolytic stability of selected ionic liquids is examined, with the goal of minimizing degradation of an IL upon exposure to gamma radiation. Imidazolium ionic liquids are shown to be unsuitable for applications involving significant radiation exposure. In contrast, phosphonium-based ILs incorporating an appropriate aromatic anion show negligible degradation under the same conditions, and accordingly, show promise for use in nuclear fuel reprocessing.

Chapter 6 considers the utility of these same phosphonium ILs as lubricants. Examination of their tribological properties and thermal stability, along with a comparison to various bio-based lubricants (*e.g.,* vegetable oil) and a conventional motor oil, suggests that the ionic liquids are in many ways superior to currently available lubricants.

Chapter 7 offers a summary of the accomplishments in this work and recommendations for further research in the field.

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CHAPTER 2:

EFFECT OF AQUEOUS PHASE ANION ON METAL ION EXTRACTION INTO ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

2.1 Introduction

In recent years, there has been growing interest in the application of environmentally benign solvents, including supercritical fluids [1] and, more recently, bio-based diluents [2] and ionic liquids (ILs) [3-5], in liquid-liquid extraction. 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 [6] or analytical-scale radionuclide separation and preconcentration for subsequent determination [7]. 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 [8-11]. 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 (*i.e.,* hydronium ion) [8-10]. 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 [9]. Other recent results suggest that the nature of the IL anion is similarly influential in determining the preferred mode of extraction [12]. 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 [13]. Along these same lines, chloride-containing aqueous phases provide the basis of several analytical-scale actinide separation schemes employing extraction chromatography [14], a form of LLE in which the extractant solution is coated into an inert polymeric support [15]. 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. Several of the results discussed in this chapter have been previously published [16, 17]. Their reproduction here has been approved by the authors.

2.2 Experimental

2.2.1 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 using established methods [18, 19]. Partitioning studies were performed using dicyclohexano-18-crown-6 (DCH18C6) as the extractant. A commercial mixture of the *cis-syn-cis* and *cis-anti-cis* isomers was used as received (Parish Chemical Company, Orem, UT). Aqueous acid solutions were prepared using Milli-Q2 water and Optima™ nitric, hydrochloric (HCl), hydroiodic (HI) or hydrobromic (HBr) acid (Aldrich, Milwaukee, WI) and standardized by titration with certified sodium hydroxide solutions (Ricca, Arlington, TX) using phenolphthalein indicator (Ricca, Arlington, TX). Radiotracers of ^{22}Na, ^{85}Sr and ^{133}Ba were purchased as nominal solutions from Eckert and Ziegler Isotope Products, Inc. (Burbank, CA).

2.2.2 Instruments

Radiometric measurements were carried out by gamma spectroscopy using a PerkinElmer model 2480 automatic gamma counter equipped with WIZARD^2 software (instrument specifications can be obtained from the manufacturer's website [20]). Ionic liquids were characterized by NMR spectroscopy using a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for protons. Spectra were obtained using solutions in chloroform-d (Acros, 100.0% atom D), and all chemical shifts were reported relative to tetramethylsilane. Nitrate and chloride concentrations were determined using a Dionex ICS-1000 ion chromatograph equipped with a 25μL fixed-loop manual injection port, an ASRS 300 cation self-regenerating eluent suppressor, a conductivity detector, Dionex AS18/AG18 analytical and guard columns (4 x 250 and 4 x 50 mm), a Dionex ASRS 300 (4 mm) conductivity suppressor, and 37 mM NaOH eluent (instrument schematics and specifications can be found in the operator's manual [21]). The instrument was operated using Chromeleon software version 6.80. The IC eluent flow rate was 1.00 mL/min and the column temperature was maintained at 30°C.

2.2.3 Methods

Distribution ratios (D_M, defined as $[M]_{org}/[M]_{aq}$ at equilibrium) were determined using commercial radiotracers assayed *via* gamma spectroscopy following standard procedures. In each metal distribution experiment, the organic phase consisted of DCH18C6 dissolved in the ionic liquid of interest. The aqueous phase acid concentration was systematically adjusted by conducting separate experiments for each condition. Unless otherwise noted, metal distribution measurements were performed at 0.1 M DCH18C6 in the organic phase. 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 water or an appropriate aqueous acid solution. Each equilibrated phase was sampled for analysis in at least duplicate, with resulting uncertainties based on counting statistics that were generally within 10%. Additionally, for radiometric measurements, the sum of the count rates in each phase yielded recoveries within 10% of the radiotracer stock solution used, indicating that equilibrium was reached with only two phases involved.

2.3 Metal Ion Extraction from Acidic Nitrate Media

2.3.1 Nitric acid and crown ether dependencies of D_M for extraction into aliphatic alcohols by DCH18C6

Prior work has established that considerable insight into the behavior of IL-based extraction systems can be obtained by comparison to results obtained under the same conditions using a conventional organic solvent, such as 1-octanol [22]. For this reason, our studies began with an examination of the extraction of various alkali and alkaline earth cations from acidic nitrate media into a series of *n*-alochols by dicyclohexano-18-crown-6 (DCH18C6). Figure 2.1 depicts the dependence of the distribution ratio (D_M) of these ions on aqueous nitric acid concentration for extraction into 0.10 M solutions of DCH18C6 in several *n*-alcohols. As can be seen, increasing metal ion extraction (as reflected in the value of D_M) is observed with rising nitric acid (*i.e.,* nitrate) concentration for all solvents studied, an observation consistent with equation 2.1. Note that in these systems, anion co-extraction is required to maintain electroneutrality.

$$Sr^{2+}_{aq} + 2\,NO_3^{-}{}_{aq} + DCH18C6_{org} \rightarrow Sr(NO_3)_2{\bullet}DCH18C6_{org} \quad (2.1)$$

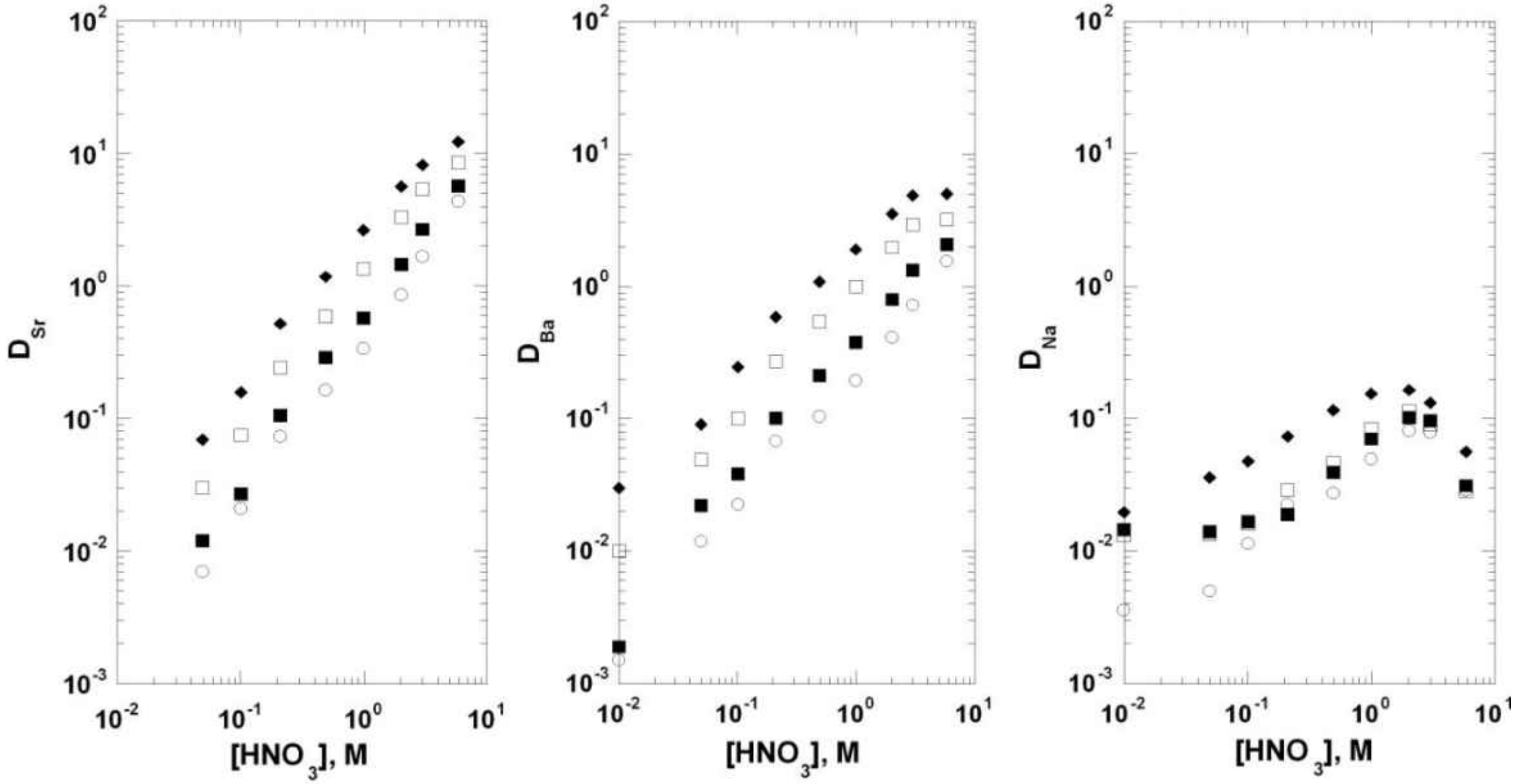

Figure 2.1: Effect of nitric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in *n*-alcohols (◆ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol) [adapted from ref. 17].

For the alkaline earth cations, a slight flattening in the dependency is observed at high nitric acid concentration. In contrast, a more dramatic rollover (*i.e.,* a decrease in D_M) is observed for sodium. This rollover can be attributed to a decrease in the free DCH18C6 concentration due to nitric acid extraction by the crown ether [22]. The absence of such a rollover under identical conditions in the case of strontium and barium is the result of their greater electrostatic charge and the accompanying increase in the metal ion-crown ether complex formation constant [23], which reduces the extent of nitric acid competition for the crown. Comparison of the acid dependencies obtained for the various alcohols shows that a decrease in extraction (D_M) occurs with increasing alcohol hydrophobicity, regardless of the metal ion examined. This decrease is due to the decline in organic phase water content that accompanies greater alcohol hydrophobicity (*i.e.,* alkyl chain length) and the concomitant decrease in the ease of anion co-extraction [24].

Like the acid dependency of D_M, the effect of crown ether concentration on the extraction of the three cations from acidic nitrate media into the *n*-alcohols (Figure 2.2) 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 equation 2.1. 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.) Taken together then, the data show that (as would be expected) the extraction of alkali and alkaline earth cations from acidic nitrate media into *n*-alcohols by DCH18C6 proceeds solely by the partitioning of a neutral metal-crown ether-nitrato complex.

2.3.2. Nitric acid dependency of D_M for extraction into $C_n mim^+ Tf_2N^-$ ILs by DCH18C6

As a next step in the determination of the effect of the aqueous phase anion on the extraction of metal ions into ILs, our studies of extraction from acidic nitrate media were extended to a series of $C_n mim^+ Tf_2N^-$ ILs. It is readily evident from measurements of metal ion extraction into these ionic liquids (Figure 2.3) that extraction here cannot proceed by the same process observed for *n*-alcohol. Interestingly, not only are significant differences observed between ionic liquids and aliphatic alcohols, but also between alkali and alkaline earth metal ions for a given IL. Prior work with strontium ion [9] has shown that a shift in the predominant mode of its transfer into various $C_n mim^+ Tf_2N^-$ ionic liquids in the presence of DCH18C6 accompanies an increase in IL cation hydrophobicity. This shift in the predominant mode of partitioning is reflected in a change in the acid dependency from one in which increasing nitric acid concentration is accompanied by falling D_{Sr} values to one in which these values generally rise as the acidity increases. This conclusion, however, was based on a somewhat limited range of acid concentrations (*i.e.*, those expected to be encountered either in the analytical-scale separation and preconcentration of Sr-89/90 from typical environmental samples [7, 25] or in the process-scale removal of radiostrontium from nuclear waste samples [6, 26]).

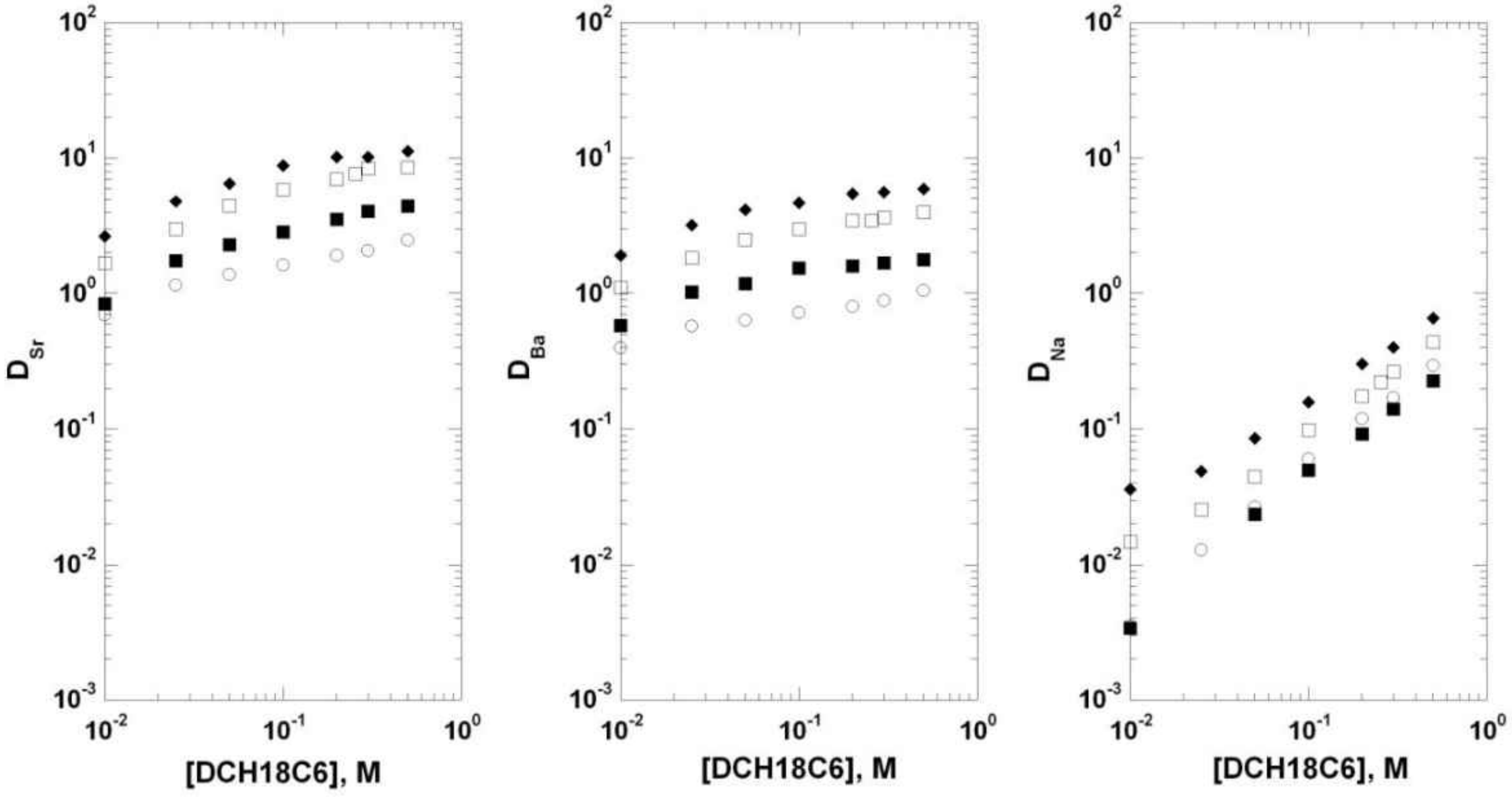

Figure 2.2: Effect of crown ether concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by HNO_3 (3.000 M for Sr^{2+}, 3.008 M for Ba^{2+} and 3.000 M for Na^+) in *n*-alcohol (◆ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

As can be seen for barium and strontium in Figure 2.3, when considered over a wider range of acidities, the variation in D_M with nitric acid concentration for alkaline earth metals is often a rather complex one. In contrast, the alkali metal cation, sodium, is seen to exhibit a steady decrease in D_M with rising aqueous acidity.

In addition to differences in the nature and complexity of the acid dependencies, differences were also observed between aliphatic alcohols and ionic liquids when the issue of the extraction of nitrate anion was considered [17]. In particular, it was found that in the extraction of various alkali and alkaline earth cations from water into a series of $C_n mim^+ Tf_2N^-$ ionic liquids in the presence of DCH18C6, the amount of co-extracted nitrate is frequently less than that required to account for the extraction of the metal ion solely as a neutral complex (Table 2.1). These results suggest that ion exchange involving the cationic constituent of the ionic liquid must also make a significant contribution to the overall extraction. This additional process, shown in equation 2.2, is one in which (in contrast to aliphatic alcohol systems) anion co-extraction is not required.

$$\mathrm{M \bullet DCH18C6^{\mathit{x}+}_{aq}} + x\,\mathrm{C}_n\mathrm{mim^+_{org}} \rightarrow \mathrm{M \bullet DCH18C6^{\mathit{x}+}_{org}} + x\,\mathrm{C}_n\mathrm{mim^+_{aq}} \quad (2.2)$$

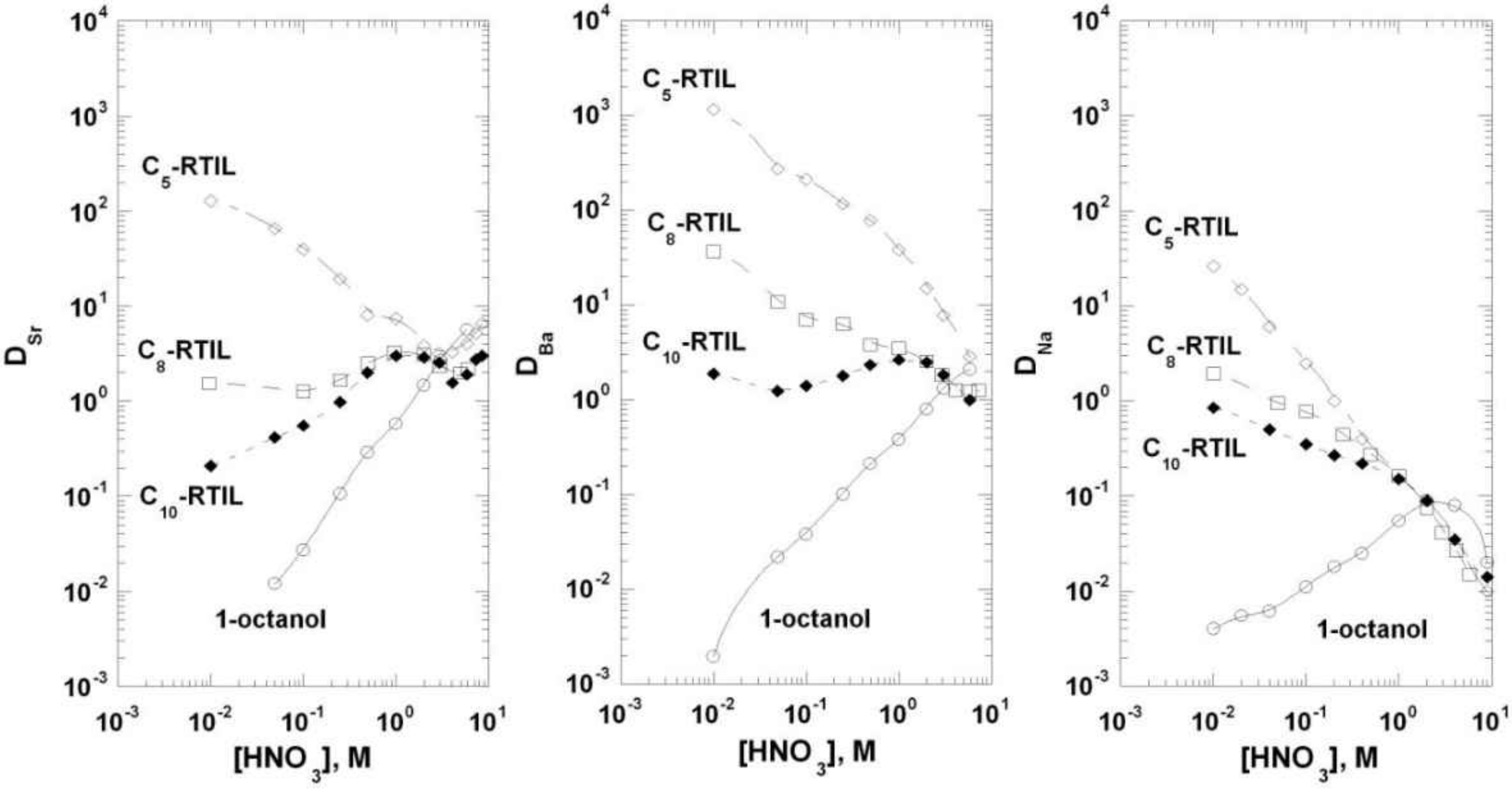

Figure 2.3: Effect of nitric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in $C_n mim^+ Tf_2N^-$ (C_n-RTIL). Data for 1-octanol are provided for purposes of comparison.

Table 2.1
The effect of IL cation chain length on sodium and strontium, nitrate ion partitioning between water and 0.20 M DCH18C6 in $C_n mim^+Tf_2N^-$

Metal	Organic Phase	$\%E_{Sr}$[a]	$\%E_{NO3-.}$[a]	Ratio $\%E_{Sr}/\%E_{NO3-}$	Partitioning Mode Indicated
Na[b]	$C_5mim^+Tf_2N^-$	94.1	1.34 ± 0.02	70.2	cation exchange
	$C_8mim^+Tf_2N^-$	50.3	12.4 ± 0.1	4.06	cation exchange
	$C_{10}mim^+Tf_2N^-$	28.2 ± 2.5	21.0 ± 0.1	1.34	mixed
Sr[c]	$C_5mim^+Tf_2N^-$	94.4 ± 12.8	10.7 ± 0.3	9.0	cation exchange
	$C_8mim^+Tf_2N^-$	45.7 ± 2.4	25.4 ± 0.8	1.8	mixed
	$C_{10}mim^+Tf_2N^-$	23.4 ± 1.0	23.1 ± 0.2	1.0	neutral complex

[a] Uncertainties were calculated at the 95% confidence interval (*n* = 3).
[b] The values shown for sodium extraction are from reference 27.
[c] The values shown for strontium extraction are from reference 17.

To interpret these results and analogous data for Ba^{2+}, K^+ and Cs^+ [9, 17], it is necessary to consider previous work involving the extraction of Sr^{2+} and Na^+ [10, 28], which suggested the presence of three distinct pathways by which a metal ion can be extracted into an ionic liquid in the presence of crown ether (Figure 2.4): the processes described by equation 2.1 and 2.2 above (*i.e.*, partitioning of a neutral metal-nitrato crown ether complex and exchange of a cationic metal-crown ether complex for the cationic component of the IL, respectively) and a third process (equation 2.3), in which the metal ion is exchanged for a hydronium ion extracted by the crown ether, as depicted for the sodium ion:

$$Na^+_{aq} + H_3O{\bullet}DCH18C6^+_{org} \rightarrow H_3O^+_{aq} + Na{\bullet}DCH18C6^+_{org} \quad (2.3)$$

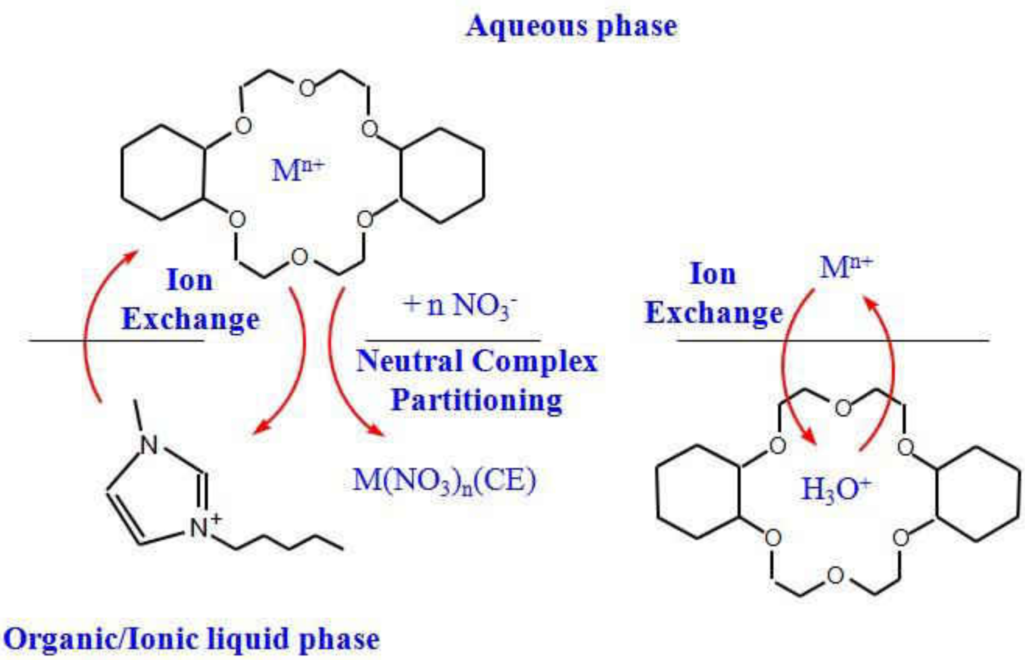

Figure 2.4: The three-path model for metal ion partitioning between nitric acid solution and $C_n mim^+Tf_2N^-$ ionic liquids in the presence of DCH18C6.

Examination of Figure 2.3 (right panel) with these possible processes in mind indicates that for sodium ion, ion-exchange is the predominant mode of partitioning, since as the concentration of nitrate increases, the extraction of sodium decreases. This trend was observed for sodium extraction regardless of the ionic liquid, indicating that IL cation hydrophobicity does not play a role in the mode of partitioning here. IL cation hydrophobicity does, however, play a role in the overall extraction efficiency (*i.e.*, D_M values). As can be seen by comparison of distribution ratios obtained for a given metal ion into C_5mim^+ and $C_{10}mim^+$, the more hydrophilic the IL cation, the greater the extraction observed, an observation consistent with the greater difficulty in transferring the more hydrophobic $C_{10}mim^+$ cation to the aqueous phase (equation 2.2). Essentially identical observations were made concerning both the IL hydrophobicity and the predominant mode of partitioning for potassium and cesium in extraction under the same conditions. Thus, the extraction of monovalent cations apparently occurs predominantly *via* ion-exchange in these systems [17].

Contrary to observations for the monovalent cations, the alkyl chain length of the ionic liquid cation does appear to affect the mode of partitioning of the divalent cations examined. As can be seen for strontium in Figure 2.3 (left panel), as the hydrophobicity of the ionic liquid cation increases, the mode of partitioning shifts from ion-exchange (*i.e.* decreasing extraction with increasing nitrate concentration, as seen with $C_5mim^+Tf_2N^-$) to neutral complex partitioning (*i.e.*, increasing extraction with increasing nitrate concentration, as seen with $C_{10}mim^+Tf_2N^-$). A similar trend is observed with barium (Figure 2.3, middle panel). Taken together, the results obtained here indicate that the extraction of all of the alkali and alkaline earth cations examined proceeds *via* the three-path scheme described in Figure 2.4, the balance among the various paths being determined by the aqueous acidity, the IL cation hydrophobicity, and the charge on the metal ion.

2.4 Metal Ion Extraction from Acidic Chloride Media

2.4.1 Hydrochloric acid and crown ether dependencies of D_M for extraction into aliphatic alcohols by DCH18C6

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 again 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 $C_n\text{mim}^+\text{Tf}_2\text{N}^-$ ionic liquids in the presence of DCH18C6 continued with an examination of their extraction into a series of aliphatic alcohols under the same conditions. As was the case for extraction from acidic nitrate media, the extraction of a metal cation by a neutral extractant (*e.g.,* a crown ether) into such solvents requires co-extraction of an aqueous phase anion to maintain electrical neutrality. Thus, extraction in these systems must involve partitioning of a neutral complex [24] as shown in equation 2.4.

$$\text{Sr}^{2+}_{\text{aq}} + 2\,\text{Cl}^-_{\text{aq}} + \text{DCH18C6}_{\text{org}} \rightarrow \text{SrCl}_2{\bullet}\text{DCH18C6}_{\text{org}} \quad (2.4)$$

Accordingly, as shown in Figure 2.5, which depicts the dependency of the distribution ratio, D_M, on the concentration of hydrochloric acid 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). This is the same general trend observed for aliphatic alcohols in extraction from acidic nitrate media (Figure 2.1). Also, as was the case in nitrate systems, 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 [23]. 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 [24, 29]. As would be expected from chlorides higher hydration energy and the accompanying greater difficulty in dehydrating the co-extracted anion [24], 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 concentrations (Figure 2.6) is also consistent with the partitioning of a neutral complex, similar to what was observed in nitrate media (Figure 2.2). 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 equation 2.4. As also seen with nitrate-containing aqueous phases, the divalent cations exhibit extractant dependencies that are nearly flat, attributed in previous work [22] to differences in the propensity of monovalent and divalent ions to form an aqueous phase complex with DCH18C6.

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

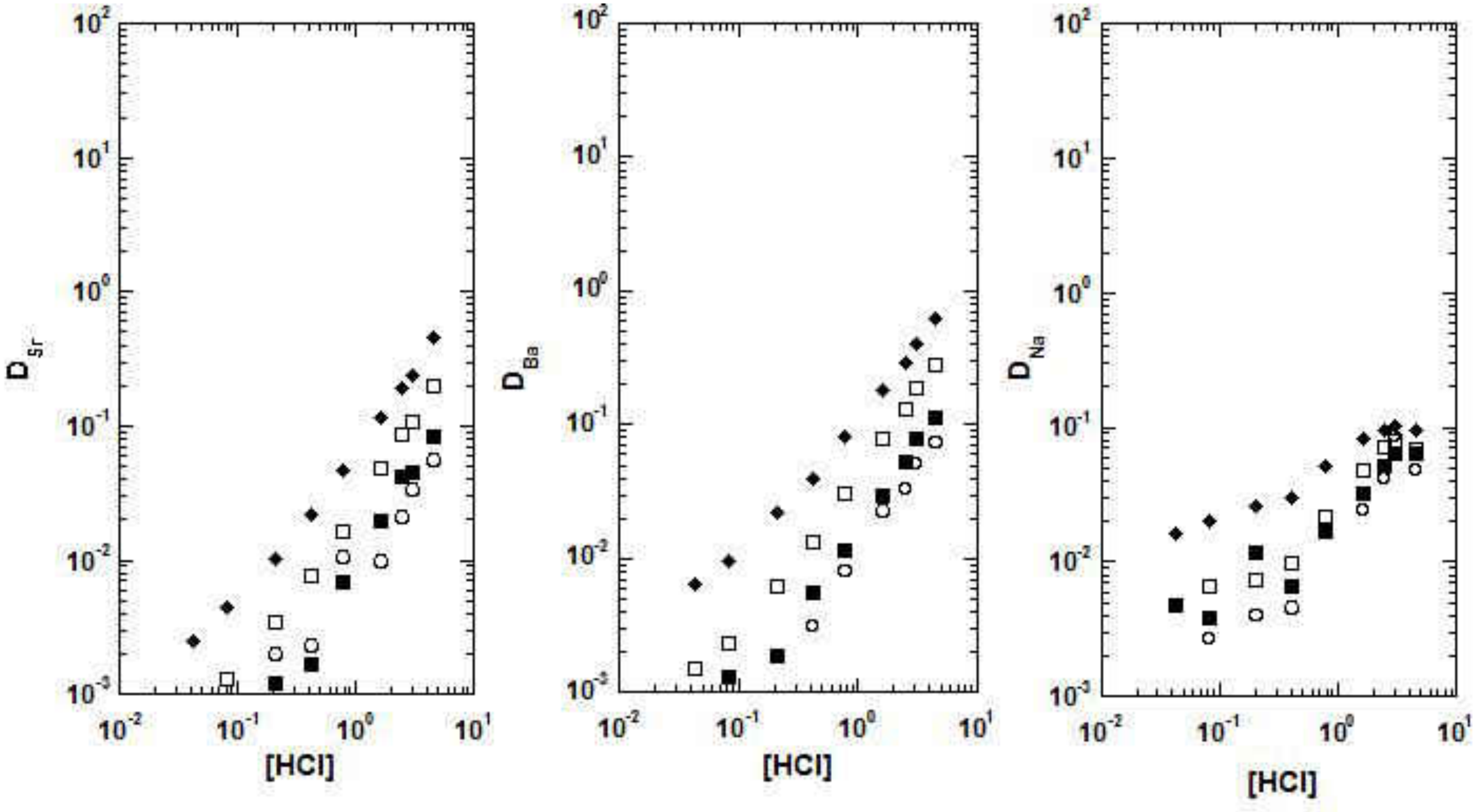

Figure 2.5: Effect of hydrochloric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^{+} (right panel) by DCH18C6 (0.10 M) in *n*-alcohol (◆ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

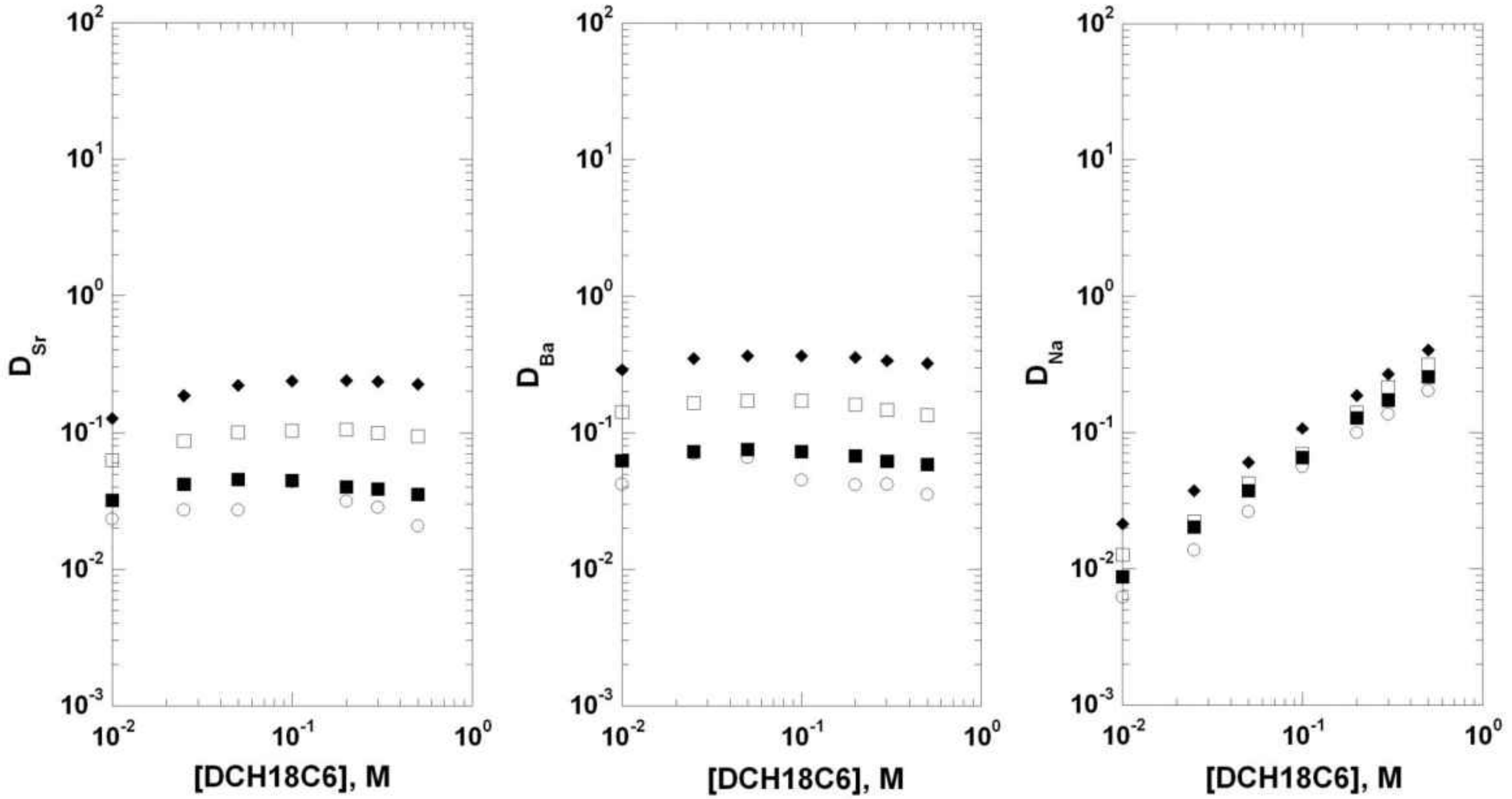

Figure 2.6: Effect of crown ether concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^{+} (right panel) by HCl (3.070 M for Sr^{2+} and Ba^{2+} and 3.286 M for Na^{+}) in *n*-alcohol (◆ = 1-pentanol, □ = 1-hexanol, ■ = 1-octanol, and ○ = 1-decanol).

2.4.2 Chloride anion co-extraction into $C_n mim^+Tf_2N^-$ ILs upon metal ion extraction by DCH18C6

That this is not the case for the ionic liquids is readily evident from an examination of the results presented in Table 2.2, which summarize measurements of the extraction of chloride, in addition to strontium, between water and several $C_n mim^+Tf_2N^-$ ILs in the presence of DCH18C6.

Table 2.2
The effect of IL cation chain length on strontium and chloride ion partitioning between water and 0.20 M DCH18C6 in $C_n mim^+Tf_2N^-$

Organic Phase	$\%E_{Sr}$[a]	$\%E_{Cl-.}$[a]	Ratio $\%E_{Sr}/\%E_{Cl-}$	Partitioning Mode Indicated
$C_5mim^+Tf_2N^-$	94.5 ± 5.3	12.6 ± 0.1	7.5	cation exchange
$C_8mim^+Tf_2N^-$	21.6 ± 1.2	6.5 ± 0.1	3.3	cation exchange
$C_{10}mim^+Tf_2N^-$	3.5 ± 0.2	10.9 ± 0.1	0.3	neutral complex

[a] Uncertainties were calculated at the 95% confidence interval ($n = 3$).

If the partitioning of a neutral complex were the sole mode of cation extraction in these systems, then the percentage extraction of chloride and of the strontium ion would correspond throughout. As can be seen, however, this is not observed. Rather, in most instances, the fraction of chloride extracted is far less than the corresponding fraction of strontium extracted, consistent with a significant contribution of ion exchange involving the cationic constituent of the IL (a process shown in equation 2.2). As shown in Table 2.1, this is also the case for nitrate extraction in these systems, further confirming that systems utilizing ionic liquids as the organic phase are far more complex than aliphatic alcohols, regardless of aqueous phase.

As shown previously for strontium extraction in nitrate media, for which increasing IL cation hydrophobicity (*i.e.*, $C_5mim^+Tf_2N^-$ to $C_{10}mim^+Tf_2N^-$) was accompanied by a diminished contribution of ion exchange to the overall extraction process, the ratio of strontium extraction to chloride extraction decreases from $C_5mim^+Tf_2N^-$ to $C_8mim^+Tf_2N^-$, a decrease consistent with a shift from cation exchange to neutral complex formation, albeit one that occurs less quickly than in nitrate media. (That is, the ratio of metal to anion extraction is greater in chloride media for $C_8mim^+Tf_2N^-$ than it is in nitrate media.) This observation can be attributed to the differences in the hydration enthalpies of the two anions (-314 kJ/mol vs. -381 kJ/mol for nitrate and chloride, respectively [30]), which results in more facile co-extraction of nitrate. Curiously, as shown in Table 2.2, for $C_{10}mim^+Tf_2N^-$, three times more chloride is extracted than strontium (*i.e.,* $\%E_{Sr}/\%E_{Cl^-} = 0.3$), an observation not consistent with the 1:1 ratio expected for extraction *via* neutral complex (ion pair) partitioning. At present, no explanation can be provided for the unexpectedly high levels of chloride present. The most likely explanation, that the ionic liquid itself extracts chloride, has been ruled out (< 0.1% chloride extracted in the absence of the crown ether). Further investigation is clearly required.

2.4.3 Acid dependency of D_{Sr} for extraction from chloride media into $C_nmim^+Tf_2N^-$ ILs by DCH18C6

Figure 2.7 shows the hydrochloric acid dependency of D_M for Na^+, Sr^{2+}, and Ba^{2+} for their extraction into $C_5mim^+Tf_2N^-$, $C_8mim^+Tf_2N^-$ and $C_{10}mim^+Tf_2N^-$. As can be seen (left panel), the extraction of strontium exhibits a significant decline as the acidity rises until *ca.* 2M HCl, above which an increase is observed. As noted previously [8], 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. This is, at low acidity, the cationic strontium-crown ether complex, $Sr{\bullet}DCH18C6^{2+}$, is exchanged for the cationic constituent of the ionic liquid, according to the following equation [8, 9]:

$$Sr{\bullet}(DCH18C6)^{2+}{}_{aq} + 2C_n\text{mim}^{+}{}_{org} \rightarrow Sr(DCH18C6)^{2+}{}_{org} + 2C_n\text{mim}^{+}{}_{aq} \qquad (2.5)$$

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 same solvents, again by DCH18C6, into nitric acid [10]:

$$Sr^{2+}{}_{aq} + 2\ H_3O{\bullet}DCH18C6^{+}{}_{org} \rightarrow 2\ H_3O^{+}{}_{aq} + Sr{\bullet}DCH18C6^{+}{}_{org} + DCH18C6_{org} \qquad (2.6)$$

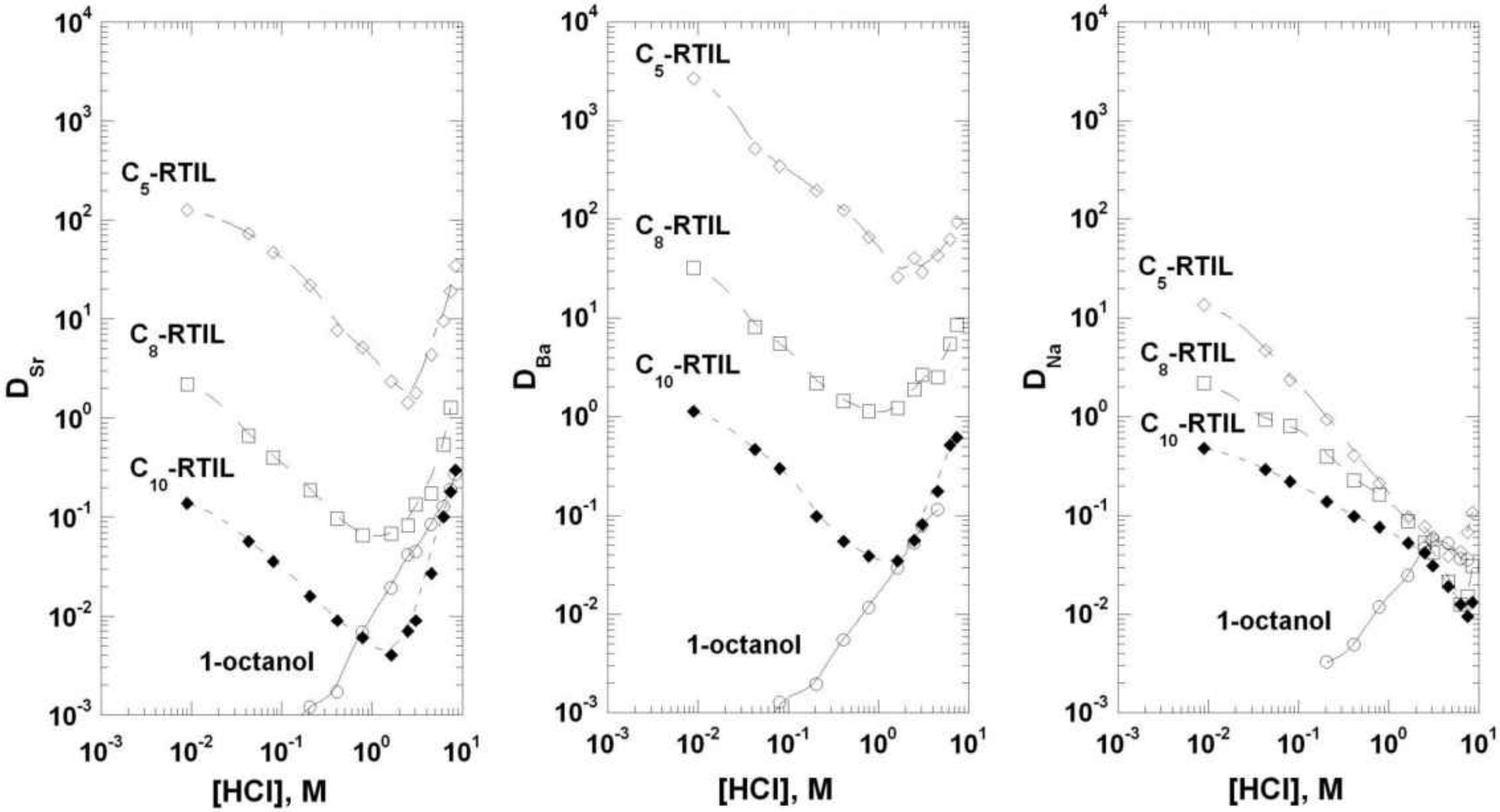

Figure 2.7: Effect of hydrochloric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in $C_n mim^+ Tf_2N^-$ (C_n-RTIL). Data for 1-octanol are provided for purposes of comparison.

At still higher acidities (*i.e.* ≥ 2M 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 (Figure 2.3, 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 (equation 2.5) [9]. 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 uptrend 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.

2.4.4 Metal ion extraction into $C_{10}mim^+Tf_2N^-$: Comparison of halide anions

In an effort to confirm this, the acid dependency of D_{Sr} was determined for two additional acids, hydroiodic acid (HI) and hydrobromic acid (HBr), whose anions are more readily dehydrated than chloride [30], which in extraction systems employing conventional solvents, would be expected to lead to higher extraction efficiency. As shown in Figure 2.8, 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 (-305 kJ/mol, -347 kJ/mol and -381 kJ/mol for I^-, Br^- and Cl^-, respectively [30]). 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.

2.4.5 Acid dependency of D_M for extraction from chloride media into $C_nmim^+Tf_2N^-$ ILs by DCH18C6

Measurements of the hydrochloric acid dependency of barium ion extraction into the $C_nmim^+Tf_2N^-$ ILs in the presence of DCH18C6 (Figure 2.7, middle panel) yield results consistent with 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).

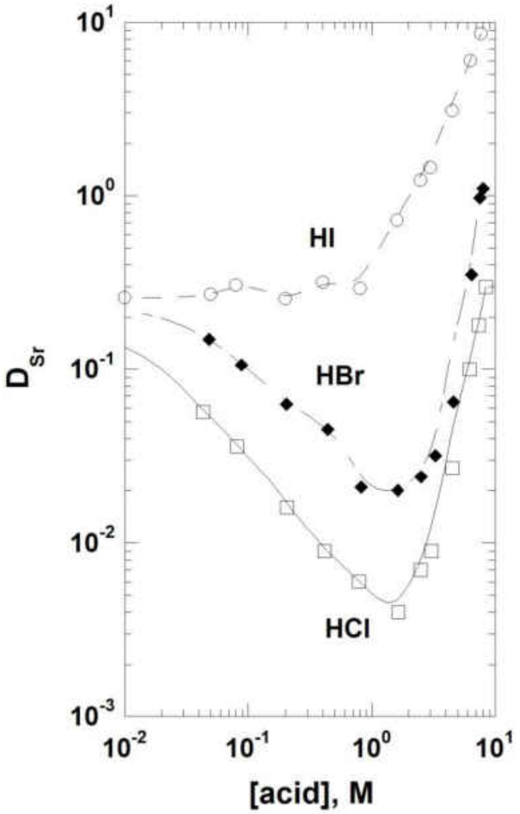

Figure 2.8: Effect of acid (hydroiodic, hydrobromic, and hydrochloric) concentration on the extraction of Sr^{2+} by DCH18C6 (0.10 M) in $C_{10}mim^+Tf_2N^-$.

Also shown in Figure 2.7 (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 *via-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), as well as with prior reports for nitrate [17] suggesting a gradual shift from ion exchange involving the IL cation to a reaction of the type depicted in equation 2.3, which involves exchange of Na^+ for a hydronium ion extracted by the crown ether. Not unexpectedly, the distribution ratios of sodium are considerably lower than those observed for strontium and barium under a given set of conditions.

2.4.6 Crown ether dependency of D_M for extraction into $C_n mim^+ Tf_2N^-$ ILs by DCH18C6

Despite obvious differences in the acid dependencies of D_M for the various alkali and alkaline earth metal ions, in all three cases the crown ether extractant dependencies observed are consistent with the partitioning of a 1:1 metal ion: crown ether complex. In particular, the log-log plot of D_M versus [DCH18C6] at constant hydrochloric acid concentration for sodium (Figure 2.9, right panel) yields a line of near-unit slope.

In contrast, strontium (Figure 2.9, left panel) exhibits an increase in extraction (*i.e.*, D_{Sr}) with increasing crown ether concentration up to *ca.* 0.1 M, above which the extraction decreases; the same trends are observed for barium (Figure 2.9, middle panel). Two possible explanations for this unusual observation come to mind. First, as the extractant concentration is raised, the ionic liquid is, in effect, increasingly "diluted" with a molecular (*i.e.,* non-ionic) species, perhaps diminishing the extractability of metal complexes. An alternative (and much more likely) explanation is found by examining equation 2.6.

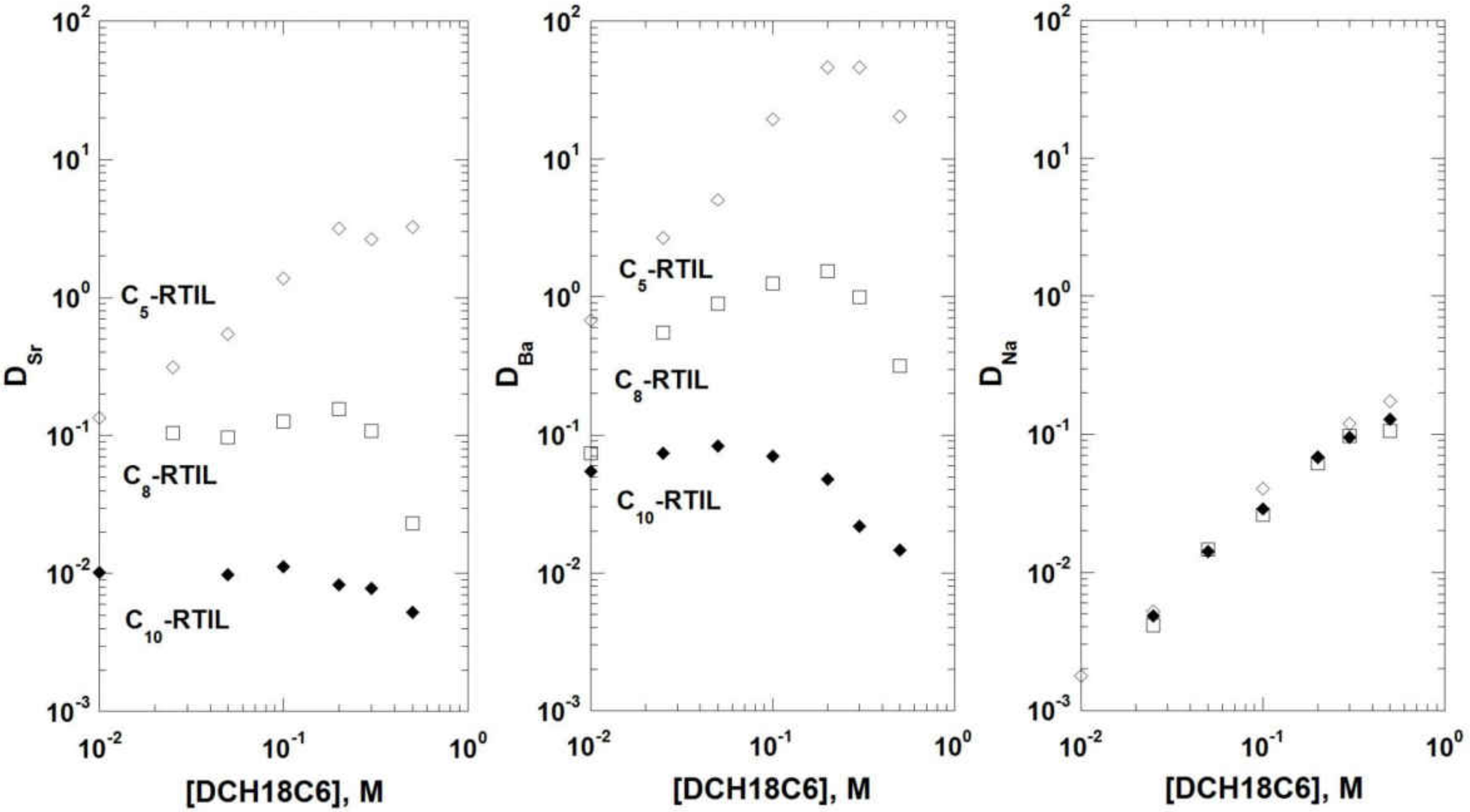

Figure 2.9: Effect of crown ether concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^{+} (right panel) from 3.070 M HCl into $C_n$mim^{+}Tf$_2$N^{-} (C_n-RTIL).

As can be seen, extraction of a divalent cation such as Sr^{2+} by the ion-exchange pathway involving its exchange for a crown ether-complexed hydronium ion is accompanied by release of a DCH18C6 molecule to the IL phase. Mass action considerations therefore mean that high $[DCH18C6]_{IL}$ actually acts against extraction. This is not the case with monovalent cations, where for every metal ion extracted, only *one* hydronium:DCH18C6 species is involved (equation 2.3), and in fact, D_{Na} extractant dependencies do not show declines at high [DCH18C6].

2.5 Conclusions

The results of this study clearly demonstrate that the extraction of alkali and alkaline earth cations from acidic 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 these 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.*, its 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 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 [8-11], 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 [8-10, 17], 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 a metal ion.

2.6 Acknowledgements

Dr. Cory Hawkins is gratefully acknowledged both for his intellectual contributions to this work and for his assistance with many of these experiments. The financial support of the Office of Basic Energy Sciences of the United States Department of Energy under the Single Investigator Small Group Research (SISGR) Program through sub-contract with Brookhaven National Laboratory is also gratefully acknowledged.

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CHAPTER 3:

EFFECT OF IONIC LIQUID ANION ON METAL ION EXTRACTION INTO ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

3.1 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. 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) [2], the extractant [3], and the ionic liquid itself [4, 5]. 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 [6]. As has recently been shown, such changes can have a significant influence on metal ion extraction efficiency and selectivity [2].

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 [7] , for example, examined the extraction of Ag^+ by dithizone into 1-butyl-3-methylimidazolium hexafluorophosphate (PF_6^-) and its *bis*[(trifluoromethyl)sulfonyl]imide (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.* [8, 9] , the suitability of 1-butyl-3-methylimidazolium-based ILs incorporating either PF_6^- or 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 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^- [5] or nonaflate (NfO^-) [4] 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.* [10] has explored IL anion (PF_6^- *vs*. Tf_2N^- *vs.* $BETI^-$, where $BETI^-$ represents the *bis*[(perfluoroethane) 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. The 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 this 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 anion hydrophobicity on the predominant mode(s) of metal ion partitioning observed.

3.2 Experimental

3.2.1 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 [11, 12] , while the PF_6^{-} ILs were purchased (IoLiTec, Tuscsaloosa, AL) and used without further purification. Partitioning studies were completed using dicyclohexano-18-crown-6 (DCH18C6) as the extractant. A commercial mixture of the *cis-syn-cis* and *cis-anti-cis* isomers was used as received (Parish Chemical Company, Orem, UT). Aqueous acid solutions were prepared using Milli-Q2 water and Optima™ nitric or hydrochloric acid (Aldrich, Milwaukee, WI) and standardized by titration with certified sodium hydroxide solutions (Ricca, Arlington, TX) using phenolphthalein indicator (Ricca, Arlington, TX). Radiotracers of ^{22}Na, ^{85}Sr and ^{133}Ba were purchased as nominal solutions from Eckert and Ziegler Isotope Products, Inc. (Burbank, CA).

3.2.2 Instruments

Radiometric measurements were carried out using gamma spectroscopy, which was performed using a PerkinElmer model 2480 automatic gamma counter equipped with WIZARD^2 software. Ionic liquid characterization was carried out by NMR spectroscopy. All spectra were acquired on a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for protons. Spectra were obtained using solutions in chloroform-d (Acros, 100.0% atom D) and all chemical shifts were reported relative to tetramethylsilane. Aqueous nitrate concentrations were determined using a Dionex ICS-1000 ion chromatograph equipped with a 25µL fixed-loop manual injection port, an ASRS 300 cation self-regenerating eluent suppressor, a conductivity detector, Dionex AS18/AG18 analytical and guard columns (4 x 250 and 4 x 50 mm), a Dionex ASRS 300 (4 mm) conductivity suppressor, and 37 mM NaOH eluent. The instrument was operated using Chromeleon software version 6.80. IC eluent flow rates were 1.00 mL/min and the column temperature was maintained at 30°C. The water content of each IL was measured using a Metrohm 870 KF Titrino Plus coulometer using hydranal (Aldrich Chemical, Milwaukee, WI) as the titrant. The solubility of each IL in water was measured by UV-visible absorption using a Shimadzu UV-2450 spectrophotometer equipped with matching 10-mm pathlength quartz cuvettes.

3.2.3 Methods

Distribution ratios (D_M, defined as $[M]_{org}/[M]_{aq}$ at equilibrium) were determined with commercial radiotracers assayed *via* gamma spectroscopy using standard procedures. In each metal distribution experiment, the organic phase consisted of DCH18C6 dissolved in the ionic liquid of interest. The aqueous phase concentration was systematically adjusted by conducting separate experiments for each condition. Unless otherwise noted, metal distribution measurements were performed at 0.1 M DCH18C6 in the organic phase. 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 water or an appropriate aqueous acid solution. Each equilibrated phase was sampled for analysis in at least duplicate, with resulting uncertainties based on counting statistics that were generally within 10%. Additionally, for radiometric measurements, the sum of the count rates in each phase yielded recoveries within 10% of that of the radiotracer stock solution added, thus indicating that equilibrium was reached with only two phases involved.

The density of each ionic liquid was determined by weighing a known volume measured by a calibrated micropipette or a volumetric flask. All measurements for "dry" ionic liquids were performed using materials that had been dried *in vacuo* at 80°C for at least 24 hours in small quantities (≤ 3 mL) to facilitate the removal of water. Samples used in the measurement of the mutual solubility of ionic liquids with water were prepared by contacting a 1 mL aliquot of the IL with a 10 mL portion of deionized (18 MΩ) water. Specifically, samples were vortexed for 10 minutes and then allowed to stand undisturbed to equilibrate for 1 hour. Following centrifugation at 3000 rpm to ensure complete disengagement, the aqueous phase was taken and diluted as needed for solubility measurements, while the organic phase was used for water content measurements. The water solubility of the ionic liquids was measured by UV-visible spectrophotometry at the wavelength characteristic of the imidazolium ring (210 nm) using standards prepared from a known weight of the dry IL. All standards and IL samples were prepared in a 50:50 (v/v) methanol:water solution. The water content of the ILs was measured using a Metrohm 870 KF Titrino Plus coulometer using hydranal (Aldrich Chemical, Milwaukee, WI) as the titrant and 18 MΩ water for calibration.

3.3 Effect of IL Anion on the Mutual Solubility of ILs and Water

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.* [10] 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 [13], a process known to be undesirable [14]. 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 formation 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 were also examined, as were the same IL anions, with the objective of understanding the interplay of all of these factors in governing the nature of the extraction process.

Table 3.1 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 $C_n\text{mim}^+$ 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 Liu *et al.*[10], specifically $PF_6^- < Tf_2N^- < BETI^-$, and are indicative of significant differences among the three anions.

Table 3.1

Effect of ionic liquid anion on the water content and water solubility for various $C_n mim^+$ ILs.

	$[C_5mim^+][X]$			$[C_8mim^+][X]$			$[C_{10}mim^+][X]$		
	PF_6^-	Tf_2N^-	$BETI^-$	PF_6^-	Tf_2N^-	$BETI^-$	PF_6^-	Tf_2N^-	$BETI^-$
Molecular weight (g/mol)	298.1	429.4	529.5	340.3	443.5	575.5	368.1	503.5	603.5
Density “dry” (g/mL)	1.29	1.35	1.51	1.22 / 1.22[b]	1.28	1.45	1.18	1.29	1.38
Water content “dry” (ppm)	425	<10	NM[a]	<10 / 388[b]	<10	NM[a]	<10	<10	NM[a]
Water content “wet” (ppm)	19260	17100	3880	15883 / 6666[b]	11500	4000	11375	10400	5600
Solubility in H_2O (ppm)	11262	2150	3779	2158	990	227	736	310	114

[a] Due to a limited quantity of sample, the water content value was not measured.
[b] Reference 15.

3.4 Metal Ion Extraction into $C_n$mim$^+$ Ionic Liquids from Acidic Chloride Media

Figures 3.1 and 3.2 show the hydrochloric acid dependency of the extraction of a representative monovalent and divalent metal cation (*i.e.* Na^+ and Sr^{2+}, respectively) by a 0.1 M solution of DCH18C6 in the various $C_n$mim$^+$ ionic liquids. For Na^+, it can be seen that for all ILs studied, a significant decline in sodium partitioning (*i.e.* the distribution ratio) generally occurs as the acidity rises, regardless of the anion hydrophobicity. This observation is consistent with results previously obtained for the same cation in its extraction from acidic nitrate media into several $C_n$mim$^+$$Tf_2N^-$ ILs [16], and suggests that ion-exchange is the predominate mode of sodium ion partitioning in these systems under most conditions. As can also be seen from Figure 3.1, for a given IL anion, D_{Na} falls as the hydrophobicity of the IL cation increases. Regardless of the IL anion, as the acid concentration increases, the magnitude of this decline generally diminishes, suggesting a gradual shift from ion-exchange involving the cationic constituent of the ionic liquid (equation 3.1) to an exchange of Na^+ for a hydronium ion extracted by the crown ether, as shown in equation 3.2:

$$\mathrm{Na{\bullet}DCH18C6_{aq}^{+}} + \mathrm{C}_n\mathrm{mim^{+}_{org}} \rightarrow \mathrm{Na{\bullet}DCH18C6^{+}_{org}} + \mathrm{C}_n\mathrm{mim^{+}_{aq}} \qquad (3.1)$$

$$\mathrm{Na^{+}_{aq}} + \mathrm{H_3O{\bullet}DCH18C6^{+}_{org}} \rightarrow \mathrm{Na{\bullet}DCH18C6^{+}_{org}} + \mathrm{H_3O^{+}_{aq}} \qquad (3.2)$$

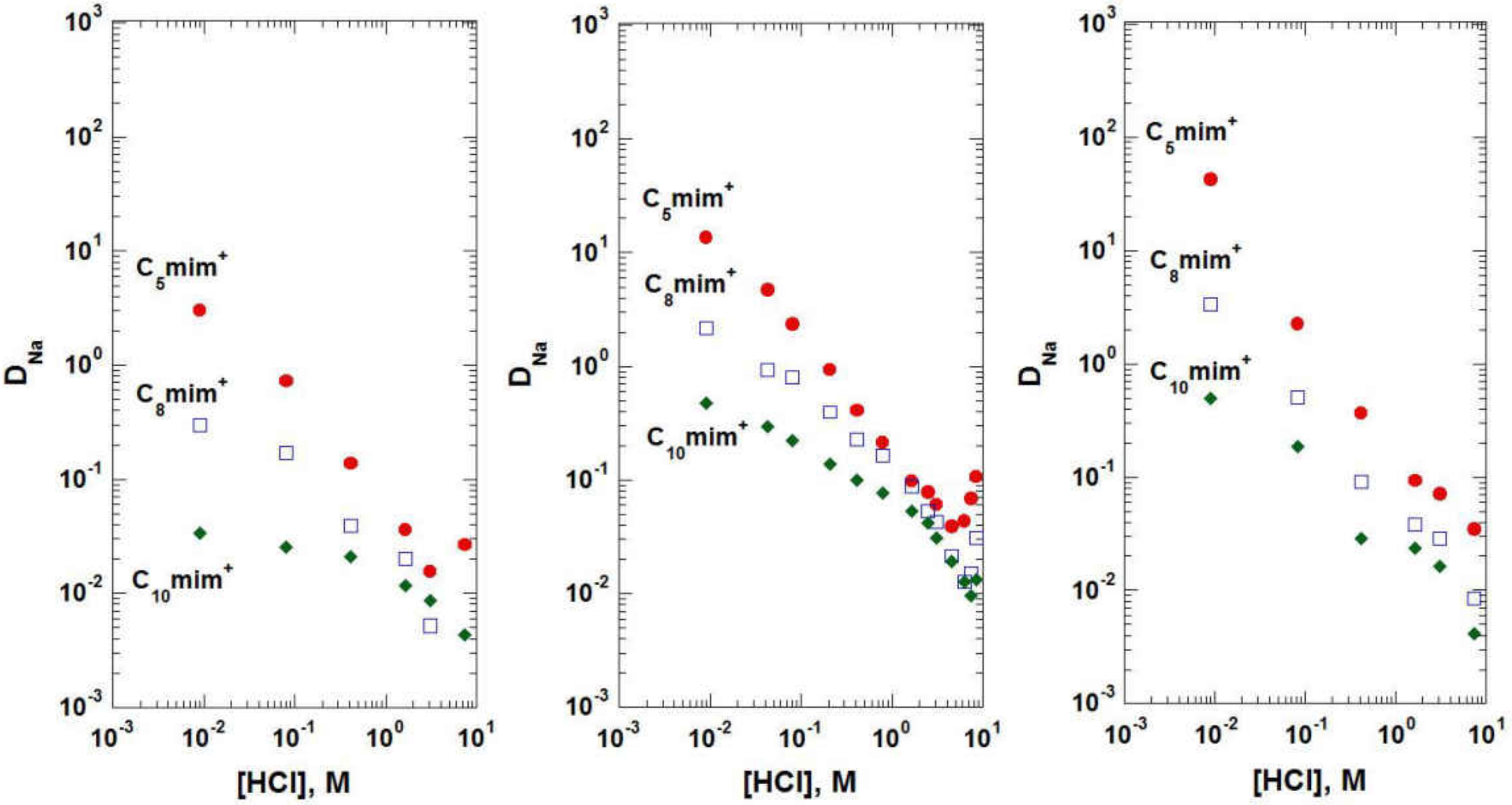

Figure 3.1: Effect of hydrochloric acid concentration on the extraction of Na^+ by DCH18C6 (0.10 M) in $C_n mim^+ PF_6^-$ (left panel), $C_n mim^+ Tf_2N^-$ (middle panel, adapted from reference 13), and $C_n mim^+ BETI^-$ (right panel).

Given the adverse effect of ion exchange (*i.e.* loss of IL cation to the aqueous phase), such processes are clearly less desirable than is the extraction of a neutral metal-chloro crown ether complex.

Interestingly, it appears that the extraction of a neutral sodium-chloro-DCH18C6 complex does occur under certain conditions. That is, close examination of the acid dependencies for two of the C_5mim^+ ILs shown in Figure 3.1 reveals an upturn in sodium extraction at very high aqueous chloride concentrations (*i.e.*, high [HCl]). In particular, at HCl concentrations exceeding *ca*. 3 M, D_{Na} rises when $C_5mim^+PF_6^-$ is employed. An analogous upturn in D_{Na} is not observed for the corresponding Tf_2N^- IL until the [HCl] exceeds 4-5 M and is not observed for the $BETI^-$ IL, even at 8 M HCl. These observations are fully consistent with the relative hydrophobicity of the three ILs. That is, for a comparatively hydrophilic IL (here, the $C_5mim^+PF_6^-$), a greater aqueous concentration of C_5mim^+ would be expected. Mass action considerations, such as described by Luo *et al.* [10], indicate that the presence of this dissolved IL cation would suppress the IX process depicted in equation 3.1, thereby favoring neutral complex extraction. For a less hydrophilic IL (here, the Tf_2N^- salt), the lower aqueous concentration of the IL cation would render ion exchange somewhat more favorable, delaying the observation of neutral complex extraction until higher aqueous chloride concentrations are present. For the even more hydrophobic BETI IL, neutral complex extraction becomes even less likely, and in fact, is not observed over the range of acidities considered.

That neutral complex extraction represents a more important mode of partitioning for a *divalent* cation from aqueous chloride solution is readily apparent from examination of the hydrochloric acid dependency of D_{Sr} for the series of ionic liquids (Figure 3.2). As can be seen, for all of the ionic liquids examined, a decrease in extraction is observed with increasing acidity only up to *ca.* 1-2 M HCl, above which a flattening or upturn in the acid dependency is observed. As noted above, such an increase in extraction with aqueous acidity is consistent with the partitioning of a neutral metal complex (equation 3.3) at high acidities (*i.e.,* high aqueous acid concentrations). At low acidities, the decline observed is likely due to a combination of two ion-exchange processes, one in which the cationic strontium-crown ether complex, $Sr{\bullet}DCH18C6^{2+}$ is exchanged for the cationic constituent of the ionic liquid (as shown in equation 3.4) and a second process (equation 3.5) analogous to that described earlier for sodium ion (equation 3.1). In the declining segment of the acid dependency, as the acidity rises, the latter process gradually replaces the former.

$$Sr^{2+}_{aq} + 2Cl^{-}_{aq} + DCH18C6_{org} \rightarrow SrCl_2{\bullet}DCH18C6_{org} \qquad (3.3)$$

$$Sr(DCH18C6)^{2+}_{aq} + 2\ C_n mim^{+}_{org} \rightarrow Sr(DCH18C6)^{2+}_{org} + 2\ C_n mim^{+}_{aq} \qquad (3.4)$$

$$Sr^{2+}_{aq} + 2\ H_3O{\bullet}DCH18C6^{+}_{org} \rightarrow Sr{\bullet}DCH18C6^{2+}_{org} + 2\ H_3O^{+}_{aq} + DCH18C6_{org} \qquad (3.5)$$

The D_{Sr} decline that is observed as the chain length on the imidazolium cation is increased (*i.e.,* from $n = 5$ to $n = 10$) is consistent with the greater difficulty encountered in transferring a more hydrophobic IL cation to the aqueous phase (equation 3.4). At higher acidities (*i.e.*, ≥ 2 M HCl), the acid dependency for strontium extraction is seen to turn up, with a sometimes-significant increase in extraction accompanying increasing acidity, consistent with the partitioning of a neutral complex (equation 3.3).

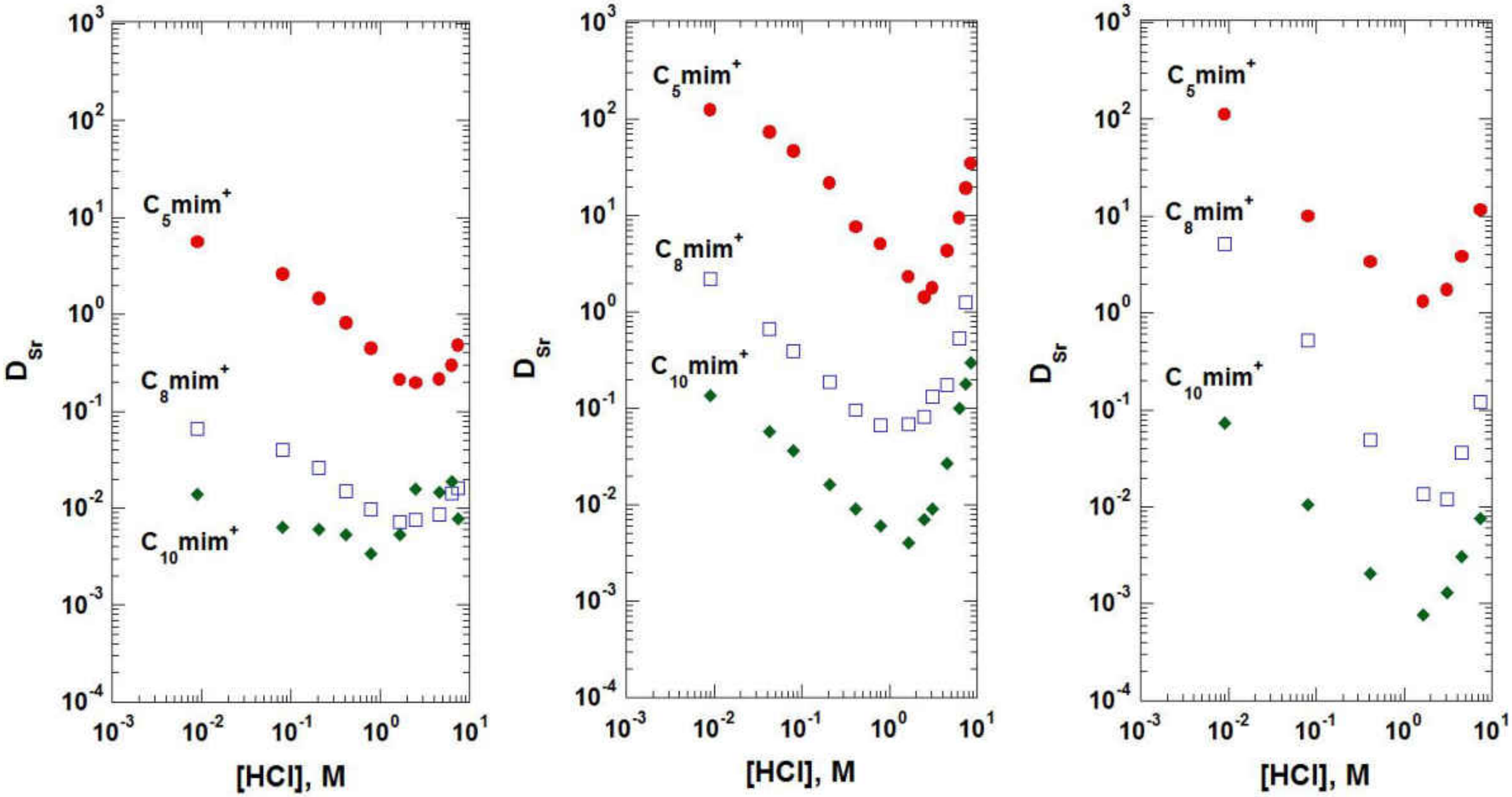

Figure 3.2. Effect of hydrochloric acid concentration on the extraction of Sr^{2+} by DCH18C6 (0.10 M) in $C_n mim^+ PF_6^-$ (left panel), $C_n mim^+ Tf_2N^-$ (middle panel, adapted from reference 13), and $C_n mim^+ BETI^-$ (right panel).

In contrast to changes in IL cation hydrophobicity, for which the effect on the acid dependency of D_{Sr} is readily evident, the effects induced by changes in IL anion hydrophobicity are less obvious. In fact, for the C_5mim^+ cation, an increase in anion hydrophobicity has little apparent effect on the extraction of strontium. That is, all three ionic liquids exhibit a decline in extraction until *ca.* 2 M HCl, above which an increase in D_{Sr} is observed. Evidently, the propensity of ILs incorporating very hydrophilic cations to undergo ion exchange is so strong as to overwhelm effects arising from changes in IL anion hydrophobicity. For the comparatively hydrophobic $C_{10}mim^+$ cation, the effect of changing the IL anion is more apparent. That is, as noted above, when PF_6^- is employed as the IL anion, relatively high (*vs*. Tf_2N^- or $BETI^-$) concentrations of the IL cation would be expected in the aqueous phase, suppressing ion exchange. Indeed, as shown in Figure 3.2 (left panel), the decline in D_{Sr} with rising aqueous acidity associated with ion exchange is far less pronounced for the PF_6^- anion than for the more hydrophobic Tf_2N^- and $BETI^-$ anions, as would be anticipated.

3.5 Metal Ion Extraction into C_nmim^+ Ionic Liquids from Acidic Nitrate Media

The effect of changes in IL anion upon the “balance of pathways” (*i.e.*, ion exchange *vs*. neutral complex formation) in the extraction process is more readily discerned from an examination of strontium extraction into the various imidazolium ionic liquids from aqueous nitrate solution (Figure 3.3). As can be seen, for the $C_nmim^+PF_6^-$ ILs (left panel), a significant decrease in extraction with increasing acidity is not observed even for the most hydrophilic IL cation (*i.e.,* C_5mim^+), consistent with a limited contribution of ion exchange to the overall partitioning process under all conditions.

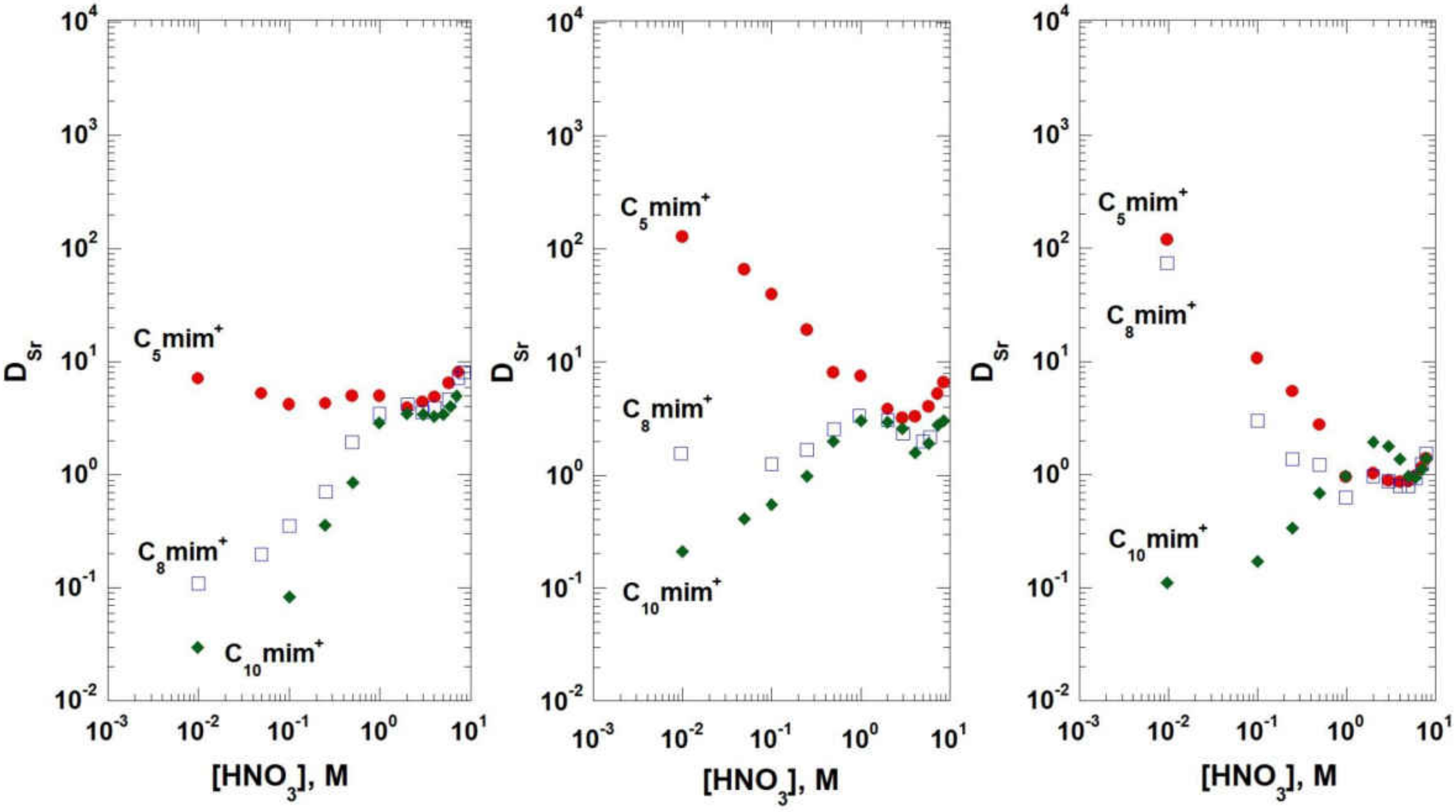

Figure 3.3: Effect of nitric acid concentration on the extraction of Sr^{2+} by DCH18C6 (0.10 M) in $C_n mim^+PF_6^-$ (left panel), $C_n mim^+Tf_2N^-$ (middle panel, adapted from reference 2), and $C_n mim^+BETI^-$ (right panel).

In contrast, for $C_n$mim$^+$BETI$^-$ (right panel), the decline in extraction with rising acidity indicative of ion exchange is seen for both of the short alkyl chain ILs examined (*i.e.,* C_5mim$^+$ and C_8mim$^+$). Interestingly, for the C_8mim$^+$ ILs, it can be seen that the increase in IL anion hydrophobicity associated with the changes from PF_6^- to Tf_2N^- to BETI$^-$ apparently leads to a systematic shift in the predominant mode of extraction from neutral complex extraction to ion-exchange, precisely as expected from the decline in the aqueous concentration of C_8mim$^+$ that accompanies this change. As seen in Table 3.2, this shift is confirmed by the results of measurements of $\%E_{NO3}$ / $\%E_{Sr2+}$, the ratio of the fraction of nitrate extracted to that of strontium in the extraction of strontium nitrate from water into a solution of DCH18C6 (0.1 M) in each of three C_8mim$^+$ ILs. This ratio falls from 0.67 for PF_6^- to 0.50 and 0.33 for Tf_2N^- and BETI$^-$, respectively, indicating an increasing contribution from ion exchange to the overall extraction process. (As less nitrate ion accompanies the extracted strontium, an increasing fraction of this strontium must partition *via* ion exchange.)

It should be noted here that significant nitrate extraction is observed in the absence of crown ether for the PF_6^- ionic liquids, but not for the other ILs, making necessary a “blank” correction for the PF_6^- data. This observation, too, is consistent with the greater hydrophilicity of PF_6^- *vs*. the other IL anions. Taken together, these results indicate that contrary to previous results for IL cations, for which increased hydrophobicity favors extraction *via* neutral complex formation, increased IL anion hydrophobicity favors extraction *via* ion exchange.

Table 3.2
The effect of ionic liquid cation chain length and anion hydrophobicity on strontium and nitrate partitioning between water and 0.20 M DCH18C6 in $C_n mim^+X^-$.

Organic phase		$\%E_{Sr}$[a]	$\%E_{NO3-}$[a]	Ratio $\%E_{Sr}/\%E_{NO3-}$	Partitioning mode indicated
IL anion	IL cation				
PF_6^-	C_5mim^+	78.3	20.3	3.9	Mixed
	C_8mim^+	22.9	15.2	1.5	Neutral complex
	$C_{10}mim^+$	10.6	4.9	2.2	Mixed
Tf_2N^- [b]	C_5mim^+	96.4 96.5	10.7 ± 0.3 9 ± 7	9.01	Cation exchange
	C_8mim^+	45.7 39.0	25.4 ± 0.8 20.9 ± 1.0	1.80	Mixed
	$C_{10}mim^+$	23.4 ± 3.0 20.2	23.1 ± 0.2 20.0 ± 1.0	1.01	Neutral complex
$BETI^-$	C_5mim^+	86.7 ± 5.0	13.0 ± 0.3	6.7	Cation exchange
	C_8mim^+	16.3 ± 0.9	8.0 ± 0.1	2.0	Mixed
	$C_{10}mim^+$	5.9 ± 0.3	6.3 ± 0.1	0.9	Neutral complex

All initial metal nitrate salt concentrations were 0.031 F.

[a] Uncertainties were calculated at the 95% confidence interval (*n* = 3).

[b] The two values shown are from previous studies in this lab, reference [2], and reference [6] respectively.

This is even more evident from an examination of the extraction of a second alkaline earth metal, barium, from acidic nitrate solution. As can be seen from Figure 3.4, for both the C_8mim^+ and $C_{10}mim^+$ ILs, the change in IL anion from PF_6^- to Tf_2N^- to $BETI^-$ leads to an obvious change in the shape of the acid dependency from one in which D_{Ba} generally rises with increasing acidity to one in which it falls. Here too then, the more hydrophobic the cation and hydrophilic the anion, the greater tendency for extraction to occur *via* partitioning of a neutral-nitrato complex.

Contrary to the changes in the shape of the acid dependency observed for divalent metal ions as the IL anion is altered, for monovalent metal ions (as shown in Figure 3.5, which depicts the nitric acid dependency of D_{Na} for the various ILs), the same general shape is observed for all of the ionic liquids studied. That is, similar to the results obtained for chloride media (Figure 3.1), a significant decline in sodium partitioning is observed with increasing acidity, regardless of the IL anion hydrophobicity. These observations provide further support for previous findings suggesting that ion-exchange is the predominate mode of sodium ion partitioning in these systems under most conditions. Furthermore, the effects of ionic liquid cation hydrophobicity on the extraction within a given anion are similar to chloride media, consistent with the shifting of ion-exchange mechanisms from one involving the cationic constituent of the ionic liquid to that involving a hydronium ion (equations 3.1 and 3.2, respectively). Similar to chloride media, a close examination of the acid dependencies for the PF_6^- anion (Figure 3.5, left panel) reveals an upturn in sodium extraction at very high nitric acid concentrations; an analogous upturn is not observed for Tf_2N^- or $BETI^-$, even at 8 M HNO_3.

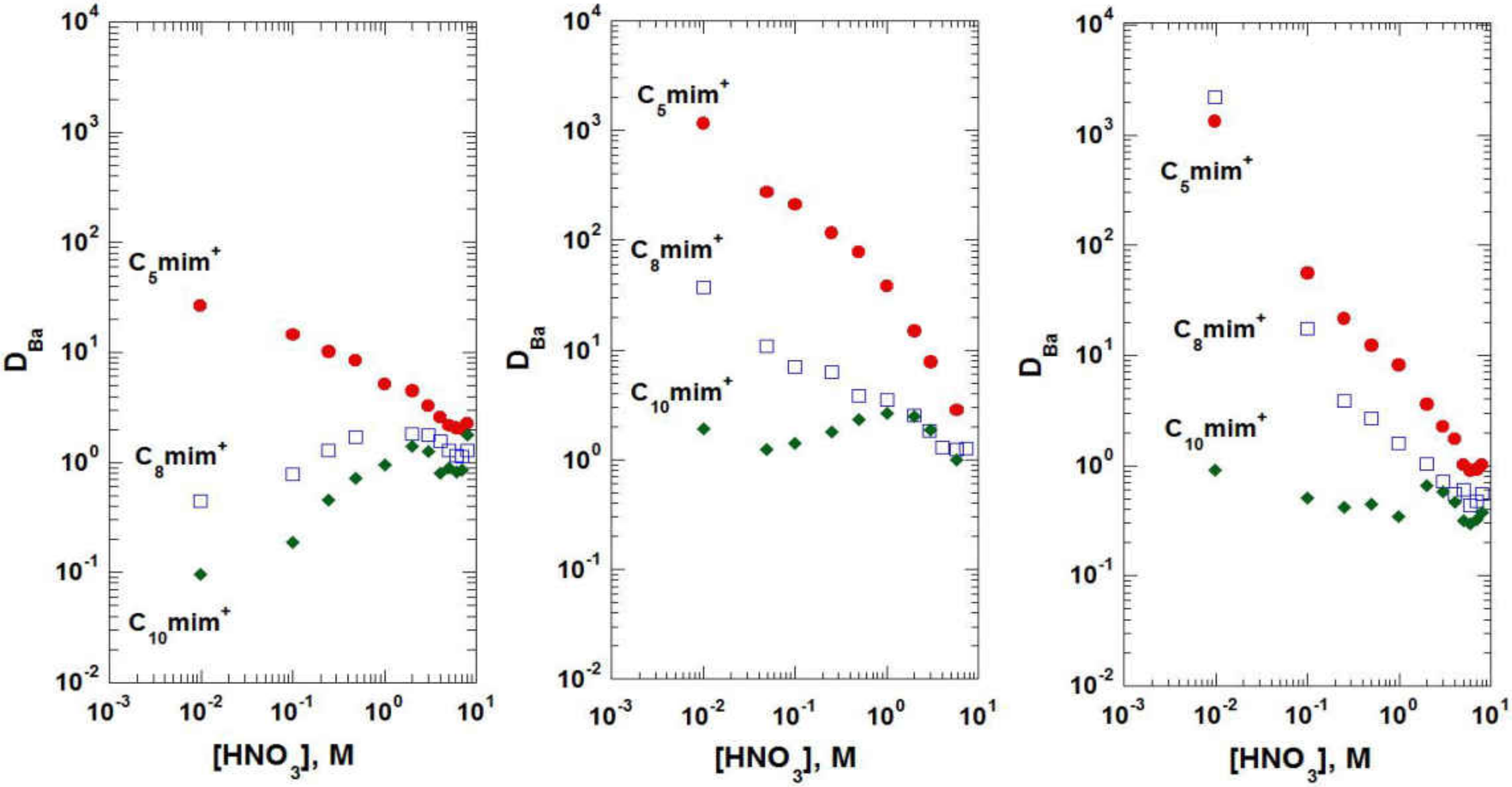

Figure 3.4: Effect of nitric acid concentration on the extraction of Ba^{2+} by DCH18C6 (0.10 M) in $C_n$mim$^+PF_6^-$ (left panel), $C_n$mim$^+Tf_2N^-$ (middle panel, adapted from reference 2) and $C_n$mim$^+$BETI$^-$ (right panel).

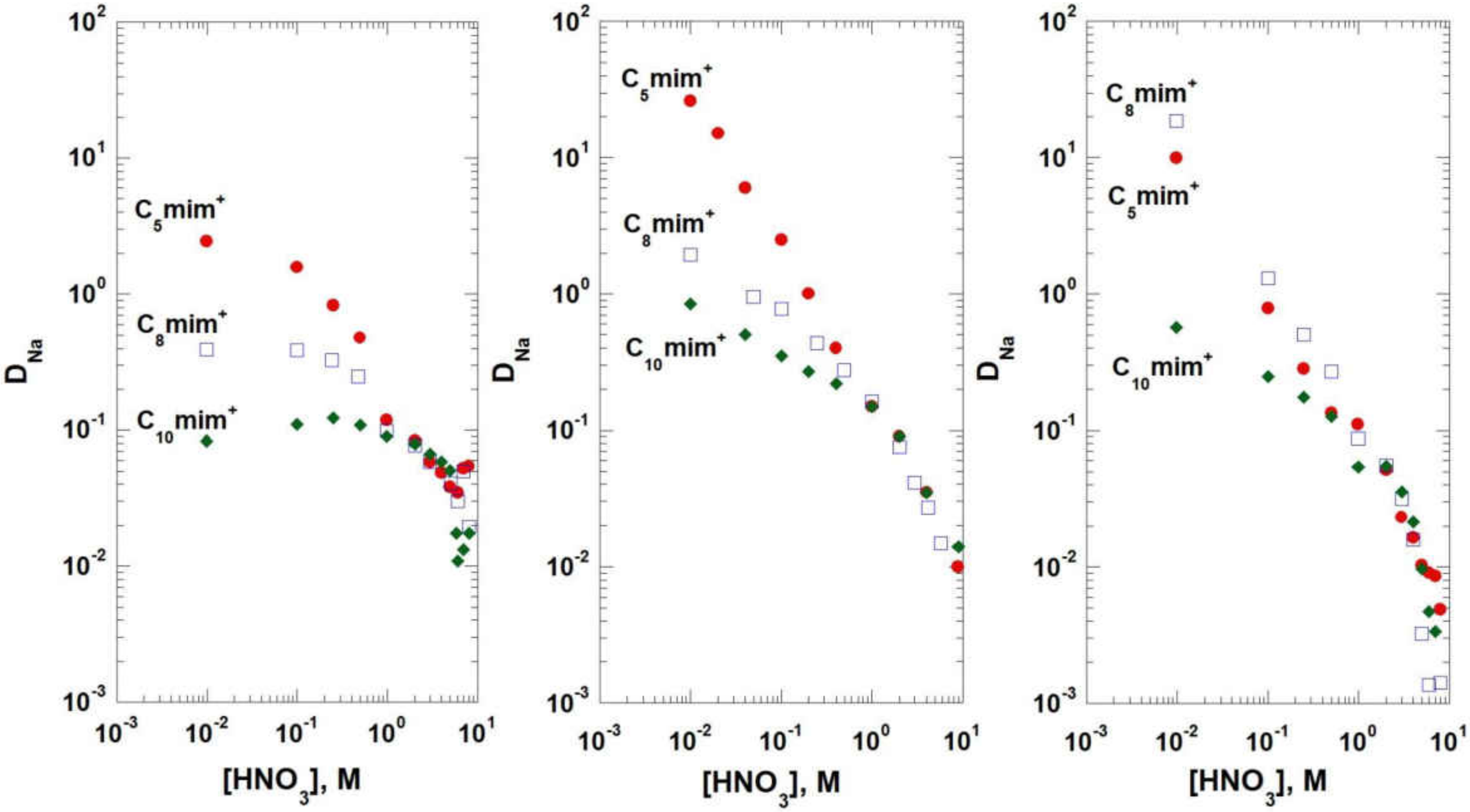

Figure 3.5: Effect of nitric acid concentration on the extraction of Na^+ by DCH18C6 (0.10 M) in $C_n mim^+PF_6^-$ (left panel), $C_n mim^+Tf_2N^-$ (middle panel, adapted from reference 2) and $C_n mim^+BETI^-$ (right panel).

3.6 Ionic Liquid Anion Effects on Extraction Efficiency and Selectivity

From a practical perspective, the design of an IL-based extraction system for the recovery of a given metal ion from aqueous solution requires not only minimal loss of the IL to the aqueous phase (*i.e.*, minimal contribution of ion exchange to the overall extraction process), but also satisfactory extraction efficiency and selectivity over potential interfering species. Prior work by Luo *et al.* [10] concerning the extraction of Sr^{2+} and Cs^+ (as $SrCl_2$ and CsCl, respectively) from water showed that for a fixed IL cation, the distribution ratios for both metal ions increase markedly with the hydrophobicity of the IL anion, in some cases (*e.g.*, $SrCl_2$ extraction into $C_4mim^+PF_6^-$ vs. $C_4mim^+BETI^-$) by as much as two orders of magnitude. Our results, best illustrated in this instance by a comparison of the nitric acid dependency of D_{Ba} for its extraction into $C_5mim^+PF_6^-$ and its Tf_2N^- analog (Figure 3.4), suggest that the situation is somewhat more complicated than previously recognized. That is, at low acidity, the difference between D_{Ba} values is indeed substantial, more than an order of magnitude at *ca.* 0.01 M HNO_3. As the acidity is increased, however, this difference diminishes until at *ca.* 6 M acid, the D_{Ba} values differ by less than a factor of two. Thus, the marked increase in D_M values with IL anion hydrophobicity noted by Luo *et al.* [10] is apparently only observed under conditions in which ion exchange involving the IL cation (equations 3.1 and 3.4) makes a significant contribution to the overall extraction process.

Related to this is the issue of the effect of IL anion hydrophobicity on the extraction selectivity (*i.e.*, separation factors). Luo *et al.* [10] observed a complex dependence of divalent vs. monovalent cation extraction selectivity on anion hydrophobicity for short-chain 1,3-dialkylimidazolium salts (C_nmim^+, with $n = 2, 4$). In particular, the Sr/Cs selectivity was found to be extremely sensitive to the choice of IL anion. In fact, while a solution of DCH18C6 in [C_4mim^+][PF_6^-] preferentially extracts Cs^+, both the analogous Tf_2N^- and $BETI^-$ ionic liquids exhibit strontium selectivity under the same conditions. Here too our results reveal additional complexity, and suggest a possible explanation for the selectivity reversal.

Figure 3.6 compares the extraction of barium and sodium ions (as representative divalent and monovalent cations, respectively) for various nitric acid solutions into several C_8mim^+ ILs incorporating PF_6^- (left panel), Tf_2N^- (center panel) or $BETI^-$ (right panel) as the counter anion. As already noted, the value of D_M observed in metal ion extraction from acidic media into $C_nmim^+X^-$ ILs is a complex function of IL cation chain length, aqueous phase acidity, and aqueous anion. In general, ion exchange processes predominate for monovalent metal ions, a fact typically reflected in declining values of D_M with rising aqueous acid concentrations. Such is the case for Na^+ extraction into each of the three ILs considered here. Close examination of the acid dependencies indicates that D_{Na} values of *ca.* 0.4, 3, and 100 are expected at very low nitric acid concentrations (*i.e.*, <0.001 M) for the PF_6^-, Tf_2N^-, and $BETI^-$ ILs, respectively. Under the same conditions, D_{Ba} values of *ca.* 0.1, 100, and $>10^4$ are expected, indicating that the system has gone from one exhibiting slight selectivity for Na^+ over Ba^{2+} to one strongly favoring extraction of the latter. This change in selectivity apparently has its origins then in the change in shape (*i.e.*, positive to negative slope) of the acid dependency of D_{Ba} as the hydrophobicity of the IL anion is increased, thus diminishing the contribution of neutral complex extraction / ion-pair extraction to the overall extraction of barium. Thus, prior observations of variations in Cs/Sr selectivity for the same extraction (*i.e.*, DCH18C6) likely stem from changes in the relative contributions of ion-exchange processes and neutral complex partitioning for the two cations that occur as the IL anion is changed.

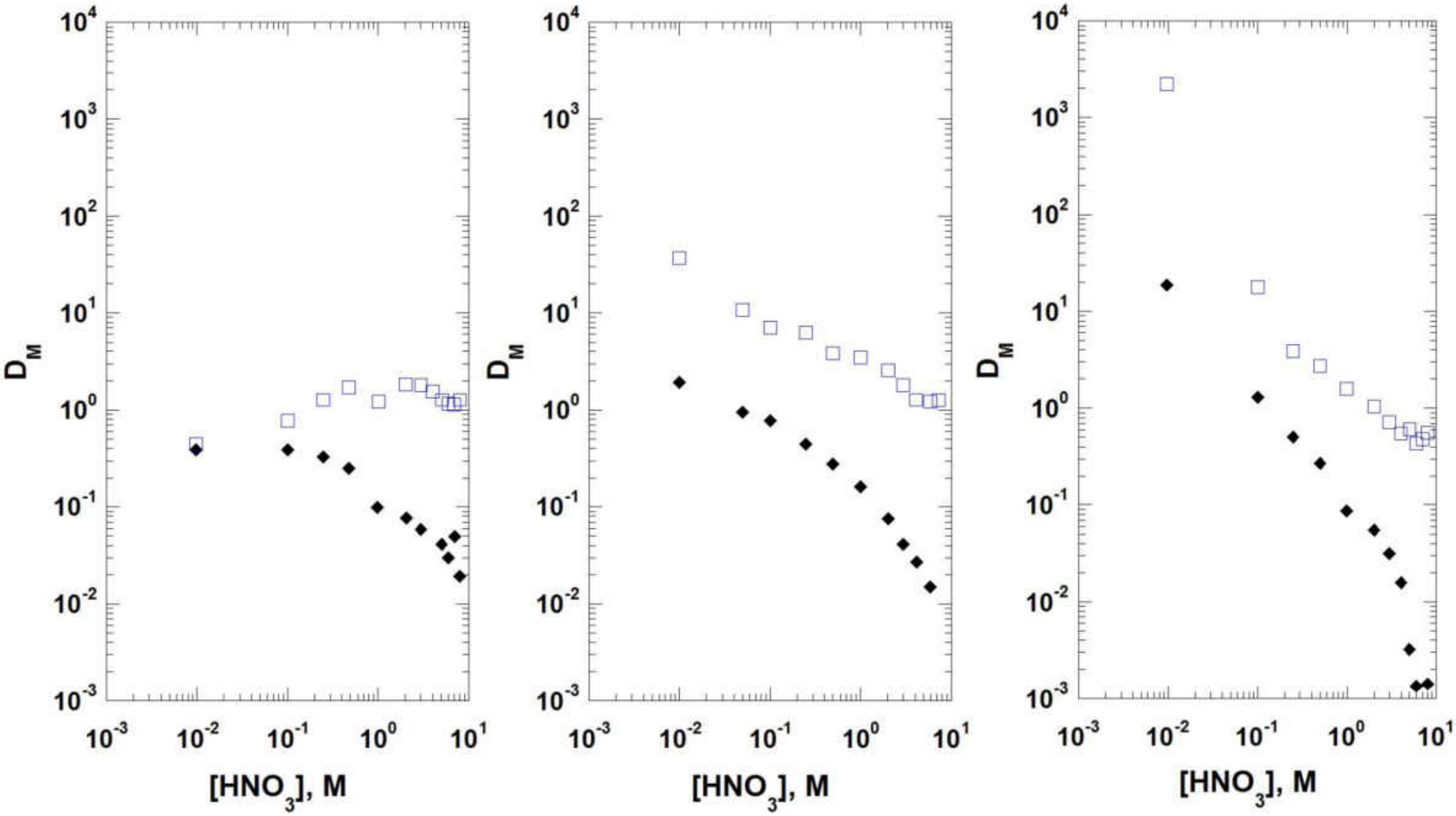

Figure 3.6: Effect of nitric acid concentration on the extraction of Ba^{2+} and Na$^+$ (represented by □ and ♦, respectively) by DCH18C6 (0.10 M) in C$_n$mim$^+$PF$_6^-$ (left panel), C$_n$mim$^+$Tf$_2$N$^-$ (middle panel, adapted from reference 2) and C$_n$mim$^+$BETI$^-$ (right panel).

3.7 Conclusions

The results of this study, by elucidating the effect of a change in IL anion upon the predominant mode(s) of alkali and alkaline earth cation extraction by a crown ether into imidazolium-based ILs from acidic aqueous phases, represent another step toward clarifying the factors governing the "balance of pathways" in metal ion extraction by various extractants in ionic liquids. In contrast to changes in the IL cation, which have typically been found to have a pronounced impact on metal ion extraction modes, IL anion effects appear to be more subtle. In certain instances, in fact, they are apparently "swamped out" by the influence of either the IL cation or the charge of the extracted metal ion. IL anion effects are seemingly most significant under conditions in which ion exchange involving the cationic constituent of the ionic liquid is the predominant mode of extraction, an undesirable situation from the perspective of devising environmentally benign alternatives to solvent extraction processes based on conventional (*i.e.*, molecular) organic solvents. Further work is needed to determine if the results obtained here represent a general description of the influence of IL anion upon metal ion extraction. Work addressing this opportunity is now underway in this laboratory.

3.8 Acknowledgements

Dr. Sheng Dai (Oak Ridge National Laboratory) is gratefully acknowledged for providing the $BETI^-$ ionic liquids necessary to complete this study. The financial support of the Office of Basic Energy Sciences of the United States Department of Energy under the Single Investigator Small Group Research (SISGR) Program through sub-contract with Brookhaven National Laboratory is also gratefully acknowledged.

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CHAPTER 4:

PERTECHNETATE EXTRACTION FROM BASIC SOLUTIONS INTO ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

4.1 Introduction

For more than a decade, hydrophobic ionic liquids have attracted attention as possible replacements for the conventional (*i.e.,* molecular) organic solvents employed in traditional solvent extraction processes for the separation of ions [1-17]. Studies of the extraction of various cations into a number of ILs have shown that these solvents can provide distribution ratios for greater than those observed in conventional solvent extraction processes employing molecular organic liquids [5, 14]. Subsequent work, however, has demonstrated that ILs suffer from certain drawbacks as extraction solvents, in particular, the loss of the constituent cations into the aqueous phase, thus limiting their utility [7, 8, 10, 11]. It has been shown, for example, that the partitioning of a metal cation (*e.g.,* Sr^{2+}) into certain 1-alkyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl] imides ($C_n mim^+ Tf_2N^-$) containing a Sr^{2+}-selective ionophore such as the crown ether (CE) dicyclohexano-18-crown-6 (DCH18C6), proceeds *via* the ion-exchange reaction depicted in equation 4.1 [7, 8, 11, 12]

$$Sr{\cdot}CE^{2+}_{aq} + 2C_n mim^{+}_{org} \leftrightarrow 2C_n mim^{+}_{aq} + Sr{\cdot}CE^{2+}_{org} \quad (4.1)$$

where the subscripts “aq” and “org” indicate a species present in the aqueous and IL phase, respectively. The release of $C_n mim^+$ to the aqueous phase results in a gradual dissolution of the IL, which has negative implications for the practical use of these ILs. While distribution ratios, D_{Sr}, of 10^4 have been reported for 1-ethyl-3-methylimidazolium ILs [5], dialkylimidazolium ILs are poorly suited for practical applications unless the alkyl side arm of the $C_n mim^+$ cation is sufficiently long ($n \geq 10$) to prevent a significant loss of the IL cation as per equation 4.1. Such an increase in hydrophobicity, however, causes the extraction efficiency for Sr^{2+} to decline until it becomes comparable to that observed for ordinary molecular liquids such as 1-octanol, thus nullifying one of the key advantages of using ILs [7, 8, 11]. Additionally, ion exchange is considered undesirable in many extraction applications due to the necessity of stripping the organic phase with concentrated acids or bases. For ILs, this is a particularly vexing problem, as, depending on the ionic composition, biphasic aqueous-IL systems incorporating these liquids are sometimes unstable at extremes of pH. Electrochemical deposition, chemical redox reactions, and precipitation thus become more attractive ways of stripping the extracted ions from such solvents [18-21].

A question of both fundamental and practical interest is whether the same potential limitation of ILs (which is obviously related to their being composed of ions) [6] adversely impacts the extraction of aqueous *anions* (A^-). That is, in analogy to the reaction in equation 4.1, does an anion exchange reaction of the type shown in equation 4.2 occur, thus resulting in the loss of the IL anion X^- to the aqueous phase and a gradual deterioration of the separations performance?

$$A^-_{aq} + C^+X^-_{org} \leftrightarrow X^-_{aq} + C^+A^-_{org} \qquad (4.2)$$

Preliminary studies by Jensen et al. [10] of the extraction of lanthanides by 2-thenoyltrifluoroacetone into an ionic liquid ($C_n mim^+ Tf_2N^-$) indicate that such anion exchange can indeed occur, but its extent and its impact on extraction performance, if any, remain unclear. Of course, aqueous anions can be extracted into *molecular* solvents (*e.g.,* 1-octanol) containing ionophores (such as crown ethers) with rings designed to accommodate ammonium and alkali cations (M^+), either by formation of a neutral coordination complex or, when the anion and/or cation are sufficiently large and of low charge, by ion-pairing, as depicted in equation 4.3 [5, 7, 8, 11, 22]

$$M^+_{aq} + A^-_{aq} + CE_{org} \leftrightarrow M\cdot CE^+ A^-_{org} \quad (4.3)$$

As will be shown below, by tuning its constituent ions, it is possible to suppress ion exchange in an IL, thereby replicating the extraction behavior typical of molecular liquids. (The main advantage of using ionic liquids for such (neutral) extractions, it should be noted, is the expected increase in the efficiency of the extraction, arising from strong solvation of the ion pair by the IL.) Specifically, it has been demonstrated that rapid (< 10 min) and efficient (> 99%) extraction of pertechnetate anion (TcO_4^-) from alkaline aqueous phases into an IL solvent can be achieved without a concurrent loss of IL ions into the aqueous phase [23].

Examination of this tetra-oxo anion is of particular importance due to its prevalence in spent nuclear fuel reprocessing streams. In fact, ^{99}Tc, a long-lived β-emitting radionuclide with high mobility in the environment, is one of the main fission products (having a yield of 6.3%) of uranium. Eliminating the release of ^{99}Tc into the environment [24-27] represents an important step toward improving the safety of spent nuclear fuel processing and restoring public confidence in the sustainability of nuclear power option [27].

The current baseline flowsheet for the processing of spent nuclear fuel in the U.S. involves co-extraction of uranium (as uranyl ion) and technetium (as pertechnetate) as one of the stages [24]. The U separation process (UREX) involves the extraction of uranyl nitrate from 1-3 M nitric acid with tri(*n*-butyl) phosphate (TBP) in *n*-dodecane. Unfortunately, it has been found that ^{99}Tc is co-extracted by this process solvent. Current procedures for TcO_4^- separation from uranyl ion involve the use of a column of a weakly basic anion exchange resin poly(vinylpyridine) (*e.g.,* Rellex HPQ), from which sorbed TcO_4^- is subsequently eluted using 1 M NH_4OH [28-30]. Although the resulting solution is ~10 times more concentrated in TcO_4^- than the initial feed, Tc/U separation processes providing much greater concentration of TcO_4^- continue to be of interest.

Improved processes for Tc separation are also of interest in the treatment of existing high-level radioactive wastes. Large volumes of these wastes are currently stored in massive underground tanks at various sites throughout the DOE complex. To prevent corrosion of the tanks, the waste solutions have been made strongly alkaline, resulting in precipitation and sludge formation [31]. Ultimately, this process yields a waste solution that is largely sodium nitrate and water [32]. Although processes based on various conventional organic solvents have been proposed for Tc removal from alkaline media [28, 32], none of them is entirely satisfactory. The use of ionic liquids represents a possible approach by which to significantly improve the performance of processes for the extraction of technetium. The present study represents an attempt to understand the fundamental aspects of Tc partitioning into ILs in the presence of a neutral extractant, and thus, to provide the basis for new processes for its recovery.

4.2 Experimental

4.2.1 Materials

One of the ionic liquids employed, 1-decyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide (hereafter abbreviated as $C_{10}mim^{+}Tf_2N^{-}$) was prepared *via* either conventional or microwave synthesis, purified and characterized using established methods [33, 34]. The other, trihexyltetradecylphosphonium *bis*[(trifluoromethyl)sulfonyl]imide (hereafter abbreviated as $P_{666,14}{}^{+}Tf_2N^{-}$) was obtained from Cytec Industries (Woodland Park, NJ) and used "as is". Partitioning studies were completed using dicyclohexano-18-crown-6 (DCH18C6) as the extractant. A commercial mixture of the *cis-syn-cis* and *cis-anti-cis* isomers was used as received (Parish Chemical Company, Orem, UT). Aqueous solutions were prepared using Milli-Q2 water and reagent grade sodium nitrate, sodium hydroxide, ammonium nitrate, and ammonium hydroxide (Aldrich, Milwaukee, WI). The aqueous base solutions (*i.e.*, NaOH and NH_4OH) were standardized by titration with potassium hydrogen phthalate (Aldrich, Milwaukee, WI) using phenolphthalein indicator (Ricca, Arlington, TX). The radiotracer ^{99}Tc (used in the form of NH_4TcO_4) was obtained from Argonne National Laboratory stocks. Optima Gold liquid scintillation cocktail was obtained from Perkin-Elmer Corporation.

4.2.2 Instruments

Radiometric measurements were carried out by liquid scintillation counting using a PerkinElmer Tri-Carb 2810 TR Series liquid scintillation counter equipped with QuantaSmart software. Ionic liquids were characterized by NMR spectroscopy using a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for protons. Spectra were obtained using solutions of chloroform-d (Acros, 100.0% atom D), and all chemical shifts were reported relative to tetramethylsilane.

4.2.3 Methods

Because ^{99}Tc is a β-emitter (E_{max} = 294 keV, $t_{1/2}$ = 2 x 10^5 years), all operations were carried out in a radiochemical laboratory equipped for handling this isotope. Distribution ratios (D_M, defined as $[M]_{org}/[M]_{aq}$ at equilibrium) were determined using a commercial radiotracer assayed *via* liquid scintillation counting following standard procedures. In each distribution experiment, the organic phase consisted of DCH18C6 dissolved in either the conventional solvent or the ionic liquid of interest. The aqueous phase salt or base concentration was systematically adjusted by conducting separate experiments for each condition. Unless otherwise noted, distribution measurements were performed at 0.1 M DCH18C6 in the organic phase. 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 water or an appropriate aqueous acid solution. Each equilibrated phase was sampled for analysis in at least duplicate with resulting uncertainties based on counting statistics that were generally within 10%.

Additionally, for radiometric measurements, the sum of the count rates in each phase yielded recoveries within 10% of the radiotracer stock solution used, indicating that equilibrium was reached with the two phases involved.

4.3 Pertechnetate Extraction from Alkaline Media

4.3.1 Salt and crown ether concentration dependencies of D_{Tc} for extraction into aliphatic alcohols by DCH18C6

As demonstrated in previous chapters in this thesis, considerable insight into the behavior of IL-based extraction systems can be obtained by examining the behavior of a conventional organic solvent, such as 1-octanol [5], under the same conditions. As a starting point in efforts to identify the possible modes of TcO_4^- partitioning in an IL, the effect of sodium nitrate concentration on the extraction of technetium into 1-octanol containing a constant concentration of DCH18C6 (abbreviated CE, crown ether) was therefore examined. As shown in Figure 4.1, TcO_4^- extraction increases with increasing $NaNO_3$ concentration up to *ca.* 0.5 – 1 M, then declines. The initial increase in D_{Tc} is consistent with ion-pair extraction of TcO_4^- according to equation 4.4

$$Na^+_{aq} + TcO^-_{4\,aq} + CE_{org} \leftrightarrow \{Na^+ \cdot CE\}\, TcO^-_{4\,org} \quad (4.4)$$

Given prior reports of sodium ion extraction from nitric acid solution by a 1-octanol/ crown ether based strontium extraction process [35], along with the relatively large size of the TcO_4^- anion (0.241 nm) [32] and the known relationship between the efficiency of ion-pair extraction and ion size, the observation of ion-pairing in this system is not unexpected.

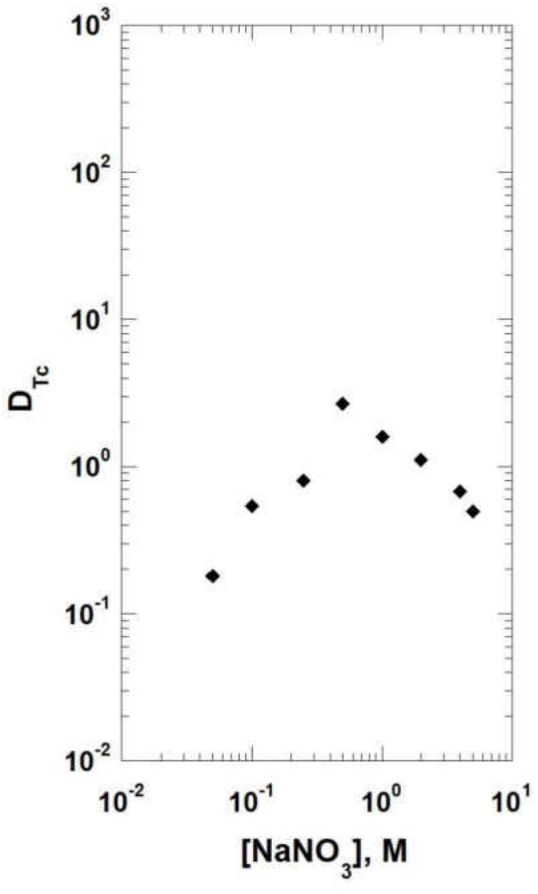

Figure 4.1: Effect of sodium nitrate concentration on the extraction of TcO_4^- by DCH18C6 (0.10 M) in 1-octanol.

The maximum in the plot is indicative of a shift in the predominant equilibrium away from ion-pair extraction to one in which further addition of $NaNO_3$ *impedes* TcO_4^- extraction. Such would be the case if the crown ether were to become appreciably loaded with $NaNO_3$. Under such conditions, the extractant would no longer be the crown ether itself, but rather the ion pair $\{Na^+ \cdot CE\}NO_3^-$, and the predominant mode of TcO_4^- partitioning would become anion-exchange as shown in equation 4.5:

$$\{Na^{+}\cdot CE\}\, NO^{-}_{3\ org} + TcO^{-}_{4\ aq} \leftrightarrow \{Na^{+}\cdot CE\}\, TcO^{-}_{4\ org} + NO^{-}_{3\ aq} \quad (4.5)$$

For extraction *via* such an anion-exchange process, a plot of log D *vs.* log $[NO_3^-]$ should yield a line of inverse unit slope (*i.e.,* -1). Indeed, close examination of the portion of Figure 4.1 to the right of the maximum shows that D_{Tc} does exhibit the expected linear decrease (slope = -0.83) with respect to $NaNO_3$ concentration. Similar observations with respect to the trend of the sodium nitrate dependency and the modes of pertechnetate partitioning into 1-octanol were observed previously [32].

Because pertechnetate is found in spent nuclear fuel waste solutions that may contain not only sodium nitrate but also either sodium or ammonium hydroxide, extraction from these aqueous phases was also examined. For comparison purposes, NH_4NO_3 was also examined. As was the case for $NaNO_3$, increasing concentrations of NH_4NO_3 (Figure 4.2, left panel), NH_4OH (Figure 4.2, middle panel), or NaOH (Figure 4.2, right panel) are initially accompanied by increasing D_{Tc}. Eventually, however, extraction reaches a maximum and then decreases significantly. Therefore, TcO_4^- partitioning in these systems is again a two-path process: ion-pair extraction at low NaOH (or NH_4OH and NH_4NO_3) concentrations and anion-exchange at higher concentrations, as described in equations 4.4 and 4.5, respectively.

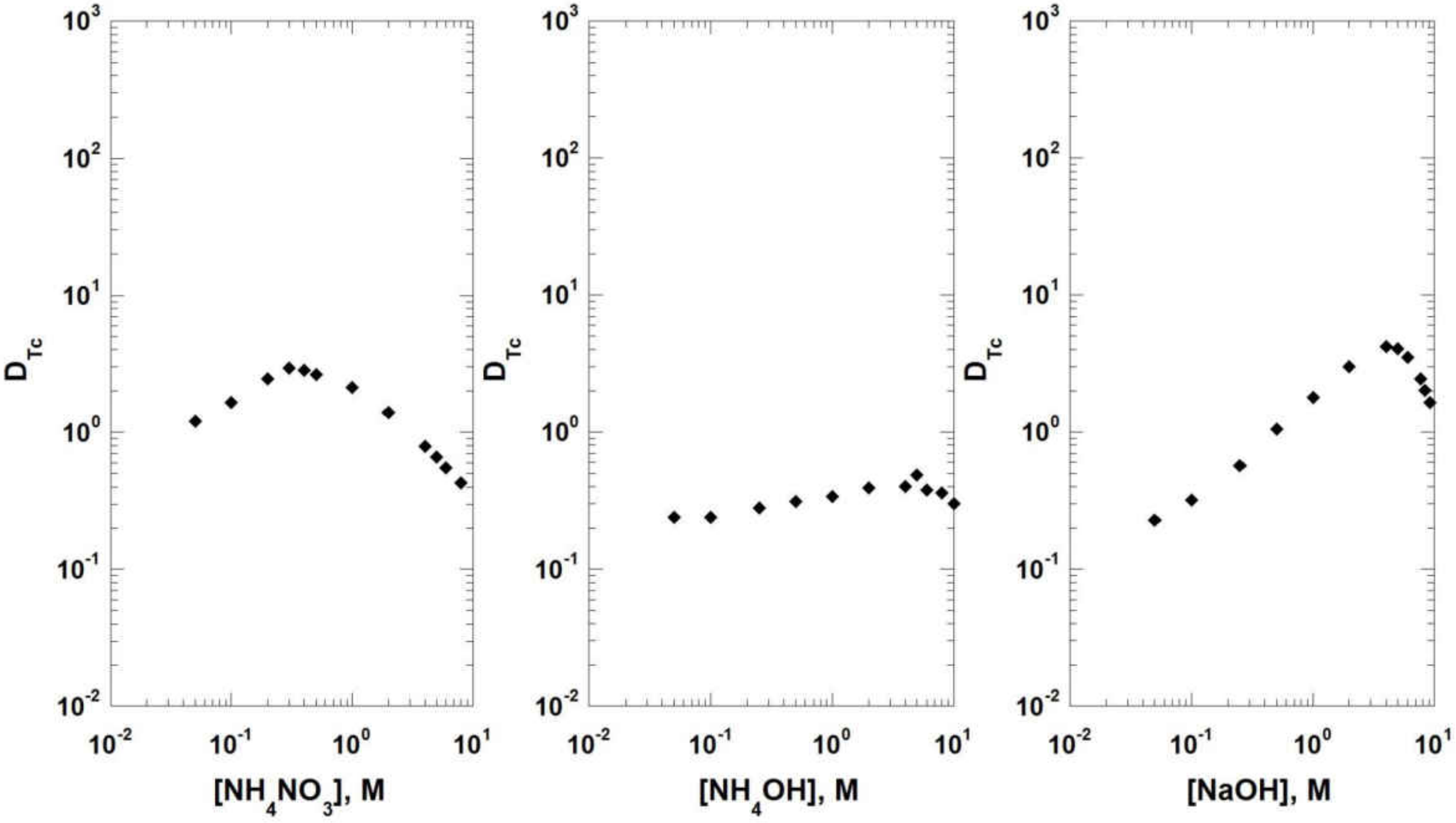

Figure 4.2: Effect of alkaline concentration (ammonium nitrate, left panel; ammonium hydroxide, middle panel; and sodium hydroxide, right panel) on the extraction of TcO_4^- by DCH18C6 (0.10 M) in 1-octanol.

It is important to note that the concentration at which the maximum D_{Tc} is observed is not the same for all four reagents. For sodium nitrate and ammonium nitrate (Figure 4.1 and 4.2, left panel, respectively), the crown ether becomes sufficiently loaded (*i.e.,* a maximum in D_{Tc} is observed) at *ca.* 0.5 M that anion-exchange becomes favorable. For the hydroxide solutions, however, the shift in the mode of partitioning (*i.e.,* the maximum in D_{Tc}) for the hydroxide solutions is not observed until *ca.* 4 M (Figure 4.2, middle and right panel). It has been shown for the extraction of strontium that the hydration energy of the aqueous phase anion plays an important role in determining the predominant mode of partitioning [36]. Here, aqueous phase anion hydration energy can account for the difference in the concentrations at which anion-exchange begins to predominate for nitrate- and hydroxide-containing aqueous phases. That is, the higher the hydration energy of the aqueous phase anion, the more difficult will be dehydrating that anion, thus rendering its co-extraction (equation 4.3) more difficult. Nitrate anion has a hydration energy significantly less than that of hydroxide anion (-314 kJ/mol vs. -460 kJ/mol) [37]. As a result, it can be dehydrated more readily and thus co-extracted. Therefore, a given level of loading of the crown will occur at a lower aqueous salt concentration for nitrates than for hydroxides, and thus, anion exchange will begin at a lower salt concentration for nitrates. This is consistent with the results shown in Figures 4.1 and 4.2.

Like the nitrate dependency of D_{Tc}, the effect of crown ether concentration on the extraction of pertechnetate from solutions containing low concentrations of sodium hydroxide or sodium nitrate (0.1 M) into 1-octanol (Figure 4.3, left and right panel, respectively) is also consistent with the partitioning of an ion-pair. That is, a log-log plot of D_{Tc} versus [DCH18C6] yields a line of near-unit slope for both aqueous solutions (1.02 and 0.98, respectively), as expected from equation 4.4. Prior work considering the extraction of potassium and sodium ion from acidic nitrate media into 1-octanol [38, 39] found much the same results. That is, the extraction of a monovalent cation into the alcohol by a crown ether also accomplished *via* neutral complex formation / ion-pairing, and the crown ether dependency (at a constant nitric acid concentration) for each of these cations also yielded a line of near-unit slope.

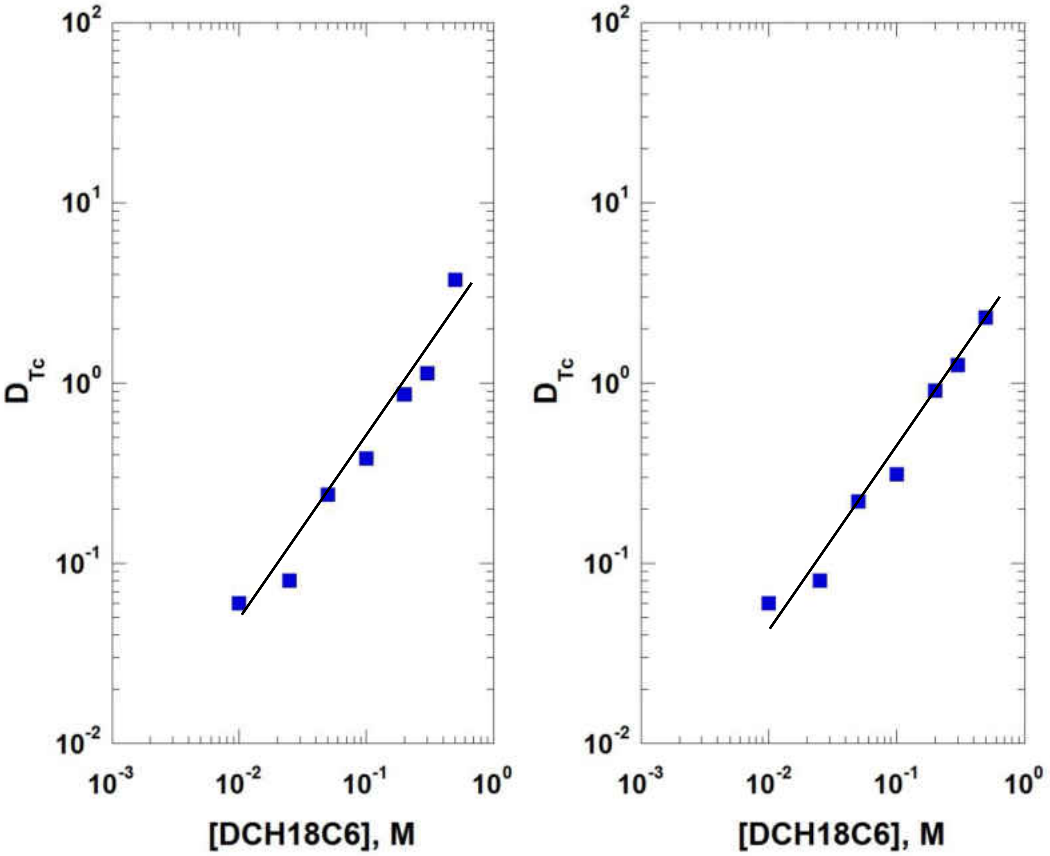

Figure 4.3: Effect of crown ether concentration on the extraction of TcO_4^- by 0.10 M NaOH (left panel) and 0.10 M $NaNO_3$ (right panel) in 1-octanol.

Taken together, the results of these experiments demonstrate that the extraction of pertechnetate into 1-octanol by DCH18C6 comprises a two-path process in which the precise balance between ion-pair extraction and anion exchange is influenced by both the identity and concentration of the aqueous phase cation and anion. In this respect, pertechnetate extraction (and by analogy, the extraction of other anions in the presence of a neural extractant) into 1-octanol is more complex than cation extraction under the same conditions, for which simple neutral complex extraction is the predominant mode of partitioning.

4.3.2 Nitrate extraction dependencies of D_{Tc} for extraction into $C_{10}mim^+Tf_2N^-$ ILs by DCH18C6

In prior work [36, 38-41], it was shown that the behavior of dialkylimidazolium ILs bearing a relatively long alkyl substituent (*e.g.,* $C_{10}mim^+Tf_2N^-$) can mimic that of 1-octanol in the extraction of cations by neutral extractants (*e.g.,* crown ethers). This is especially evident in the extraction of divalent cations from nitric acid solutions [36, 38, 39]. As a next step in our investigation of pertechnetate extraction into ILs, we therefore chose to examine its partitioning between selected aqueous phases and $C_{10}mim^+Tf_2N^-$. Figure 4.4 shows the effect of $NaNO_3$ concentration on the extraction of TcO_4^- into this IL, both in the presence and absence of added (0.1 M) crown ether. As can be seen, the parabolic dependency exhibiting a maximum at intermediate sodium nitrate concentrations observed for 1-octanol has been replaced by one in which D_{Tc} gradually decreases as the $NaNO_3$ concentration increases. A similar, albeit steeper decrease is observed in the absence of crown ether. Such a decrease is inconsistent with an appreciable contribution of ion-pair extraction to the observed partitioning, but rather is indicative of ion-exchange processes. There are, in fact, three possible ion-exchange processes in this system. First, as shown in equation 4.6, TcO_4^- can be exchanged for the IL anion (*i.e.,* the IL can function as a conventional liquid anion exchanger):

$$C_{10}mim^+Tf_2N^-_{org} + TcO^-_{4\ aq} \leftrightarrow C_{10}mim^+TcO^-_{4\ org} + Tf_2N^-_{aq} \quad (4.6)$$

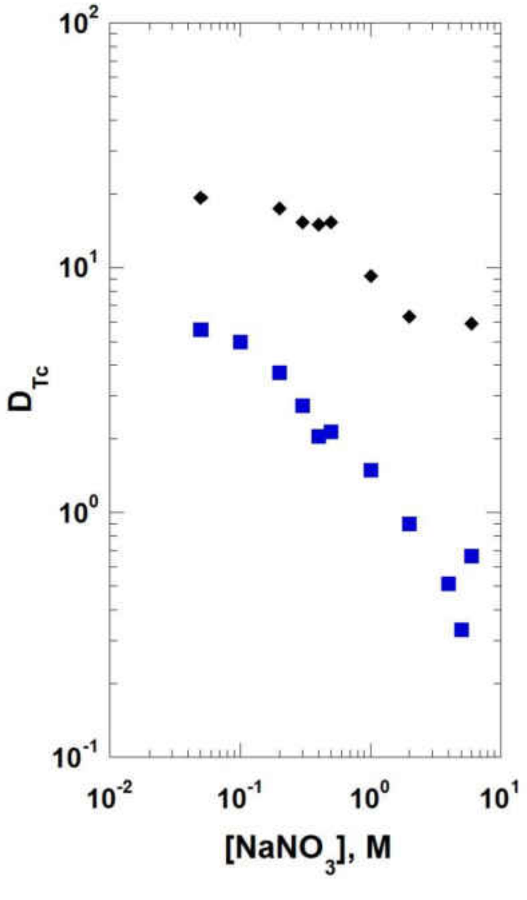

Figure 4.4: Effect of sodium nitrate concentration on the extraction of TcO_4^- by $C_{10}mim^+Tf_2N^-$ both in the presence (♦) and absence (■) of added DCH18C6 (0.10 M).

Because preconditioning of the IL phase prior to the measurement of TcO_4^- partitioning involves repeated contact of the ionic liquid with a $NaNO_3$ solution and because prior work has shown that contact of certain ILs with an aqueous phase containing high salt concentrations (*e.g.,* 6 M $NaNO_3$) can lead to partial conversion of the IL to another form (here, for example, to $C_{10}mim^+NO_3^-$), however, it is conceivable that the extraction solvent is actually a mixture of $C_{10}mim^+Tf_2N^-$ and $C_{10}mim^+NO_3^-$. Thus, as shown in equation 4.7, a second possible pathway involves exchange of TcO_4^- for NO_3^- rather than Tf_2N^-:

$$C_{10}mim^+NO^-_{3\ org} + TcO^-_{4\ aq} \leftrightarrow C_{10}mim^+TcO^-_{4\ org} + NO^-_{3\ aq} \quad (4.7)$$

Finally, TcO_4^- could be exchanged for NO_3^- present as part of extracted $\{Na^+\cdot CE\}NO_3^-$ (equation 4.5).

Examination by NMR of the IL before and after repeated equilibration with a 4 M $NaNO_3$ solution revealed no evidence for the formation of $C_{10}mim^+NO_3^-$, apparently ruling out a contribution from a process involving that form of the IL. Comparison of the results obtained in the presence and absence of added ionophore (Figure 4.4), however, indicates that the two other ion-exchange processes (equations 4.5 and 4.6) must contribute to the observed extraction in this system. That is, even in the absence of crown ether, measurable TcO_4^- extraction is observed over the entire range of $NaNO_3$ concentrations examined. In this case, the only viable route for TcO_4^- partitioning is exchange of TcO_4^- for Tf_2N^- (*i.e.,* equation 4.6). If this were the only route, then the results obtained in both the presence and absence of crown ether would be identical. In fact, however, addition of crown ether boosts D_{Tc} significantly at high $NaNO_3$ concentrations, with a lesser effect being observed as the salt concentration falls. This result is consistent with the presence of a contribution from the anion exchange process depicted in equation 4.5. Thus, TcO_4^- extraction into $C_{10}mim^+Tf_2N^-$ from $NaNO_3$ solution differs somewhat from that seen in 1-octanol (*e.g.,* ion-pairing predominating at low aqueous concentration and anion-exchange at high concentration), despite prior reports indicating that the behavior of the two solvents is often similar. In contrast to 1-octanol, *two* ion-exchange reactions (equation 4.5 and 4.6), their relative importance governed by the $NaNO_3$ concentration, apparently determine the observed extraction efficiency, and over the range of $NaNO_3$ concentrations considered, no region of rising D_{Tc} with increasing salt concentration is observed.

Efforts to extend these studies to extraction of pertechnetate from sodium hydroxide media were unsuccessful, as alkaline solutions led to deprotonation of the imidazolium cation in the C(2) position (*i.e.,* the carbon directly between the two nitrogen groups in the imidazolium ring), forming a reactive carbene [42, 43].

4.3.3 Sodium nitrate and hydroxide dependencies of D_{Tc} for extraction into $P_{666,14}^+Tf_2N^-$ ILs by DCH18C6

Although useful from a fundamental perspective, studies of dialkylimidazolium salts are of limited *direct* utility in the development of workable extraction / electrodeposition processes for pertechnetate [23] . Our studies were therefore extended to a second, more practical class of hydrophobic ILs, tetraalkylphosphonium salts. In an examination of the effect of $NaNO_3$ concentration on the extraction of TcO_4^- into neat $P_{666,14}^+Tf_2N^-$, both in the presence and absence of added (0.1 M) crown ether, results similar to those for $C_{10}mim^+Tf_2N^-$ were obtained (Figure 4.5, left panel), suggesting that in this system also, pertechnetate partitioning proceeds *via* a combination of two forms of ion exchange. One ion-exchange process involves the exchange of pertechnetate for nitrate that is present as part of the extracted sodium-crown ether-nitrate complex (equation 4.5), while a second process involves exchange of pertechnetate for the anionic constituent of the ionic liquid (equation 4.6).

In the course of these experiments, it became obvious that the viscosity of phosphonium ionic liquids is too high to permit their use in an undiluted form. Our subsequent studies therefore focused on mixtures of $P_{666,14}{}^+Tf_2N^-$ and *m*-xylene, a solvent shown to combine satisfactory physiochemical properties and acceptable pertechnetate extraction efficiency. Figure 4.5 (right panel) shows the sodium nitrate dependency for the dilute $P_{666,14}{}^+Tf_2N^-$ / *m*-xylene solution containing 0.1 M crown ether. As can be seen, comparable extraction efficiency is observed for the solution and the neat IL, indicating that dilution to facilitate handling does not lead to significant adverse effects on the extraction.

In contrast to imidazolium cations in alkaline solutions, deprotonation is not a concern for the phosphonium cation. Therefore, the efficiency of TcO_4^- extraction was examined in sodium hydroxide media (Figure 4.6). It is immediately evident that the shape of the dependency (hence the mode of partitioning for technetium from hydroxide media into the phosphonium IL) is not the same as in nitrate media. That is, for 0.1 M DCH18C6 in $P_{666,14}{}^+Tf_2N^-$, an increase in extraction is observed with increasing NaOH concentration, which is indicative of extraction *via* ion-pairing (equation 4.4). At high hydroxide concentrations, a flattening of the dependency is observed.

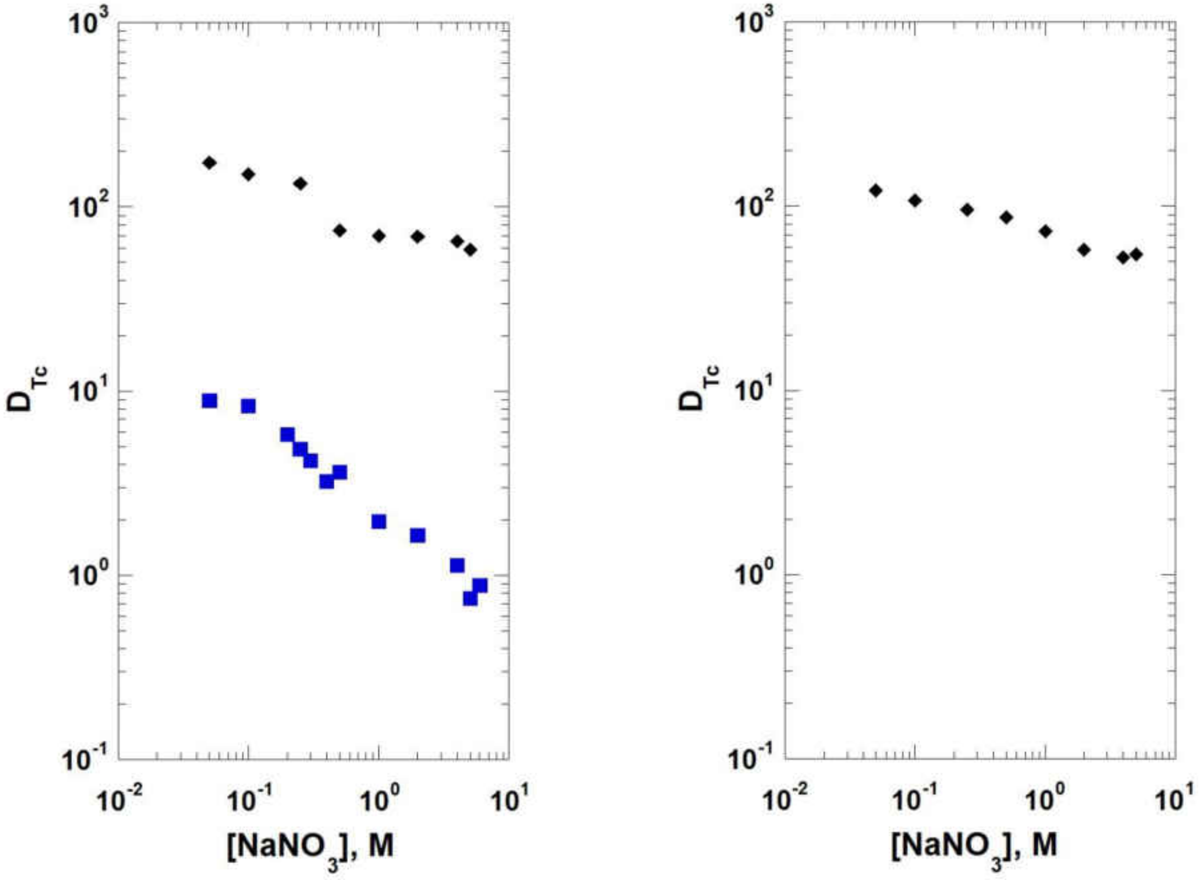

Figure 4.5: Effect of sodium nitrate concentration on the extraction of TcO_4^- by $P_{666,14}^+Tf_2N^-$ both in the presence (♦) and absence (■) of added DCH18C6 (0.10 M), left panel; 0.10 M DCH18C6 in $P_{666,14}^+Tf_2N^-$ (0.40 M solution diluted with *m*-xylene), right panel.

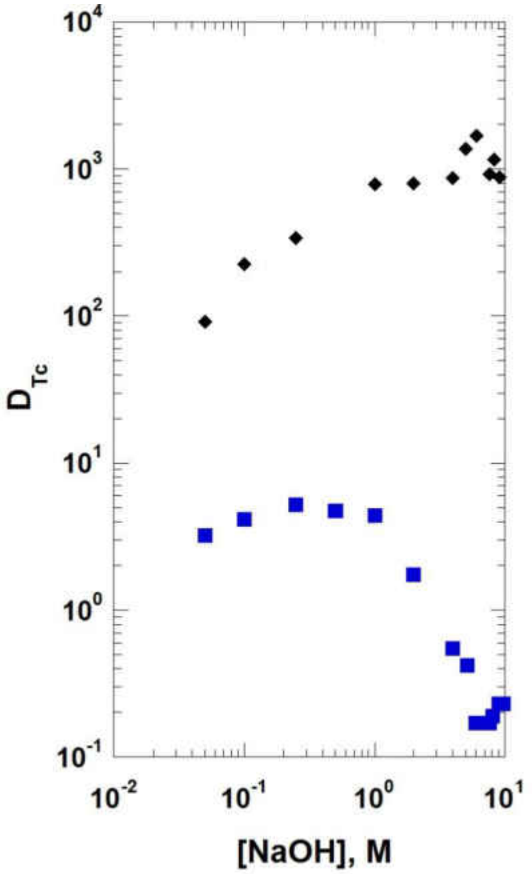

Figure 4.6: Effect of sodium hydroxide concentration on the extraction of TcO_4^- by $P_{666,14}{}^+Tf_2N^-$ (diluted with *m*-xylene) both in the presence (♦) and absence (■) of added DCH18C6 (0.10 M).

As was the case for the imidazolium IL, extraction is observed even in the absence of crown ether for the phosphonium IL, however, the mode of partitioning has shifted from extraction by ion-pairing to anion exchange, similar to the behavior of the extraction system in nitrate media. When the ionophore is absent from the system, the mode of partitioning is limited to that involving the ionic liquid (equation 4.6).

The differences observed between the nitrate and hydroxide media in the extraction of pertechnetate from 0.1 M DCH18C6 in $P_{666,14}{}^+Tf_2N^-$ can again be explained by the hydration energy of the anions. For the anion-exchange processes to predominate (*i.e.,* equation 4.5) co-extraction of the anion needs to occur to allow formation of the sodium-crown ether complex. Given that nitrate has a lower hydration energy, it will co-extract much sooner and thus anion-exchange will be observed over a wide range of salt concentrations than for hydroxide (which will thus exhibit ion-pairing longer).

4.4 Conclusions

In summary, our efforts to identify the modes of pertechnetate ion partitioning in IL-based extraction systems containing a macrocyclic polyether (crown ether) have led to the conclusion that three modes occur, with the particular mode predominating varying with the system of interest. That is, when a conventional molecular solvent, 1-octanol, was employed with sodium nitrate media, two modes of partitioning were observed: ion-pairing (at low nitrate concentrations) and anion-exchange between pertechnetate anion and the nitrate associated with the sodium-crown ether complex (at high nitrate concentrations). Very similar results were obtained for other aqueous media (*i.e.,* sodium hydroxide, ammonium hydroxide and ammonium nitrate) in that the same modes of partitioning were identified. A slight shift in the concentration at which each mode predominated was observed due to differences in the hydration energies of the aqueous phase anion, however.

Examination of a hydrophobic imidazolium ionic liquid ($C_{10}mim^+Tf_2N^-$) showed that the modes of partitioning for the extraction of pertechnetate from sodium nitrate solution differ from those observed for 1-octanol. Specifically, anion exchange was the only mode of partitioning observed for the IL system over the range of aqueous salt concentrations examined. Two different types of ion exchange were identified in the presence of DCH18C6: exchange of pertechnetate for the anionic constituent of the IL and its exchange for nitrate ion co-extracted with a sodium-DCH18C6 complex (as observed in 1-octanol). In the absence of the crown ether, extraction is observed only *via* anion-exchange involving the ionic liquid anion. Attempts to extend these investigations to other aqueous media were unsuccessful due to the instability of the IL cation in strongly alkaline solutions. Contrary to what has been observed in the extraction of metal cations, the modes of partitioning observed for anion extraction utilizing $C_{10}mim^{+}Tf_2N^{-}$ do not mimic those observed with 1-octanol.

An examination of the extraction of pertechnetate from sodium nitrate media into a phosphonium ionic liquid yielded results similar to those obtained for the imidazolium ionic liquid. That is, the same two anion exchange processes were observed in the presence of crown ether, while in the absence of the ionophore, only one mode of partitioning (involving the ionic liquid anion) was observed. When the aqueous phase was changed to sodium hydroxide, an ion-pairing mechanism predominated for the ionic liquid in the presence of crown ether, while only anion exchange was observed when no ionophore was present. These differences in the modes of partitioning can be attributed to the higher hydration energy of the hydroxide ion. Contrary to the imidazolium ionic liquid, similarities to 1-octanol were observed for the phosphonium IL for alkaline aqueous phases.

The results obtained here, in addition to being of obvious fundamental interest, are of considerable practical significance. That is, objections have frequently been raised to the use of ILs as extraction solvents due to the loss of the IL constituents to the aqueous phase that can accompany cation/anion partitioning *via* ion exchange. The results obtained here suggest that it may be possible to avoid these losses by careful selection of experimental conditions.

4.5 Acknowledgements

Dr. Diab Qadah is gratefully acknowledged for his assistance in completing many of these studies and for his intellectual contributions to the project. The financial support of the Office of Basic Energy Sciences of the United States Department of Energy (US-DOE) under the Single Investigator Small Group Research (SISGR) Program through sub-contract with Brookhaven National Laboratory and of the Office of Nuclear Energy of US-DOE through the Advanced Fuel Cycle Initiative is gratefully acknowledged.

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CHAPTER 5:

EFFECT OF RADIOLYSIS ON METAL ION EXTRACTION INTO CARBOXYLATE-BASED ROOM-TEMPERATURE IONIC LIQUIDS (RTILs)

5.1 Introduction

Under certain conditions, room-temperature ionic liquids have been shown to yield vast improvements over conventional organic solvents in the efficiency of extraction of metal ions, especially when a neutral extractant is employed [1]. This improved extraction efficiency, together with their low volatility, wide liquidus range [2-5] and ready tunability have led to considerable interest in the application of ionic liquids in separations processes, among them, the reprocessing of spent nuclear fuel. In such an application, extraction efficiency is not the only factor to consider when selecting a process solvent. Satisfactory radiation stability is also an essential requirement.

The first assessments of the radiation stability of ionic liquids were reported more than a decade ago [6]. In one of the earliest, an examination of the effect of alpha, beta and gamma radiation (up to a maximum of 400 kGy) on the stability of 1,3-alkylmethylimidazolium ionic liquids incorporating nitrate or chloride as the anion, results consistent with high radiation stability were obtained. That is, although sample discoloration was observed, <1% of the sample actually decomposeed. Subsequent studies of several 1-methyl-3-butylimidazolium ionic liquids using hexafluorophosphate (PF_6^-), tetraflurorоborate (BF_4^-) or *bis*(trifluoromethyl sulfonyl)imide (Tf_2N^-) as the counter ion showed that changes in viscosity and conductivity accompanied the sample discoloration in all cases [7-11]. Studies of various imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium cations, paired with the Tf_2N^- anion, also suggest that ionic liquids exhibit good radiation stability. Although hydrogen gas is produced when these materials are irradiated [12], the amount is less than that observed for conventional organic solvents under the same conditions.

Several studies have examined the effect of irradiation on the performance of ILs as extraction solvents [13, 14]. For example, it has been observed that the extraction of strontium by a crown ether into $C_4mim^+PF_6^-$ is decreased by gamma irradiation. This effect was attributed to hydrogen ions generated by the radiation process, which would compete with the strontium for the crown ether [13]. Similar results (*i.e.,* a decrease in strontium partitioning) were observed for $C_4mim^+Tf_2N^-$. In this instance, strontium extraction was also diminished by the presence of SO_4^{2-} produced by oxidation of SO_3^{2-}, a degradation product of the Tf_2N^- anion [14].

Subsequent studies have shown that the accumulation of degradation products from solvent (IL) or extractant fragmentation may compromise the performance of extraction systems involving ILs based on BF_4^-, PF_6^- or Tf_2N^-, which have been found to fragment appreciably upon exposure to high levels of gamma radiation (1200 -2000 kGy) [15]. (Such levels approximate the upper limit of radiation exposures anticipated for reprocessing systems.) In common organic solvents (such as *n*-dodecane) used for nuclear separations, solvent degradation is seldom a concern. Rather, due to its lower ionization potential (IP), deterioration of the extracting agent is more likely [15]. Because ionic liquid systems generally have much lower IPs than alkanes, the situation is reversed, and ionic liquid degradation is more likely than deterioration of the extractant [15]. The chemical make-up of the ionic liquid thus becomes particularly important in development of a radiolytically stable process solvent. It has been shown that ILs incorporating aromatic cations (*e.g.,* imidazolium and pyridinium) tend to degrade more readily than those that do not, as these cations readily trap electrons (creating competition with the electron-accepting anions), and therefore fragment more easily [15-17]. The effect of structure on the radiolytic stability of an IL anion has also been investigated [15]. Extensive fragmentation has been observed for the widely used Tf_2N^- anion by electron paramagnetic resonance (EPR) [15, 18]. A larger aromatic anion, benzoate, was found to be more stable due to the suppression of oxidative fragmentation. Also, this anion was found to serve as a hole scavenger as well as an electron and H-atom acceptor [15]. DFT calculations on these systems indicate that the benzoate anion does not fragment. Other aromatic carboxylate anions (*e.g.,*salicylate) were found to display similar stability, making such anions good candidates as the basis of a radiolytically stable ionic liquid.

In the present study, we present a detailed examination of the effect of gamma radiation on the extraction of strontium from acidic nitrate media by dicyclohexano-18-crown-6 (DCH18C6) into a series of phosphonium carboxylate ILs. For purposes of comparison, several 1,3-dialkylimidazolium ILs were also examined. In addition, the effect of irradiation on the physical and thermal properties of these systems is also examined.

5.2 Experimental

5.2.1 Materials

Three 1-alkyl-3-methylimidzolium *bis*[(trifluoromethyl)sulfonyl]imide ionic liquids (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 [19, 20]. The phosphonium ionic liquids (*i.e.,* [trihexyl(tetradecyl)phosphonium cation with benzoate, salicylate and saccharinate anions) employed in this study were synthesized, purified, and characterized according to a published method [21] with minor modifications. Specifically, a dichloromethane solution of $P_{666,14}^+Cl^-$ was mixed for two hours at room temperature with a saturated aqueous (D.I. water) solution of the sodium salt of the anion of interest. The IL (lower) layer was separated from the aqueous layer and washed with D.I. water three times. A silver nitrate test was used to ensure removal of excess NaCl. The organic phase was evaporated to dryness at 80°C and the residue (*i.e.,* the IL) was examined by ^1H NMR. Partitioning studies were performed using dicyclohexano-18-crown-6 (DCH18C6) as the extractant. A commercial mixture of the *cis-syn-cis* and *cis-anti-cis* isomers (Parish Chemical Company, Orem, UT) was used as received. Aqueous acid solutions were prepared using Milli-Q2 water and Optima™ nitric acid (Aldrich, Milwaukee, WI) and standardized by titration with certified sodium hydroxide solutions (Ricca, Arlington, TX) using phenolphthalein indicator (Ricca, Arlington, TX). The ^{85}Sr radiotracer was purchased as a nominal solution from Eckert and Ziegler Isotope Products, Inc. (Burbank, CA).

5.2.2 Instruments

Radiometric measurements were carried out using gamma spectroscopy, which was performed using a PerkinElmer model 2480 automatic gamma counter equipped with WIZARD^2 software. NMR spectra of the ILs were acquired on a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for protons. Spectra were obtained using solutions in chloroform-d (Acros, 100.0% atom D) and all chemical shifts were reported relative to tetramethylsilane. The water content of each IL was measured using a Metrohm 870 KF Titrino Plus coulometer using hydranal (Aldrich Chemical, Milwaukee, WI) as the titrant. The solubility of each IL in water was measured by UV-visible absorption using a Shimadzu UV-2450 spectrophotometer equipped with matching 10-mm pathlength quartz cuvettes.

Surface tension measurements were carried out using a Surface Tensiomat 21 (Fisher Scientific) utilizing a Du Nouy Tensiometer Ring (CSC Scientific, Fairfax, VA) with a circumference of 6.158 cm. Thermogravimetric analysis (TGA) was performed using a TA Instruments Model Q50. Experiments were run using a platinum pan containing 8.0-8.7 mg samples under a nitrogen atmosphere from room temperature to 600°C at a scan rate of 10°C/min. Differntial scanning calorimetry (DSC) measurements were performed with a TA Instruments DSC Model Q20. Experiments were run under a nitrogen atmosphere. Samples (6-9 mg) were first frozen at -90°C and then heated to 100°C at a rate of 5°C/min in a hermetically sealed aluminum pan.

5.2.3 Methods

The ionic liquid irradiation was carried out in two separate series of experiments performed at two different locations. In the first series, carried out at Argonne National Laboratory, samples were placed in 10-mm NMR tubes and irradiated (at 25°C) with a beam (1.0 μA) of 3 MeV electrons from a Van de Graaff accelerator using either 12 ns pulses at a repetition rate of 180 Hz or 25 ns pulses at a repetition rate of 120 Hz. Samples were cooled by flowing water (20°C) around the sample during the radiolysis. Due to the deposited heat, the temperature of the liquid sample at the center of the tube increased to 40°C during the irradiation process. These irradiated samples were used for all extraction and solubility studies. The irradiation time and corresponding dose for each sample are shown in Table 5.1. The typical dose in these experiments was 50-244 Mrad (500-2440 kGy) at a dose rate of 2440 ± 50 kGy/hr.

The second group of samples was irradiated at Idaho National Laboratory. In these experiments, samples were placed in glass scintillation vials, which were then irradiated at 25°C utilizing a Fricke Dosimetry Irradiation Jig and a Co-60 source. This set of samples was used for viscosity, surface tension and water content studies. The irradiation time and corresponding dose quantity for each sample is shown in Table 5.2. The typical dose was approximately 2400 kGy at a dose rate of 7.3 – 9.44 kGy/hr.

Table 5.1
Irradiation time (mins) and corresponding dose (kGy) for irradiated imidazolium and phosphonium ionic liquids.

IL:	$C_n$mimTf$_2$N			0.1M DCH18C6 in $C_n$mim$^+$Tf$_2$N$^-$			0.1M DCH18C6 in $P_{666,14}{}^+X^{-a}$					
Time	$n = 5$	8	10	$n = 5$	8	10	Tf$_2$N	Sal.	Benz.	Sacc.	Cl	NO$_3$
15	464	488	488	550	550	550	610	550	610	610	610	NM[b]
30	928	976	928	1100	1100	1100	1220	1100	1220	1220	1220	1220
45	1428	1410	1428	1650	1650	1650	1831	1650	1830	1831	1831	NM[b]
60	1958	1855	1806	2200	2200	2200	2441	2200	2440	2441	2441	2441

[a] Sal., Benz., and Sacc. represent salicylate, benzoate and saccharinate respectively.
[b] Due to limited quantity of material, these time intervals were not completed.

Table 5.2
Dose rate (kGy/hr) and dose (kGy) for irradiated phosphonium ($P_{666,14}{}^{+}X^{-}$) ionic liquids.

X	Benzoate	Saccharinate	Salicylate
Dose Rate[a]	8.72 / 8.44	8.71 / 8.85	8.84 / 8.47
Dose	2472.3 / 2395.5	2469.8 / 2509.5	2401.6 / 2507.6

[a]Decay corrected dose rate.
Note: Two samples of each of IL were irradiated. The samples were combined for characterization.

Distribution ratios (D_M, defined as $[M]_{org}/[M]_{aq}$ at equilibrium) were determined with a commercial radiotracer assayed *via* gamma spectroscopy using standard procedures. In each metal distribution experiment, the organic phase consisted of DCH18C6 dissolved in a given ionic liquid. The aqueous phase acid concentration was systematically adjusted by conducting separate experiments for each condition. Unless otherwise noted, metal distribution measurements were performed with 0.1 M DCH18C6 in the organic phase. 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 water or an appropriate aqueous acid solution. Each equilibrated phase was sampled for analysis in at least duplicate, with resulting uncertainties based on counting statistics that were generally within 10%. Additionally, for radiometric measurements, the sum of the count rates in each phase yielded recoveries within 10% of that of the radiotracer stock solution added, thus indicating that equilibrium was reached with only two phases involved.

All physical and thermal characterization of the ionic liquid samples was carried out in the absence of crown ether. The density of each ionic liquid was determined by weighing a known volume measured by a calibrated micropipette or a volumetric flask. All measurements for "dry" ionic liquids were performed using materials that had been dried *in vacuo* at 70°C for at least 24 hours in small quantities (≤3 mL) to facilitate the removal of water. The water solubility of the ionic liquids (ILs) was measured by UV-visible spectrophotometry at the wavelength characteristic of the imidazolium ring (210 nm) using standards prepared from a known weight of the dry IL. Both the standards and the ionic liquid solutions were prepared in 50:50 (v/v) methanol:water. 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 minutes, and allowed to stand undisturbed at 25 ± 2°C to equilibrate for 1 hour. Following centrifugation at 3000 rpm, the aqueous phase was removed and diluted as needed for solubility measurements, while the organic phase was used for water content measurements. The water content of the ILs was measured using a Metrohm 870 KF Titrino Plus coulometer using hydranal (Aldrich Chemical, Milwaukee, WI) as the titrant and 18 MΩ water for calibration.

5.3 Influence of γ-Radiation on Ionic Liquids used in the Extraction of ^{85}Sr.

5.3.1 Evaluation of the effect of radiation on the extraction mechanisms utilizing imidazolium ionic liquids

Although considerable effort has been expended to determine the effect of ionic liquid structure on the mode of partitioning of extracted metal ions, little attention has been devoted to the effect of radiation stability on extraction mechanisms. A generalization has previously been made that aromatic compounds are more stable than non-aromatic ones due to their ability to absorb energy, with a combination of the two (*i.e.,* an aliphatic IL cation plus an aromatic anion) showing the most promise towards stability [6]. Imidazolium ionic liquids (*i.e.,* $C_n\text{mim}^+$ ILs) have been studied the most extensively for radiation stability due to their aromatic nature. Previous studies have found that gamma irradiation has minimal effect on the extraction efficiency of strontium from aqueous solutions into these solvents by DCH18C6. In particular, it was found that solutions of DCH18C6 in $C_4\text{mim}^+\text{Tf}_2\text{N}^-$ or $C_4\text{mim}^+\text{PF}_6^-$ exhibit only a slight decrease in extraction efficiency after irradiation [11, 13, 14]. It was determined that radiation-generated protons interact with the neutral extractant (introduced to the ionic liquid after irradiation), decreasing its efficiency. It was found that this effect could be eliminated by washing the irradiated ionic liquids with water to remove the degradation products [13]. These studies, by focusing on systems employing short-chain (*i.e.*, relatively hydrophilic) imidazolium cations ($C_n\text{mim}^+$, with $n = 4$) chose conditions known to favor extraction *via* ion-exchange (see Chapter 2), a process known to be undesirable [22]. Moreover, these studies focused upon extraction efficiency, rather than considering the effect of radiolysis 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. In an effort to build on prior work, the same class of ionic liquids was examined (*i.e.*, $C_n mim^+Tf_2N^-$) incorporating more hydrophobic cations (where n = 5-10).

Figure 5.1 shows the nitric acid dependency of the extraction of strontium by a 0.1 M solution of DCH18C6 in $C_5mim^+Tf_2N^-$ under various irradiation conditions. As shown in panel A of the figure, for $C_5mim^+Tf_2N^-$ in the absence of irradiation, the extraction of strontium (*i.e.,* D_{Sr}) exhibits a significant decline as the acidity (*i.e.,* nitrate concentration) rises until *ca.* 2 M HNO_3, above which an increase is observed. As noted previously by Dietz *et al.* [22], a decline in the extraction of strontium with increasing nitrate concentration is consistent with a combination of two ion-exchange processes (equation 5.1) one involving exchange of the cationic strontium-crown ether complex ($Sr{\bullet}DCH18C6^{2+}$) for the cationic constituent of the ionic liquid ($C_n mim^+$) [23, 24] and a second (equation 5.2) in which the strontium ion is exchanged for hydronium ions complexed by the crown ether, analogous to previous results for the extraction of Na^+ in the same systems [24, 25].

$$Sr{\cdot}(DCH18C6)_{aq}{}^{2+} + 2\ C_n mim_{org}{}^{+} \rightarrow Sr(DCH18C6)_{org}{}^{2+} + 2\ C_n mim_{aq}{}^{+} \qquad (5.1)$$

$$Sr_{aq}{}^{2+} + 2\ H_3O{\cdot}DCH18C6_{org}{}^{+} \rightarrow Sr{\cdot}DCH18C6_{org}{}^{2+} + 2\ H_3O_{aq}{}^{+} + DCH18C6_{org} \qquad (5.2)$$

At acidities greater than 2 M HNO_3, an increase in the extraction of strontium is observed suggesting that the metal cation is being extracted as a neutral strontium-extractant-nitrato complex (or ion pair), as shown in equation 5.3 [26]:

$$Sr_{aq}^{2+} + 2\ NO_3^-{}_{aq} + DCH18C6_{org} \rightarrow Sr(NO_3)_2 \cdot DCH18C6_{org} \quad (5.3)$$

To facilitate comparison to previous work, the $C_5mim^+Tf_2N^-$ ionic liquid was initially irradiated in the absence of extractant for periods of 15 to 60 minutes, corresponding to doses ranging from 500 to 2000 kGy. Following irradiation, a 0.1 M DCH18C6 solution was prepared for the irradiated ionic liquid at each time/dose interval and the extraction of strontium measured. As can be seen from Figure 5.1, trends in the nitric acid dependency for the 0.1 M DCH18C6 in irradiated $C_5mim^+Tf_2N^-$ (panel B) similar to those seen with the non-irradiated IL are observed. In particular, a decrease in strontium extraction is observed with increasing acidity up to *ca.* 2 M HNO_3. Unlike the non-irradiated ionic liquid, for which an upturn is observed at higher acidities, a flattening of the acid dependency is observed for the irradiated material. This change in the acid dependency indicates that some degradation of the IL has occurred. In addition to the effects at high acidity, a decrease in the extraction efficiency is also observed at low acidities. Overall, however, the general trends in extraction are maintained upon irradiation of the IL. Thus, although the irradiation process does affect ionic liquids (consistent with observations made previously with $C_4mim^+Tf_2N^-$ [11, 14]), the effects are not so substantial as to preclude their use.

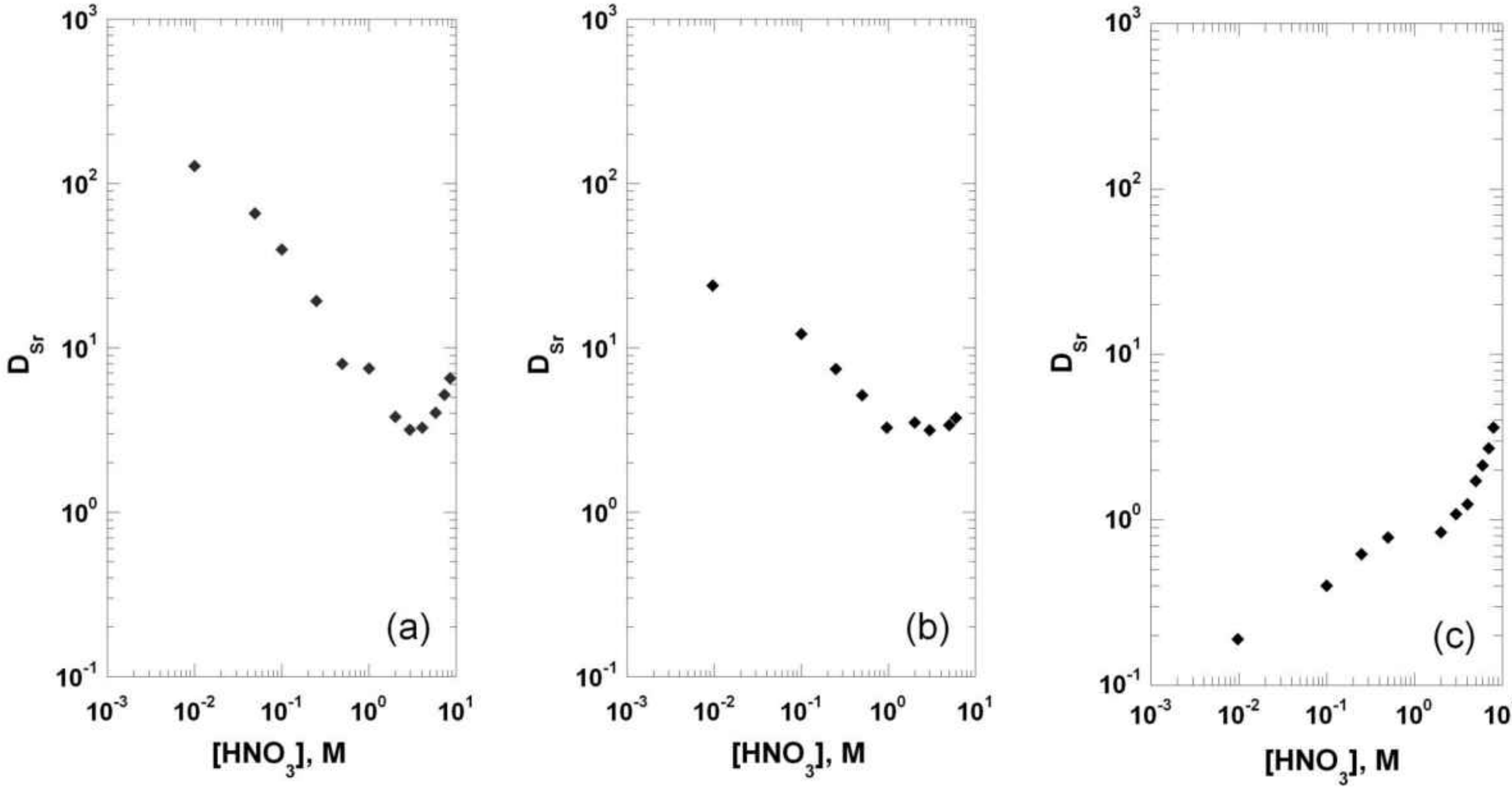

Figure 5.1: Nitric acid dependency of 0.10 M DCH18C6 in $C_5mim^+Tf_2N^-$: (a) no irradiation of IL (b) IL irradiated in absence of crown ether at 1950 kGy (c) IL irradiated in presence of crown ether at 2200 kGy.

In addition to the degradation of the solvent, possible deterioration of the extracting agent [15] must also be considered. To examine the effect of radiolysis on the extractant, solutions of 0.1 M DCH18C6 in several $C_n$mim$^+$Tf$_2$N$^-$ (where $n = 5$, 8 and 10) ILs were prepared and irradiated for varying times and at several doses. These solutions were then used (with no further modifications) for the extraction of strontium from nitric acid solutions. Contrary to observations made for irradiated imidazolium ILs in the absence of extractant, substantial changes were observed in the nitric acid dependency of D_{Sr} for 0.1 M DCH18C6 in C_5mim$^+$Tf$_2$N$^-$ upon irradiation (Figure 5.1, panel c). Specifically, the strontium distribution ratios (*i.e.,* D_{Sr}) decreased for all nitric acid concentrations, with a more dramatic decrease at low nitrate concentrations, where the values dropped by nearly three orders of magnitude. These changes lead to an acid dependency whose shape is consistent with extraction by neutral complex formation (ion-pairing), which is signaled by increasing extraction with increasing nitrate concentration. Of course, without identification of the degradation products, a definitive statement cannot be made concerning precisely what changes induced by irradiation have led to the apparent change in the mode of partitioning. It is interesting to note, however, that the observed changes could be accounted for by a diminution in the ability of the crown ether to extract nitric acid. It is, obviously, the extraction of acid that makes possible partitioning *via* exchange of the metal ion for crown-complexed hydronium ions. Without acid extraction, this mode of strontium partitioning (equation 5.2) would clearly not be observed, and the acid dependency of D_{Sr} would not decline with rising acidity. If radiolysis were to result in opening of the crown ether ring, one would anticipate a decrease in the ability of the extractant to take up acid. Of course, the ability of the crown ether to extract strontium would also be altered. An indication of the extent to which this may occur is found in a comparison of the barium (as a representative divalent cation) formation constant for 18C6 and an open chain analog, pentaglyme ($\log K = 6.56$ and $\log K = 2.33$, respectively) [27].

Figures 5.2 and 5.3 summarize analogous results obtained for two ionic liquids with more hydrophobic cations, $C_8mim^+Tf_2N^-$ and $C_{10}mim^+Tf_2N^-$, respectively. As noted previously (chapter 2), as the hydrophobicity of the IL cation increases, the primary mode of extraction shifts, from ion exchange to neutral complex extraction (ion-pairing). Such a trend is observed for the non-irradiated ionic liquids (Figure 5.1–5.3, panel A) in the three systems. As was observed for $C_5mim^+Tf_2N^-$, minimal changes are observed when the ionic liquid is irradiated in the absence of crown ether, while more dramatic effects are noted when the crown is present during irradiation.

Interestingly, for all three systems examined, the acid dependencies for the ionic liquids irradiated with crown ether present (panel C in Figures 5.1, 5.2 and 5.3) exhibit a similar trend. That is, in all three cases, strontium extraction increases with increasing nitrate concentration, suggesting that the extraction occurs primarily by neutral nitrato complex formation / ion-pairing. It is important to note that among the most important characteristics of a workable process for the treatment of nuclear wastes is consistent process performance. Ideally then, radiolysis should have no discernible effect on the values of D_{Sr} across the entire range of acidities. Thus, although our results indicate that radiolysis of DCH18C6 in $C_n mim^+Tf_2N^-$ ILs leads to an improvement in the shape of the acid dependency of D_{Sr}, such an improvement is actually less desirable than is unchanged extraction behavior.

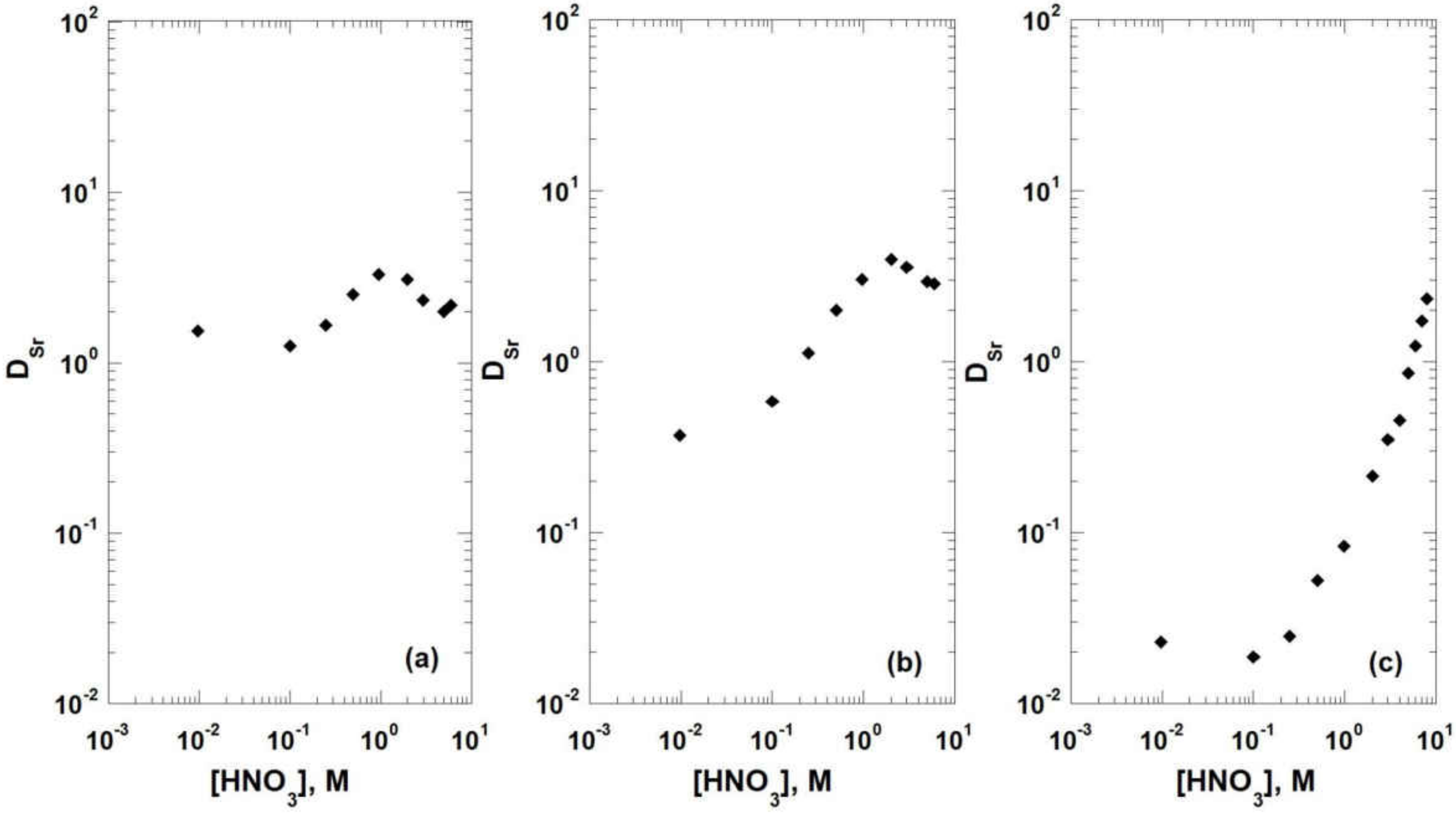

Figure 5.2: Nitric acid dependency of 0.10 M DCH18C6 in $C_8mim^+Tf_2N^-$: (a) no irradiation of IL (b) IL irradiated in absence of crown ether at 1860 kGy (c) IL irradiated in presence of crown ether at 2200 kGy.

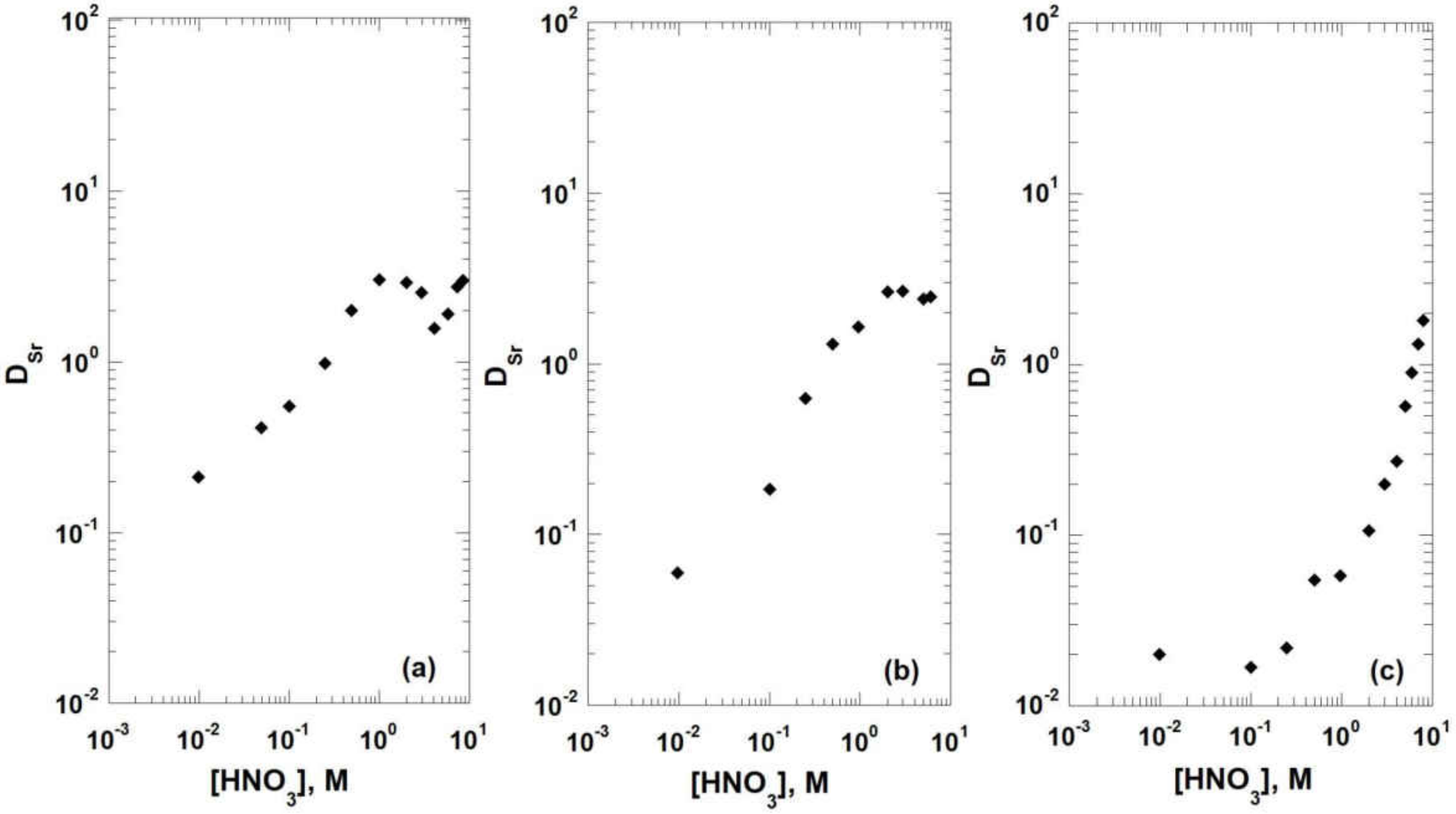

Figure 5.3: Nitric acid dependency of 0.10 M DCH18C6 in $C_{10}mim^+Tf_2N^-$: (a) no irradiation of IL (b) IL irradiated in absence of crown ether at 1810 kGy (c) IL irradiated in presence of crown ether at 2200 kGy.

5.3.2Evaulation of the effect of radiation on the extraction mechanisms utilizing phosphonium ionic liquids

The changes in extraction efficiency observed for the imidazolium ionic liquids made it necessary to extend our studies of IL radiolysis to a different family of cations, one hopefully less prone to degradation than 1,3-dialkylimidazolium salts. As already noted, in addition to the absence of degradation, it would be desirable that the ionic liquid also facilitate the extraction of a neutral metal-crown ether-nitrato complex (or ion-pair). That is, the acid dependency for metal ion extraction should exhibit an increase with rising acidity. It has been previously shown that the more hydrophobic the IL cation is, the greater the tendency toward ion-pair extraction. For this reason, phosphonium ionic liquids were regarded as promising candidates, and were therefore investigated. In our initial experiments, the cation of the ionic liquid was changed from imidazolium to phosphonium while the anion remained unchanged. Specifically, trihexyl(tetradecyl) phosphonium *bis*(trifluorosulfonyl)imide ($P_{666,14}^{+}Tf_2N^{-}$; Cytec Industries) was evaluated. The acid dependency of D_{Sr} for this IL is shown in Figure 5.4. Panel A depicts the results obtained before radiolysis. As can be seen, an increase in strontium extraction (*i.e.,* D_{Sr}) is observed as the nitrate concentration increases. As previously shown for the imidazolium ionic liquids, such a trend is consistent with partitioning *via* neutral complex formation (ion-pairing) as shown in equation 5.3. In contrast to the significant changes in the acid dependency observed for the imidazolium ionic liquids, only a modest alteration was observed for the phosphonium IL (Figure 5.4, panel B). That is, as the nitrate concentration increases, the extraction also continues to increase. Some flattening of the acid dependency is observed for the lower nitrate concentrations, however. In addition, a decrease in the distribution ratios (but not a change in their trend) is observed at any given high nitrate concentration, as was observed for the imidazolium ionic liquids. Because the Tf_2N^- anion has been shown to fragment upon radiolysis to yield sulfur-containing species that precipitate strontium sulfate or sulfite at the water-IL interface [14], some change in extraction behavior is not entirely unexpected here.

Preliminary evidence suggests that certain aromatic anions, such as benzoate and salicylate, are relatively radiolytically stable [15], and for this reason, phosphonium ILs incorporating these anions were also evaluated. Figure 5.5 (panel A) depicts the nitric acid dependency of $P_{666,14}{}^{+}$benzoate^{-}. As can be seen, the extraction of strontium is apparently accomplished *via* ion-pairing. That is, as the nitrate concentration rises, the extraction of strontium also increases. From the results in panel B, which depicts the effect of radiolysis upon the extraction, it is clear that the use of a hydrophobic aliphatic cation and an aromatic anion (*i.e.,* benzoate) provides both the desired extraction mechanism and satisfactory radiation stability. That is, after maximum irradiation, the acid dependency still exhibits a linear increase in the extraction of strontium, and contrary to the imidazolium ionic liquids, where a decrease in extraction is observed after irradiation, minimal change in the D_{Sr} values were observed for the system.

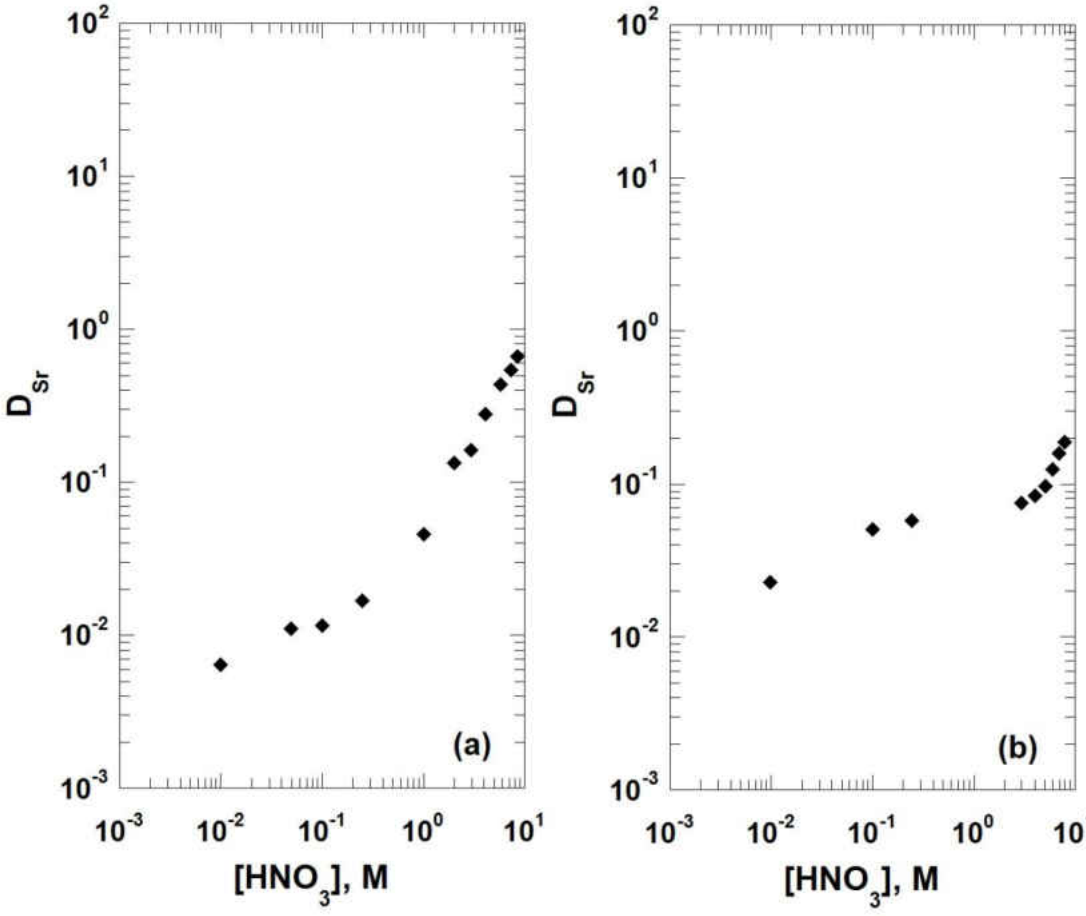

Figure 5.4: Nitric acid dependency of 0.10 M DCH18C6 in $P_{666,14}{}^{+}Tf_2N^{-}$: (a) no irradiation of IL and (b) IL irradiated in presence of crown ether at 1830 kGy.

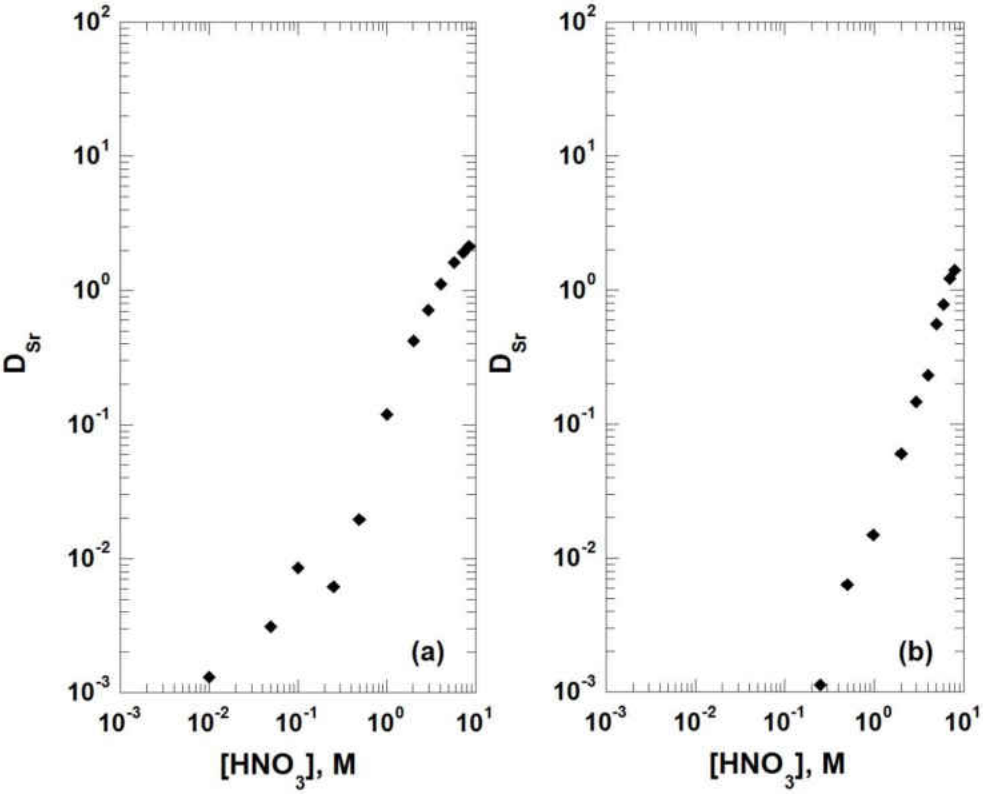

Figure 5.5: Nitric acid dependency of 0.10 M DCH18C6 in $P_{666,14}^{+}$benzoate^{-}: (a) no irradiation of IL and (b) IL irradiated in presence of crown ether at 2440 kGy.

Similar trends were observed for the other phosphonium carboxylate ionic liquids studied. Figures 5.6 and 5.7 show the nitric acid dependencies for strontium extraction for $P_{666,14}^{+}$salicylate^{-} and $P_{666,14}^{+}$saccharinate^{-}, respectively. As can be seen, in both cases, the predominant mode of partitioning is apparently extraction of a neutral nitrato complex (ion-pair extraction), and radiation has little, if any, effect on the preferred extraction mode.

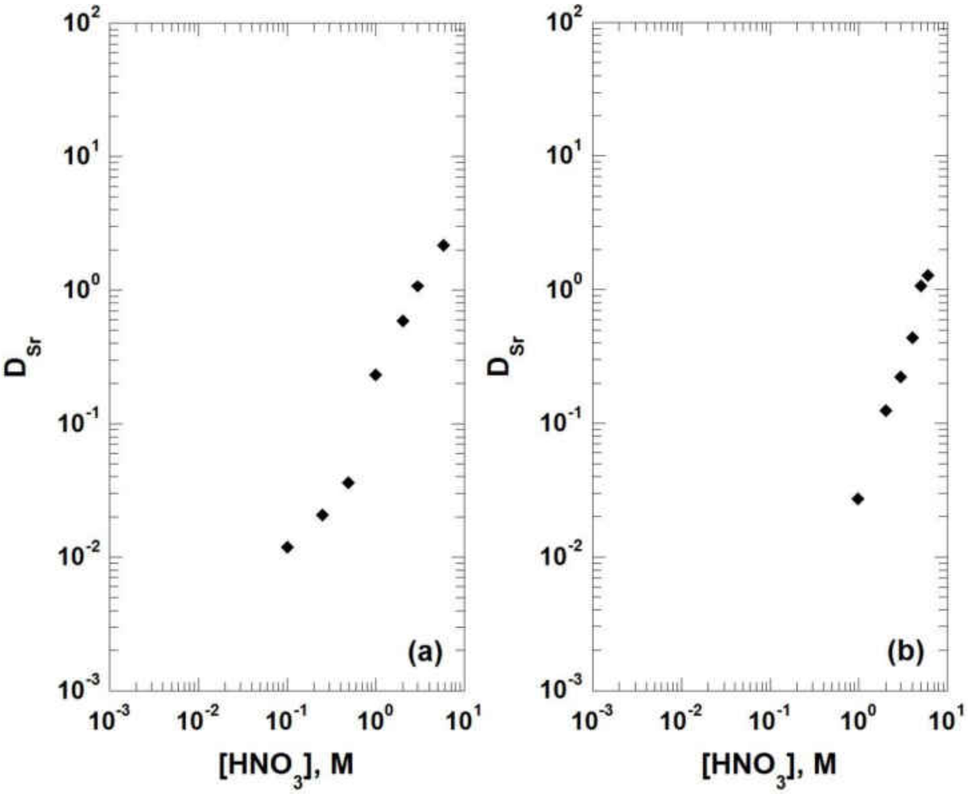

Figure 5.6: Nitric acid dependency of 0.10 M DCH18C6 in $P_{666,14}^{+}$salicylate^{-}: (a) no irradiation of IL and (b) IL irradiated in presence of crown ether at 2440 kGy.

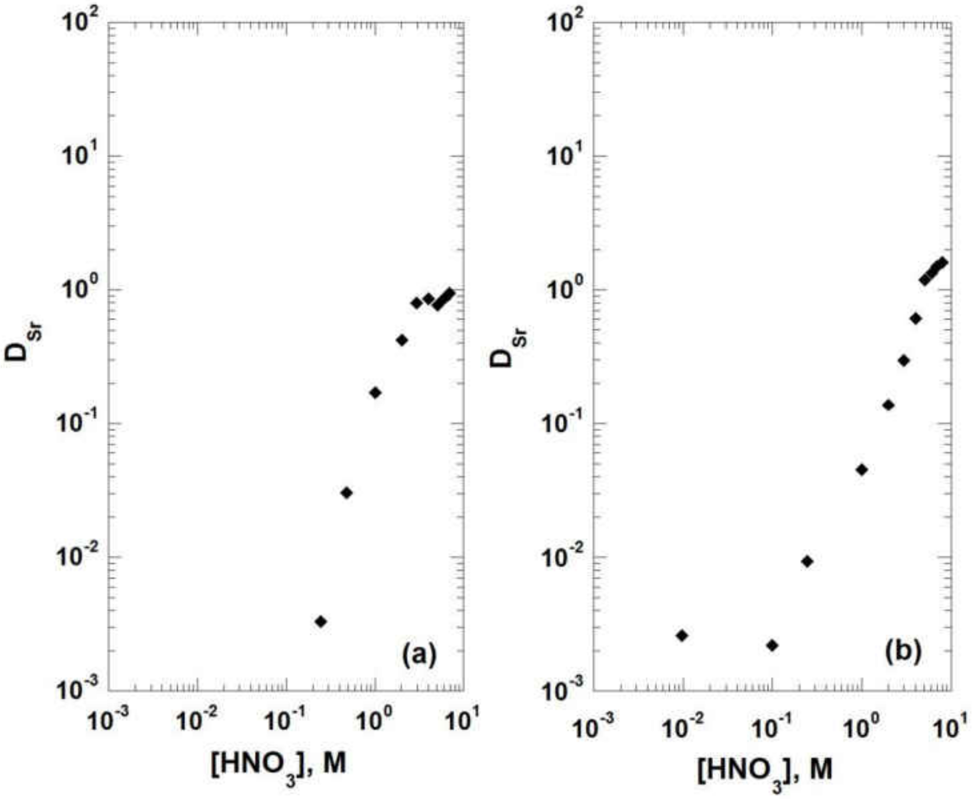

Figure 5.7: Nitric acid dependency of 0.10 M DCH18C6 in $P_{666,14}^+$saccharinate$^-$: (a) no irradiation of IL and (b) IL irradiated in presence of crown ether at 2440 kGy.

These findings indicate that by combining a hydrophobic aliphatic cation with an aromatic anion (*e.g.,* carboxylate anion), both the preferred mode of partitioning and radiation stability can be achieved. These systems thus show promise for nuclear fuel reprocessing applications. Accordingly, they were further investigated to determine the effect of radiolysis on various other properties relevant to large scale liquid-liquid extraction processes.

5.4 Influence of γ-Radiation on the Physical and Thermal Properties of Imidazolium and Phosphonium Ionic Liquids.

5.4.1 Physical characterization of phosphonium ionic liquids

Gamma irradiation of the imidazolium ionic liquids caused a readily evident change in their appearance. Prior to irradiation, the ILs were pale yellow in color, while after irradiation, each was dark red. Such color changes are consistent with observations made for other imidazolium ionic liquids, including $C_4mim^+PF_6^-$ [9], $C_4mim^+BF_4^-$ [10], $C_2mim^+Cl^-$, and $C_4mim^+NO_3^-$ [6], all of which showed considerable darkening upon irradiation. Contrary to prior results, however, where the degree of darkening varied, here the high radiation dose to which the samples were exposed meant that all of the samples were comparably dark. (In prior studies involving irradiation of short chain ionic liquids, doses ranged from 2 – 400 kGy. In contrast, here the radiation doses were up to 5 times greater.) Contrary to $C_4mim^+PF_6^-$ [9], where toxic and corrosive HF fumes were formed, no pungent odors where detected upon irradiation of the ILs examined here. In contrast to the imidazolium ionic liquids, no effect on physical appearance was observed upon irradiation for the phosphonium carboxylate ionic liquids. Both before and after irradiation, all were pale yellow.

^{1}HNMR spectra of the imidazolium and phosphonium ionic liquids collected before and after irradiation showed no discernible changes, even at a dose of 2000 kGy. This finding is consistent with prior results described for $C_4mim^+PF_6^-$ [9], $C_4mim^+BF_4^-$ [10], $C_2mim^+Cl^-$, and $C_4mim^+NO_3^-$ [6], for which no changes were observed. This indicates that less than 1% of the sample was decomposed in each case. Despite the apparent lack of NMR evidence of IL degradation, the changes in physical appearance and extraction behavior observed for the imidazolium ionic liquids suggests that they are insufficiently stable to radiolysis to be suitable for use in nuclear waste processing. Further physical and thermal characterization of irradiated ILs was therefore carried out only for the phosphonium ionic liquids.

Table 5.3 compares the water content, solubility in water, density and surface tension of the phosphonium ionic liquids before and after exposure to gamma radiation. (Note that the surface tension and water content measurements were made without subjecting the material to drying.) As can be seen, there is no significant change in these physical properties after gamma radiation at the dose considered. Prior studies of various pyrrolidinium [28] and imidazolium [7] ionic liquids before and after radiolysis also showed negligible change in the physical properties up to a radiation dose of 700 kGy. This indicates that these properties are less susceptible to radiation damage than other properties such as extraction efficiency. Contrary to these physical properties, changes in viscosity were observed for both the pyrrolidinium and imidazolium ionic liquids examined. Specifically, an increase in sample viscosity was observed with increasing radiation dose [7, 28]. Similar results were noted when handling the irradiated imidazolium ionic liquids in this study, but the amount of materials available was insufficient to permit data to be obtained.

Table 5.3

Physical properties of phosphonium carboxylate ionic liquids, before and after irradiation (2440 kGy).

		Density (g/mL)[a]	Water Content (ppm)			Solubility in water (ppm)	Surface Tension (mN/m)
			"wet"[a]	"dry"	Lit.		
[$\mathrm{P}_{666,14}$][benzoate]	No irradiation	0.916 / 0.920[1]	112950	2675[b]	36[1]	224	30.8
	Irradiated	0.935	107725	12840[c]		626	30.9
[$\mathrm{P}_{666,14}$][salicylate]	No irradiation	0.923 / 0.922[1]	62150	1467[b]	80[1]	237	31.3
	Irradiated	0.970	94167	1767[c]		238	32.3
[$\mathrm{P}_{666,14}$][saccharinate]	No irradiation	0.961 / 0.968[2]	23917	425[b]	230[2]	4570	32.5
	Irradiated	0.924	46150	6250[c]		589	31.1

[a] 4 mL of IL was contacted with 15 mL of 18MΩ water at 24±2°C for 1 week, slow mixing was required.

[b] Ionic liquids (not irradiated) were dried at 70°C for 96 hours.

[c] Irradiated "dry" materials were measured as received.

[1] Reference 29

[2] Reference 30

Table 5.4
Thermal properties of phosphonium carboxylate ionic liquids, before and after irradiation (2440 kGy).

		T_d (°C)[a]	Measured mass loss/wt% (Isothermal Decomposition)		T_g (°C)[d]
			Temp. 1[b]	Temp. 2[c]	
$[P_{666,14}]$[benzoate]	No irradiation	327 / 360[1]	23	62	-66.4 / -75.5[3]
	Irradiated	322			-65.9
$[P_{666,14}]$[salicylate]	No irradiation	341 / 340[1]	9.5	55	-67.6
	Irradiated	331			-64
$[P_{666,14}]$[saccharinate]	No irradiation	376 / 197[2]	7	76	-56 / -56[1]
	Irradiated	373			-47.5

[a] T_d: onset decomposition temperature based on TGA measurement. The estimated errors are ±5°C.
[b] Isothermal temperature 1 was measured 100°C below T_d.
[c] Isothermal temperature 2 was measured 50°C below T_d.
[d] T_g: glass transition temperature based on DSC measurement. The estimated errors are ±5°C.
[1] Reference 29
[2] Reference 30
[3] Reference 31

5.4.2 Thermal characterization of phosphonium ionic liquids

A comparison of various thermal properties (*i.e.,* glass transition and decomposition temperatures), before and after gamma irradiation is shown in Table 5.4. Like their physical properties, the thermal properties of the phosphonium ILs show negligible change after gamma irradiation. In addition to a comparison of properties before and after irradiation, isothermal decomposition data was obtained for the phosphonium ionic liquids. Initially, measurements were made to determine the onset temperature for decomposition. Once this had been determined, each IL was held at either 50°C or 100°C below the onset temperature for eight hours to determine if prolonged exposure to these temperatures results in decomposition. Minimal weight loss was observed for the salicylate and saccharinate ILs, and a slightly greater mass loss for the benzoate. The extent of mass loss is consistent with the loss of the hydroxyl group and oxygen atoms from the salicylate and saccharinate ILs, respectively, while the weight loss for the benzoate IL apparently corresponds to the destruction of the benzoate anion itself. The temperatures observed for the glass transition did not change significantly before and after irradiation.

5.5 Conclusions

The results of this study clearly demonstrate that the mode of partitioning for the extraction of strontium from acidic nitrate media into 1,3-dialkylimidazolium ionic liquids by a crown ether is affected by gamma irradiation. For the systems analyzed, a decrease in extraction (*i.e.,* D_{Sr}) was observed in addition to a change in the shape of the acid dependency after the extractant was irradiated. Changing the ionic liquid to incorporate a more hydrophobic cation and an aromatic anion (*i.e.,* $P_{666,14}^{+}$ carboxylate) led to extraction *via* neutral complex extraction / ion-pair formation and negligible change in either the extraction efficiency or the shape of the acid dependency upon gamma irradiation. In addition to the effect on extraction, the physical and thermal properties were examined before and after radiolysis. Negligible change in these properties was observed for the phosphonium ionic liquids examined. These findings indicate that the phosphonium carboxylate ionic liquids may be good candidates for use in nuclear fuel reprocessing. Additional study of these ILs is clearly warranted.

5.6 Acknowledgements

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CHAPTER 6:

TRIBOLOGICAL PROPERTIES OF IMIDAZOLIUM AND PHOSPHONIUM IONIC LIQUIDS INCORPORATING CARBOXYLATE ANIONS: A PRELIMINARY EVALUATION

6.1 Introduction

The depletion of the world's crude oil reserves, increasing oil prices, and issues concerning environmental contamination have led to increasing interest in the use of materials that are environmentally benign and renewable, and that provide feasible and economical alternatives to petroleum-based oils [1]. For example, natural oils, typically plant or animal-based, have recently attracted growing attention as lubricants and hydraulic fluids, a result of their biodegradability, low ecotoxicity [2, 3], high lubricity, carrying capacity, shear stability, and lower volatility [4]. The reduced ecotoxicity of these materials *vs.* traditional lubricants is especially important given that approximately 50% of all lubricants ultimately end up in the environment due to loss during use, spills, volatility, accidents and improper disposal [5], and that more than 95% of these consist of petroleum-based oils that are hazardous to the environment.

Liquid biolubricants derived from plant-oils typically consist of triacylglycerol molecules made up of esters derived from glycerol and long chains of polar fatty acids. The fatty acids are desirable in boundary lubrication for their ability to adhere to metallic surfaces due to their polar carboxyl group, remain closely packed, and create a monolayer film that is effective at reducing friction and wear by minimizing the asperity contact [6]. Much of the work with bio-based oils has concentrated on understanding the fundamental behavior of saturated and unsaturated fatty acids as additives in mineral oils and bio-based feedstock for chemically-modified lubricants [7]. Recently, biolubricants have found use as carrier fluids for lamellar powder additives in sliding contact [8]. Lamellar powders have been shown to be useful over a broad range of pressures and temperatures, and thus, in applications ranging from automotive to aerospace where reduced friction and minimization of wear are crucial [1, 9].

For practical applications, lubricants must exhibit protection against wear and corrosion and must provide effective heat removal [2]. Natural oils, particularly those that are plant-based, have shown superiority in these areas. Despite these benefits, the applications of these materials in industry and motor vehicles has been limited due to low stability and high pour points [10], which has led to the development of modified synthetic biolubricants [4], the use of stabilizing additive [2, 10] and more recently, ionic liquids.

Ionic liquids (ILs), a novel class of solvents typically consisting of a bulky, asymmetric organic cation in combination with any of a wide variety of organic or inorganic anions, exhibit a number of unique and useful characteristics, including high thermal stability, low melting point, a broad liquidus range, and negligible vapor pressure. The last of these properties, by minimizing solvent losses due to volatilization (*i.e.*, fugative emissions), has led many to regard ionic liquids as “green solvents”, and over the last decade, they have been evaluated in a wide range of applications, including the fabrication of dye-sensitized solar cells [11], the preparation of electrolytes for electrochemical storage devices [12] and batteries, the electrodeposition of metals [13], the recovery of metal ions from aqueous solutions *via* liquid-liquid extraction (LLE) [14, 15], and the development of separation processes for various organic compounds [16]. Many of the same properties that make ILs useful in these applications also make them good candidates as high-performance lubricants [17].

The use of ionic melts as lubricants was first reported in 1961, when fluoride-containing molten salts (*i.e.* LiF and BeF_2) were subjected to high-temperature (650-815°C) bearing tests [18]. Four decades later, low-melting analogs of classical molten salts, room-temperature ionic liquids (RTILs), were first evaluated as synthetic lubricating fluids [19]. Since this time, considerable attention has been devoted to the application of ILs as lubricants. Three applications have been the most extensively explored: the use of ILs as base oils, as additives, and as thin films [20]. When employed as base oils, ILs have been reported to exhibit good tribological performance for steel/steel, ceramic/ceramic, and steel/aluminum sliding pairs [20]. ILs are also effective as additives to the main lubricant (*e.g.,* mineral oils), where because of their tendency to form strong boundary films, they will enhance the tribological performance of the primary lubricant [20, 21]. Thin-film lubrication employing ILs has been studied by many researchers with the goal of replacing conventional perfluoropolyether (PFPE) lubricants [22-28].

Although the chemical structure of the cationic and anionic substituents of an IL can vary greatly, the most commonly studied ILs in tribological processes have been those containing a tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) anion [29, 30], a result of their ready availability, reasonable cost, and the good tribological properties under the high pressures and elevated temperatures that lubricants can encounter [31-34]. The frequent use of boron- and phosphorus-containing ILs as lubricants does not imply that either of them is optimum, however. In fact, BF_4^- and PF_6^- have been found to cause corrosion of steel under humid conditions. Moreover, other hydrophobic anions, such as *bis*(trifluoromethanesulfonyl) amide (TFSA) and tris(tetrafluoroethyl)trifluorophosphate (FAP), actually exhibit better tribological properties for steel-steel contact [35, 36]. In general, as the hydrophobicity of the anion increases, both the thermo-oxidative stability and the tribological properties improve [36].

Among the many possible IL cations, the imidazolium ion has probably been studied in the most detail, a result of the high thermal stability of imidazole-based rings [37]. Additionally, the chain length on the imidazolium cation can be readily altered. Increasing the chain length to make the IL more hydrophobic will decrease the friction coefficient in a manner similar to that observed when the anion is made more hydrophobic. In contrast to the improvement in thermo-oxidative stability observed with hydrophobic anions, however, a decrease in stability is observed with more hydrophobic cations [36]. Nonetheless, ILs with longer alkyl chains and lower polarity have been reported to have excellent tribological properties from low to relatively high temperature (-30°C to 200°C) [38]. Other ILs that have been studied with the goal of improving tribological properties include phosphonium [17, 39-41] and ammonium [27, 42-44] salts.

To date, the use of natural oils and ionic liquids as lubricants has been extensively investigated *independently*. To the best of our knowledge, however, these two families of lubricants have not been examined simultaneously under the same experimental conditions. In this study, the tribological properties of various natural oils and conventional ionic liquids have been evaluated utilizing the same instrument and experimental parameters. Specifically, a comparison of the tribological properties (*e.g.,* coefficient of friction and wear volume) of these two systems and a representative petroleum-based oil was made. In addition, the stability of the materials at elevated temperatures was evaluated.

6.2 Experimental

6.2.1 Materials

The conventional ionic liquids employed (1-pentyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide and its 1-hexyl-, 1-octyl- and 1-decyl-analogs, hereafter abbreviated as $C_n mim^+ Tf_2N^-$, where $n = 5$, 6, 8 or 10) were prepared *via* either conventional or microwave synthesis, purified and characterized using established methods [45, 46]. Phosphonium-based ionic liquids consisting of a [trihexyl(tetradecyl)] phosphonium cation paired with a benzoate, salicylate or Tf_2N anion were synthesized, purified, and characterized according to a published method [47] with slight modifications. In the method employed, a dichloromethane solution of $P_{666,14}^+Cl^-$ was contacted for two hours at room temperature with a saturated aqueous solution (in D.I. water) of either the sodium or lithium salt of the anion of interest to permit ion exchange. The IL (lower) layer was separated from the aqueous phase (upper) and washed three times with D.I. water to ensure complete removal of NaCl (or LiCl). The methylene chloride was then removed at 80°C and the chemical composition of the residue remaining (*i.e.,* the IL) was determined by ^1H NMR.

For comparison purposes, natural oils consisting of canola (rapeseed), olive, vegetable (soybean), peanut, sesame, avocado, corn, and safflower (high oleic acid) oil were purchased from a grocery store and used “as is”. In addition, SoyGold, a commercial soybean derived biolubricant, as well as SAE 10W-30 motor oil, a petroleum-based oil, were tested.

6.2.2 Instruments

Ionic liquid characterization was carried out by NMR spectroscopy. All spectra were acquired on a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for protons. Spectra were obtained using solutions in chloroform-d (Acros, 100.0% atom D) and all chemical shifts were reported relative to tetramethylsilane. Thermogravimetric analayis (TGA) was performed using a TA Instruments Q50. Experiments were run in a nitrogen atmosphere from room temperature to 600°C using a platinum pan at a temperature scan rate of 10°C/min using 8.35 ± 0.35 mg samples.

Pin-on-disk and friction measurements were conducted on a Ducom Instruments (Bangalore, India) Material Characterization System tribometer (up to 20 N) containing a unidirectional rotational disk spinning against a pin). The tribometer utilized a hanging mass load with a linear variable differential transformer (LVDT) to measure the wear rate.

6.2.3 Methods

In the pin-on-disk experiments, aluminum pins were used with a hemispherical-shaped pin tip with a diameter of 6.35 mm and a length of 50 mm. Stainless steel (440C) disks 70 mm in diameter and 6.35 mm in thickness were employed. Prior to use, the disks were polished to a surface roughness, R_a, of 0.3 ± 0.05 μm. The experiments were conducted under ambient conditions (T = 23°C) for a sliding distance of 0.5 km under a constant normal load of 10 N at a linear velocity of 36 mm/s.

A thermogravimetric analysis (TGA) was completed for each of the lubricants to determine its thermal stability. Prior to analysis, the samples were dried under vacuum (-28 in Hg) at 60°C to remove residual water. The TGA was performed by measuring the mass loss for both dynamic and isothermal decomposition. In the dynamic tests (*i.e.,* measuring the onset temperature, T_d, of decomposition), the samples were heated at a rate of 10°C/min from room temperature to *ca*. 800 to 1000°C. The experiment was stopped after T_m (maximum decomposition temperature) had been measured and a plateau at 0 wt% was observed for at least 200°C. In the isothermal decomposition tests, the samples were heated at a rate of 20°C/min from room temperature to a temperature approximately 50°C - 100°C below the T_d measured during the dynamic test and held for *ca*. 480 minutes.

6.3 Tribological Properties of Natural Oils and Ionic Liquid Lubricants

6.3.1 Lubricity properties of conventional imidazolium and phosphonium ionic liquids

The effect of altering the hydrophobicity of the IL (*i.e.,* the alkyl chain length of the IL cation) on the tribological properties exhibited by it at the aluminum-steel interface is shown in Table 6.1, where the measured steady-state coefficient of friction values are summarized.

Table 6.1
The measured steady-state coefficient of friction (μ) of a variety of conventional imidazolium and phosphonium ionic liquids and natural oils.

Lubricant	Coefficient of Friction (μ)[a]
Vegetable Oil	0.0690 ± 0.0023
Olive Oil	0.0706 ± 0.0028
Sesame Oil	0.0713 ± 0.0026
Peanut Oil	0.0718 ± 0.0025
Avocado Oil	0.0729 ± 0.0023
Safflower Oil	0.0738 ± 0.0020
$C_{10}mim^+Tf_2N^-$	0.0746 ± 0.0127
$P_{666,14}{}^+Tf_2N^-$	0.0951 ± 0.0333
Canola Oil	0.0956 ± 0.0013
Corn Oil	0.1003 ± 0.0025
SoyGold	0.1060 ± 0.0017
$C_8mim^+Tf_2N^-$	0.1094 ± 0.0270
$C_5mim^+Tf_2N^-$	0.1200 ± 0.0170
$C_6mim^+Tf_2N^-$	0.1348 ± 0.0167
10W-30 Motor Oil	0.1734 ± 0.0119

[a] IL and motor oil data adapted from reference 48.

It can be seen that as the alkyl chain length on the ionic liquid cation increases (*i.e.,* as cation hydrophobicity rises), the coefficient of friction decreases. In going from the shortest alkyl chain length to the longest (*i.e.,* $C_5mim^+Tf_2N^-$ to $C_{10}mim^+Tf_2N^-$), in fact, a nearly 60% decrease in the coefficient is observed. When a more hydrophobic cation (*i.e.,* $P_{666,14}^+$) was examined, the coefficient of friction improved further, by *ca.* 10%. Previous results [38] have shown imidazolium cations bearing longer alkyl chains tend to exhibit good tribological properties, an observation supported by these results. Interestingly, all of the ionic liquids tested outperform the petroleum-based 10W-30 motor oil.

Prior studies of the tribological properties of various natural oils, such as vegetable and canola oil, have shown that plant-based oils are able to maintain high lubricity, a result of their high fatty acid content (>70% oleic acid (C18:1) and linoleic acid (C18:2) [1]). The steady-state coefficient of friction for the natural oils tested is also shown in Table 6.1, enabling a comparison to be made to the conventional ionic liquids. As can be seen, the natural oils yield results similar to those obtained for the conventional imidazolium ionic liquids and almost the same as that of the phosphonium ionic liquid. All of the results represent a vast improvement over the motor oil.

In addition to the coefficient of friction, the wear volume (Table 6.2) was determined for the conventional room-temperature ionic liquids at ambient conditions. The imidazolium ($C_nmim^+Tf_2N^-$) ionic liquids, particularly those with comparatively hydrophobic cations, demonstrated superior wear resistance. As was the case in the previous study, the hydrophobicity of the ionic liquid cation appears to correlate with superior lubricity properties. Curiously, however, the wear volume efficiency decreased, in some cases, by a factor of 2, for the phosphonium ($P_{666,14}^{+}Tf_2N^{-}$) ionic liquid.

Contrary to the trend in the coefficient of friction observed for the natural oils and the ionic liquids, the opposite trend is observed in the case of wear volume (Table 6.2). That is, the ionic liquids have wear resistance superior to that of the natural oils. Friction and wear are two independent responses from a tribo-system, related to each other in the state of contact in the system. Nonetheless, a simple relationship between the two is not to be expected. Inconsistent trends (*e.g.,* natural oils have both lower friction and wear) are not uncommon, as often times lower friction is indicative of a soft material that will wear away rapidly [49]. Despite the difference in trend observed, both the natural oils and the ionic liquids still exhibit wear resistance superior to that of the conventional motor oil.

Table 6.2
The measured pin wear volume (mm^3) of a variety of conventional imidazolium and phosphonium ionic liquids and natural oils.

Lubricant	Pin Wear Volume (mm^3)[a]
$C_{10}mim^+Tf_2N^-$	0.0675 ± 0.0630
$C_6mim^+Tf_2N^-$	0.0689 ± 0.0226
$C_8mim^+Tf_2N^-$	0.0857 ± 0.0385
$C_5mim^+Tf_2N^-$	0.1226 ± 0.0739
$P_{666,14}{}^+Tf_2N^-$	0.2215 ± 0.0182
Peanut Oil	0.2787 ± 0.0303
Safflower Oil	0.3084 ± 0.0382
Olive Oil	0.3151 ± 0.0386
Canola Oil	0.3177 ± 0.0351
Avocado Oil	0.3220 ± 0.0312
SoyGold	0.3265 ± 0.0558
Vegetable Oil	0.3300 ± 0.0023
Corn Oil	0.3604 ± 0.0438
10W-30 Motor Oil	0.4628 ± 0.1640
Sesame Oil	0.6667 ± 0.0777

[a] IL and motor oil data adapted from reference 48.

6.3.2. Lubricity properties of phosphonium carboxylate ionic liquids

In many applications, a lubricant must be able to withstand prolonged use at high temperatures. Previous work examining the stability of ionic liquids to gamma irradiation (Chapter 5) showed that radiolytic stability is enhanced by the use of an aliphatic cation (*i.e.,* $P_{666,14}^{+}$) and an aromatic (especially a carboxylate) anion (*e.g.,* benzoate and salicylate). It seemed reasonable, given that radiolysis can cause significant heating of an irradiated sample, to assume that the structural features of an ionic liquid yielding high radiolytic stability would also provide good thermal stability. For this reason, our studies were extended to include a pair of carboxylate ionic liquids. In our initial experiments, the lubricity of these ionic liquids was determined and compared with that of both "conventional" ionic liquids and various natural oils. The thermal properties of all of the compounds were then evaluated.

Table 6.3 shows the steady-state coefficient of friction and pin wear volume of the phosphonium carboxylate ionic liquids. Comparison of these results to those of the conventional imidazolium ionic liquids, natural oils and motor oil as shown in Table 6.1 and 6.2 indicate that the phosphonium carboxylate ionic liquids exhibit a lower steady-state coefficient of friction. In fact, $P_{666,14}^{+}$benzoate^{-} and $P_{666,14}^{+}$salicylate^{-} have coefficient of friction values approximately half that of the natural oils and a third that of the conventional imidazolium ionic liquids.

Table 6.3
The measured steady-state coefficient of friction and pin wear volume (mm^3) of the phosphonium carboxylate ionic liquids.

Lubricant	Coefficient of Friction (μ)[a]	Pin Wear Volume (mm^3)[a]
$P_{666,14}^+$benzoate$^-$	0.04033 ± 0.0051	0.2117 ± 0.1321
$P_{666,14}^+$salicylate$^-$	0.0419 ± 0.0161	0.2819 ± 0.1494

[a] IL data adapted from reference 48.

The wear volume measurements for the phosphonium carboxylate ionic liquids show that $P_{666,14}^+$benzoate$^-$ exhibits a wear volume lower than that of the natural oils and higher than that of the imidazolium ionic liquids, while the $P_{666,14}^+$salicylate$^-$ has a higher wear volume than both the natural oils and the imidazolium ionic liquids. This indicates that neither the aromaticity of the anion nor the hydrophobicity of the cation is as important in determining wear volume as it was for friction.

6.4 Thermal Properties of Natural Oils and Ionic Liquid Lubricants

As already noted, in certain applications, a lubricant (*e.g.,* motor oil) must be able to withstand elevated temperatures for extended periods of time without significant decomposition. The thermal stability of the natural oils and ionic liquids was therefore examined by thermogravimetric analysis (TGA), yielding the results shown in Table 6.4. Two different sets of decomposition experiments were carried out on the ionic liquids and the natural oils. First dynamic decomposition measurements, in which the temperature of the sample is increased at a constant rate, were made to determine the temperature at which decomposition (as indicated by mass loss) begins and the temperature at which decomposition is complete. Once the temperature corresponding to the onset of decomposition (T_d) was determined, the material was then subjected to isothermal decomposition measurements, in which samples are held at 50°C or 100°C below T_d for an eight hour period to determine stability over an extended period of time.

As can be seen from the Table, the conventional imidazolium and phosphonium ionic liquids exhibit decomposition temperatures *ca.* 40°C higher than the natural oils, while the phosphonium carboxylate ionic liquids exhibit decomposition temperatures comparable to or lower than the natural oils. Of course, unlike natural oils, ILs do not exhibit a smoke point. Several prior studies have suggested that decomposition temperatures measured in dynamic experiments provide an inaccurate estimate of the thermal stability of ionic liquids [50-53]. In the opinion of these investigators, only isothermal measurements yield a true assessment of this characteristic. As shown in the Table, in a series of decomposition experiments carried out at a temperature 50°C below the temperature corresponding to the onset of decomposition, all of the natural oils were found to exhibit substantial (and in some instances, nearly complete) decomposition over an eight-hour period. In contrast, the conventional imidazolium ionic liquids exhibited complete decomposition at 100°C below the temperature, with a systematic decrease in decomposition observed at 50°C. An increase in the alkyl chain length resulted in a decrease in the tendency toward decomposition. Similarly, the conventional phosphonium ionic liquid showed complete decomposition at the higher isothermal temperature (*e.g.,* 50°C below T_d), with less than 50% decomposition at the lower temperature.

The most striking results were found in the evaluation of the phosphonium carboxylate ionic liquids. Although approximately half of the material decomposed at the higher temperature, minimal decomposition was observed at the lower temperature. The extent of weight loss in these cases can be attributed to the benzoate anion for $P_{666,14}{}^{+}$benzoate^{-} and the hydroxyl group for $P_{666,14}{}^{+}$salicylate^{-}. These results are encouraging, as minimal destruction of the lubricant is observed at elevated temperatures over an extended period of time. In addition, these materials also exhibited low friction and minimal pin wear.

Table 6.4
Thermogravimetric analysis results for natural oils and ionic liquid lubricants.

Natural Oil / RTIL	T_d / T_m (°C)[a]	% decomposition (50°C below T_d)[b]	% decomposition (100°C below T_d)[b]	Smoke Point (°C)[c]
Avocado Oil	376 / 410	82	21	271
Canola Oil	377 / 410	79	20	226
Corn Oil	372 / 407	76	16	165
Olive Oil	377 / 411	86	27	160
Peanut Oil	378 / 411	92	18	107
Safflower Oil	376 / 410	91	19	160
Sesame Oil	370 / 407	72	32	177
Vegetable	371 / 409	76	13	225[d]
$C_5mim^+Tf_2N^-$	409 / 446	100	100	N/A
$C_6mim^+Tf_2N^-$	409 / 448	100	100	N/A
$C_8mim^+Tf_2N^-$	404 / 450	100	91	N/A
$C_{10}mim^+Tf_2N^-$	409 / 451	100	87	N/A
$P_{666,14}{}^+Tf_2N^-$	406 / 408	100	43	N/A
$P_{666,14}{}^+$benzoate$^-$	327 / 371	65	24	N/A
$P_{666,14}{}^+$salicylate$^-$	376 / 410	53	10	N/A

[a] T_d and T_m refer to the onset and complete decomposition temperatures, respectively.
[b] The % decomposition values were rounded to the nearest whole number.
[c] Reference 54.
[d] Reference 55.
N/A ≡ not applicable

6.5 Conclusions

This study sought to elucidate the factors that determine the lubricity of two families of environmentally friendly lubricants, natural oils and room-temperature ionic liquids. It has been found that increasing the alkyl chain length of an imidazolium cation leads to a decrease in the coefficient of friction for an ionic liquid incorporating the cation. Changing to an even more hydrophobic cation, a phosphonium cation comprising 32 carbon atoms, decreases the coefficient of friction still further. When the anion was made aromatic, the coefficient of friction was also found to decrease. Overall, natural oils exhibited lower coefficients of friction than the conventional imidazolium ionic liquids, and phosphonium carboxylate ionic liquids yielded values lower than either of these materials.

In addition, the decomposition of each of the lubricants was measured. It was found that the conventional imidazolium and phosphonium ionic liquids exhibited the most decomposition. In some cases, in fact, essentially complete decomposition was observed. The natural oils showed more stability, as only a fourth of the material was found to decompose. The best results were again exhibited by the phosphonium carboxylate ionic liquids, for which only *ca*. 10% decomposition occurred in some instances. Given their superior thermal stability and favorable lubricity properties, the phosphonium carboxylate ionic liquids appear to show promise as possible replacements for petroleum-based oils.

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CHAPTER 7:

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In this work, the use of ionic liquids as replacements for conventional solvents in metal ion extraction has been examined. It has been shown that extraction into conventional solvents and ionic liquids often occurs by very different pathways. Specifically, while a single mechanism (*i.e.,* neutral complex formation / ion-pairing) is observed for metal cation extraction into conventional solvents, multiple pathways (*i.e.,* neutral complex formation and ion-exchange) are observed for the same extractant and metal cation in an ionic liquid system [1, 2]. Understanding the factors that determine the pathway by which a particular metal is extracted is especially important to aid in the design of an ionic liquid for the system of interest. Ionic liquids can consist of a variety of cations and anions, and alteration of either (or both) has been shown to drastically change the extraction efficiency of the system. For example, it has been shown that progressively increasing the alkyl chain length on a 1,3-dialkyl-imidazolium ionic liquid decreases the metal ion extraction (D_M) [2, 3]. In addition, increasing the hydrophobicity of the cation tends to promote a change in the predominant mechanism (*i.e.,* a shift from ion-exchange to neutral complex formation) for extraction of divalent cations in nitrate media [2, 3].

The effect on the mode of partitioning observed upon altering the ionic liquid anion has been studied less extensively, and for this reason, this task was undertaken in the present work. Evaluation of various ionic liquids comprising a 1,3-

dialkylimidazolium cation and any of several anions of varying hydrophobicity as the extracting solvent (vs. nitric acid) has been completed, and the effect of the hydrophobicity of the IL anion on both the extraction efficiency and the predominant mode of partitioning observed has been assessed. For the extraction of divalent cations, increasing the hydrophobicity of the IL anion has been found to lead to greater metal extraction (D_M) and a greater tendency for ion-exchange to predominate. This trend is opposite to that observed for increasing the IL cation hydrophobicity. It has been determined that a hydrophobic cation and a hydrophilic anion favor neutral complex formation (the desired extraction mechanism) as the predominant mode of partitioning. Changing the IL anion has a lesser effect on the extraction of a monovalent cation. That is, for all ILs examined, ion-exchange predominated as the mode of partitioning. This is not surprising given the lower charge density of the sodium cation and the accompanying diminished electrostatic attraction between the cation and aqueous phase anion [2].

A thorough examination of the effect of the aqueous phase constituents metal ion extraction into ILs has also been completed. In particular, comparison of alkali and alkaline earth cation extraction into both conventional solvents and ionic liquids from nitric and hydrochloric acids has been performed. For conventional solvents, regardless of aqueous phase, only extraction *via* neutral complex formation is observed, and a decrease in the extraction efficiency (*vs.* nitrate-containing aqueous phases) is observed for chloride media due to the higher hydration energy of the chloride ions. In contrast, ILs show drastic differences in the acid dependencies for nitrate and chloride media. Contrary to nitrate, where a shift in the predominant mode of partitioning is observed as the IL cation hydrophobicity increased, ion-exchange has been found to be the predominant mode at low chloride concentration and neutral complex formation at high chloride concentration for all ILs examined. The extraction of monovalent cations occurrs predominantly *via* ion-exchange for both the nitrate and chloride media. These results indicate that ion-exchange is the predominant mode of partitioning for ILs in chloride media, an effect again attributed to the high hydration energy of the anion and the need for co-extraction of the aqueous phase anion for neutral complex formation.

The extraction of a metal anion (TcO_4^-) into both conventional solvents and ILs from varying aqueous media has also been examined. Contrary to results for metal cation extraction for conventional solvents, two modes of partitioning were observed from sodium nitrate media (ion-pairing at low nitrate concentration and ion-exchange at high nitrate concentration). Similar trends were observed in hydroxide media. The concentration at which the mode of partitioning changes is shifted due to the hydration energy of the aqueous phase anion, however. Extraction into ILs occurred primarily *via* ion-exchange for the systems analyzed.

Evaluation of ionic liquids as extraction solvents in high radiation fields was completed by determining the effect of gamma radiation on the stability of various ILs. It has been found that 1,3-dialkylimiadzolium ionic liquids degrade upon irradiation, and that this degradation manifests itself as a decrease in both the strontium extraction efficiency (D_{Sr} values) and a change in the shape of the D_{Sr} acid dependency. Collaborative studies indicate that a more radiolytically stable IL can be prepared from an aliphatic cation and an aromatic anion. In fact, when phosphonium carboxylate ILs were examined, negligible changes were observed in the acid dependencies following irradiation. In addition, no substantial changes in the physical properties considered were observed for these ILs due to radiolysis, indicating that these materials could be of use in highly irradiated systems.

Finally, studies of the tribological properties of conventional imidazolium- and phosphonium-based ionic liquids indicate that 1,3-dialkylimidazolium ILs are comparable to natural oils in terms of friction and superior in terms of wear volume. Phosphonium carboxylate ionic liquids exhibit better wear and friction properties than either the conventional ionic liquids or natural oils. In addition, these ILs are the most stable at the temperatures examined.

While the studies reported in this work have led to a better understanding of the behavior of IL-based metal ion extraction systems, many important questions remain unanswered. It is hoped that the knowledge gained through this work will provide a foundation for the continued development of improved IL-based separation schemes for a variety of metal ions.

7.2 Recommendations

In an effort to expand the knowledge base of IL-based extraction systems, several recommendations are made in the following sections. Although these do not represent a complete list of possible areas of research, they include both the ongoing studies in this laboratory and experiments that may significantly improve this field.

7.2.1 Examination of other ionic liquid families

The majority of this work was completed with either a 1,3-dialkylimidazolium or phosphonium ionic liquid paired with a small number of anions (particularly the Tf_2N,

PF_6 or BETI salts). Examination of other IL cations (*e.g., N*-alkylpyridinium, *N*-alkylquinolium or *N*-dialkylpyrrolidinium) and a wider range of IL anions (*e.g.,* a more hydrophilic anion) could easily be accomplished using the same approaches employed here. In addition, the use of other ionophores (*e.g.,* crown ethers other than DCH18C6) should be examined to establish the impact of the choice of extractant on the observed trends. The incorporation of somewhat less common, but more "green" components (*e.g.,* amino acids or aspirin) could be examined for efficiency and use in other applications (*i.e.,* lubricants).

7.2.2 Examination of ionic liquids incorporating the nonaflate anion

Preliminary work has been carrier out in this to determine the extraction efficiency of alkali and alkaline earth metals using a solution of DCH18C6 in several 1,3-dialkylimidazolium nonafluorobutanesulfonates (abbreviated as *nonaflate* or *NfO*). A representative structure of this type of IL is shown in Figure 7.1.

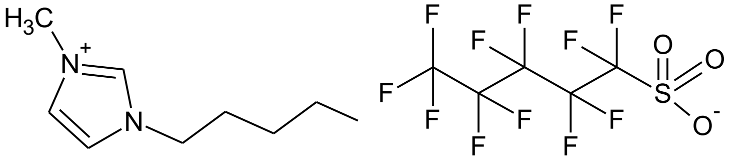

Figure 7.1: Structure of 1-methyl-3-pentylimidazolium nonafluorobutanesulfonate ($C_5mim^+NfO^-$).

Although initial investigations suggested that the nonflate anion is more hydrophobic than the *bis*[(trifluoromethyl)sulfonyl]imide anion (Tf_2N^-) measurements of the solubility of the IL in water and of the IL water content (Table 7.1) indicates otherwise.

Table 7.1
Water content and water solubility measurements for $C_n mim^+ NfO^-$ ILs.

	$[C_n mim^+][NfO^-]$		
	C_5mim^+	C_8mim^+	$C_{10}mim^+$
Molecular weight (g/mol)	448.4	462.5	522.51
Density "dry" (g/mL)[a]	1.36	1.30	1.24
Water content "dry" (ppm)[a]	1267	<10	<10
Water content "wet" (ppm)[b]	108700	96850	101500
Solubility in water (ppm)[b]	11687	2158	785

[a] Samples were dried *in vacuo* at 80°C for at least 24 hours prior to measurement.
[b] 1 mL of IL was contacted with 10 mL of 18 MΩ water for 1 hour, phases were separated and organic phase used for water content measurements while aqueous phase used for solubility measurements.

As was reported in Chapter 3 [4, 5] for other types of ILs, as the alkyl chain length (*i.e.,* hydrophobicity of the cation) increases, the water content and solubility in water of the IL decreases. Previous results in this dissertation (Chapter 3) also indicate that as the hydrophobicity of the IL anion increases (anion hydrophobicity order: $PF_6^- < Tf_2N^- < BETI^-$), both the water content and solubility in water decrease. The most hydrophobic anion previously studied ($BETI^-$) yielded water content and solubility values (for C_5mim^+) of 3880 ppm and 3779 ppm, respectively, while the most hydrophilic anion (PF_6^-) yielded 19260 ppm and 11262 ppm, respectively. Based on the measurements obtained in Table 7.1, the NfO^- anion thus appears to be more hydrophilic than the PF_6^- anion. Previous results for $C_4mim^+NfO^-$ (containing 0.5 M 2-thenoyltrifluoroacetone) showed that this solution equilibrated with water contained 142,000 ppm water, while a neat sample of $C_4mim^+NfO^-$ contained 207,000 ppm [6]. These results are consistent with the trend observed here, where by a shorter alkyl chain imidazolium cation leads to a higher water content.

An examination of the nitric acid dependency for various alkali and alkaline earth metals utilizing the NfO^- anion (Figure 7.2) shows a decrease in extraction (D_M) as the concentration of nitric acid increases for all ILs and metal ions examined, which is indicative of ion-exchange as the predominant mode of partitioning [7] (as represented in equations 3.1 and 3.2 for monovalent cations and equations 3.4 and 3.5 for divalent cations). Due to emulsion formation, sampling was difficult at low nitrate concentrations for $C_{10}mim^+NfO^-$.

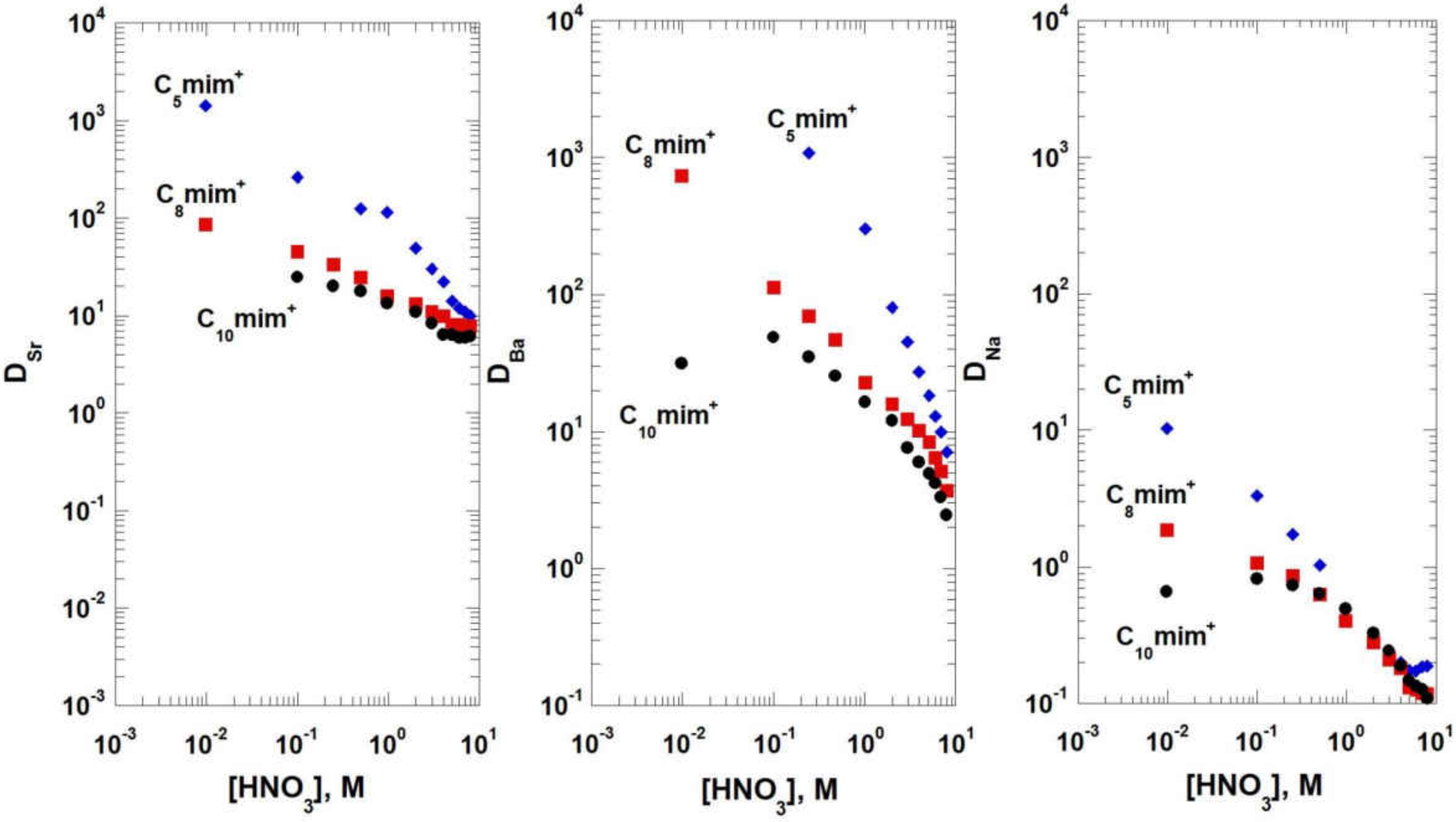

Figure 7.2. Effect of nitric acid concentration on the extraction of Sr^{2+} (left panel), Ba^{2+} (middle panel) and Na^+ (right panel) by DCH18C6 (0.10 M) in $C_n$mim$^+$NfO$^-$ (where n = 5, 8 and 10).

As previously indicated (Chapter 3) for extraction into nitrate media, the more hydrophilic the IL anion, the greater the tendency for extraction to occur *via* neutral complex formation (*i.e.,* an increase in extraction is observed with increasing nitrate concentration). This is not the case for the nonalfate anion, however, where a greater propensity towards ion-exchange is observed.

As seen in Table 7.2, for a series of $C_n$mim$^+$ nonaflates, the mode of partitioning for a given metal ion systematically changes from one in which approximately 5 times as much metal is extracted versus nitrate (*i.e.,* cation exchange) to one in which equal amounts of metal and nitrate are extracted (*i.e.,* neutral complex / ion-pairing). Consistent with previous results [2-4], an increase in the alkyl chain length of the cation is associated with an increase in the nitrate extraction and a corresponding decrease in metal extraction (*i.e.,* a decrease in the ratio of $\%E_{M}/\%E_{NO3-}$). The values obtained previously for $\%E_{Sr}/\%E_{NO3-}$ for C_{10}mim$^+$X$^-$ (where X = PF_6^-, Tf_2N^- and BETI$^-$) show that as the hydrophobicity of the anion increases (*i.e.,* switching from PF_6^- to Tf_2N^- or BETI$^-$), the ratio of extraction decreases, 2.2, 1.01 and 0.9, respectively. The values obtained in the study of NfO (Table 7.2) are again consistent with a hydrophilic anion, as the $\%E_{Sr}/\%E_{NO3-}$ for C_{10}mim$^+$NfO$^-$ is 1.1.

Table 7.2

The effect of ionic liquid cation chain length on metal (*i.e.*, strontium, barium and sodium) and nitrate partitioning between water and 0.20 M DCH18C6 in $C_n mim^+ NfO^-$ ILs.

Metal	IL cation	$\%E_M$ [a]	$\%E_{NO3-}$ [a]	Ratio $\%E_M/\%E_{NO3-}$	Partitioning mode indicated
Sr^{2+}	C_5mim^+	99.8 ± 0.1	17.4 ± 0.1	5.7 ± 0.3	Cation exchange
	C_8mim^+	85.5 ± 3.9	55.4 ± 0.2	1.5 ± 0.1	Mixed
	$C_{10}mim^+$	73.0 ± 4.8	67.0 ± 0.0	1.1 ± 0.1	Neutral complex
Ba^{2+}	C_5mim^+	100.0 ± 8.2	23.6 ± 0.0	4.2 ± 0.3	Cation exchange
	C_8mim^+	91.9 ± 6.2	59.6 ± 0.1	1.5 ± 0.1	Mixed
	$C_{10}mim^+$	74.7 ± 5.1	70.0 ± 0.1	1.1 ± 0.1	Neutral complex
Na^+	C_5mim^+	94.0 ± 7.0	21.4 ± 0.1	4.4 ± 0.3	Cation exchange
	C_8mim^+	59.2 ± 4.4	40.4 ± 0.1	1.5 ± 0.1	Mixed
	$C_{10}mim^+$	45.7 ± 3.4	54.6 ± 0.1	0.8 ± 0.1	Neutral complex

All initial metal nitrate salt concentrations were 0.031 F.

[a] Uncertainties were calculated at the 95% confidence interval ($n = 3$).

Note: Data was collected by using IC, instrument information and experimental conditions are described in Chapter 3.

Thus, seemingly contradictory results have been obtained in this study as to the hydrophobic nature of the NfO^- anion. That is, while the water content/solubility study indicates that the NfO^- anion is more hydrophilic than the PF_6 anion, the predominant mode of partitioning observed for metal ion extraction (based on the shape of the acid dependencies) in nitrate media indicates that NfO^- is more hydrophobic (similar to the BETI anion), given its tendency to ion-exchange. Similar results were obtained with the extraction of U(VI) in nitric acid where the 1-butyl-3-methylimidazolum nonafluorobutanesulfonate ($C_4mim^+NfO^-$) IL utilizing a *N*-dodecyl-2-pyrrolidone extractant, where anion exchange was also found to be the predominant mode of extraction [8]. However, data from an extraction system comprising an IL with a NfO^- anion is much more difficult to interpret than previously studied systems. For example, when $C_4mim^+NfO^-$ (containing 0.5 M Htta) was used for extraction of lanthanide species, anion exchange reactions were not observed as has been previously reported. Instead, lanthanide complexes were observed with metal:extractant stoichiometries of 1:0, 1:2, and 1:3 depending on the extractant concentration and solution pcH [6]. Taken together, these studies illustrate the important and hard-to-predict effects that changing the anion of an IL can have on the mechanisms of metal ion extraction in liquid-liquid systems. Further examination of this system will be necessary before a clearer understanding of the results can be obtained.

7.2.3 Expand the knowledge base for aqueous solutions to other solutions and/or metals

Valuable information was gained from the examination of the effect of altering the aqueous phase anion on metal ion extraction. As already stated, it was found that the anion hydration energy plays a significant role in determining the predominant mode of partitioning. Systems comprising an aqueous phase anion with a lower hydration energy (*e.g.,* perchlorate anion, -229 kJ/mol) could be examined to determine if neutral complex formation would predominate for a wider range of concentrations. Additionally, as observed with the extraction of pertechnetate, hydration energy plays a significant role encouraging ion-pairing. Extraction of other metals (*e.g.,* lanthanides/actinides) could potentially be prompted to follow a particular pathway by careful choice of aqueous phase anions.

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CURRICULUM VITAE

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Education

Ph.D. in Chemistry, University of Wisconsin-Milwaukee May 2013

Dissertation: "Anion Effects in the Extraction of Metal Ions into Room-Temperature Ionic Liquids (RTILs)", Advisor: Mark L. Dietz, Ph.D.

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Experience

Marquette University, Milwaukee, WI 2012-date
Adjunct Faculty

- Prepared and delivered lectures for Arts and Science Colloquium courses.
    - ARSC 1020 – Major Concepts in Modern Science 1
        - Concepts covered: Physics and Chemistry
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        - Concepts covered: Astronomy, Biology and Geology
- Developed demonstrations for use in lecture and laboratory.
- Prepared, administered, and graded exams.

University of Wisconsin-Milwaukee, Milwaukee, WI 2007-date
Teaching Assistant

- Taught laboratories and discussions for Analytical and General Chemistry courses including: Chem 100 (Chemical Science), Chem 102 (General Chemistry), Chem 105 (General Chemistry II – Engineering Majors), Chem 221 (Elementary Quantitative Analysis), and Chem 582 (Advanced Chemistry Laboratory).
- Designed experiments for the Analytical laboratory which has been implemented into the curriculum.

Guest Lecturer

- Chemistry 221, Elementary Quantitative Analysis

Research Assistant

- Assisted in the start-up of a new research laboratory.
- Led a research group aimed at elucidating the factors at which alkali and alkaline earth metals extract from aqueous media into room temperature ionic liquids.
- Synthesized new ionic liquids.
- Supervised undergraduate researchers and trained junior graduate research assistants.

Project Assistant

- Implemented a department-wide chemical inventory system.
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Society for Applied Spectroscopy, University of Wisconsin-Milwaukee Chapter 2011-date
Teaching Assistant

- Designed, coordinated and implemented an IRB-certified forensic science experiment at Milwaukee area high schools.

12th Annual National School on Neutron and X-ray Scattering, Oak Ridge National Laboratory and Argonne National Laboratory 2010
Invited Participant

- Participated in hands-on experiments utilizing the Advanced Photon Source at ANL in addition to the Spallation Neutron Source and the High Flux Isotope Reactor at ORNL.

Aldrich Chemical Company, Sheboygan Falls, WI 2006-2007
Production Chemist

- Developed procedures for large-scale chemical production and custom pharmaceuticals.
- Served as shift leader.
- Served as a member of the emergency response medical team.

Inorganic Laboratory Research University of Wisconsin-Oshkosh 2005
Undergraduate Research Assistant

- Synthesized, analyzed and characterized (*via* x-ray diffraction) nanoscale materials for improved cutting tools.

Science Outreach Program, University of Wisconsin-Oshkosh 2003-2005

Teaching Assistant

- Led science discussions and performed chemical demonstrations.
- Coordinated and judged events for the Wisconsin Middle School Science Olympiad

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Publications

- S.L. Garvey, G. Shahmohammadi, D.R. McLain and M.L. Dietz, "Determination of Calcium in Dietary Supplements: Statistical Comparison of Methods in the Analytical Laboratory" *Journal of Chemical Education*, 2013 (In Preparation).
- S.L. Garvey and M.L. Dietz, "Ionic Liquid Anion Effects in the Extraction of Metal Ions by Macrocylic Polyethers" *Separation and Purification Technology*, 2013 (submitted).
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Invention Disclosure

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Honors and Awards

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- University of Wisconsin-Milwaukee Graduate Student Travel Award, 2012
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- Marshallton Achievement Award, 1st Place Poster Presentation for the 17th Symposium on Separation Science and Technology for Energy Applications, 2011
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- Student Leadership Award, University of Wisconsin-Oshkosh, 2005
- Chemistry Alumni Research Award, University of Wisconsin-Oshkosh, 2005
- Gilbert F. and Katherine L. Pollnow Tuition Scholarship Award, University of Wisconsin-Oshkosh, Chemistry Department, 2005
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Presentations

- Sarah L. Garvey, C. A. Hawkins, Anna Rud, and Mark L. Dietz "Modes of metal ion transfer into ionic liquids (ILs): Implications for the application of ILs as extraction solvents", 243rd ACS National Meeting, San Diego, CA (March 2012). {oral presentation}

- Sarah L. Garvey, Mark L. Dietz, Ilya A. Shkrob, and Tim W. Marin. "Phosphonium carboxylate ionic liquids: Preparation, characterization and evaluation as extraction solvents", 17th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN (October 2011). {poster} – 1st Place Student Poster Award.

- Sarah L. Garvey and Mark L. Dietz. "Ionic Liquid-Based Solvent Extraction Systems for Improved Actinide and Fission Product Separations", 42nd Meeting of the American Chemical Society Central Region, Indianapolis, IN (June 2011). {poster}

- Sarah L. Garvey, Diab T. Qadah, Cory A. Hawkins, Mark L. Dietz, Dominique C. Stepinski, Ilya A. Shkrob, George F. Vandegrift, James F. Wishart, Sheng Dai, and Huimin Luo. "Ionic Liquid-based Extraction Systems for the Recovery of Pertechnetate from Aqueous Solutions ", Chemistry in Southeastern Wisconsin Poster Mixer, Milwaukee, WI (October 2009). {poster}

Contributed Presentations, Co-Author

- Mark L. Dietz, Cory A. Hawkins, Anna Rud, and Sarah L. Garvey. "Mechanisms of Metal Ion Transfer into RTILs: Implications for their Use as Extraction Solvents", 245th American Chemistry Society National Meeting, New Orleans, LA (April 2013). {oral presentation}

- Carlton J. Reeves, Sarah L. Garvey, Pradeep L. Menezes, Mark L. Dietz, Tien-Chien Jen and Michael R. Lovell. "Tribological Performance of Environmentally Friendly Ionic Liquid Lubricants for Energy Conservation and Sustainability", ASME/STLE 2012 International Joint Tribology Conference, Denver, CO (October 2012). {oral presentation and poster} – 1st Place Student Poster Award.

- Cory A. Hawkins, Anna Rud, Derek R. McLain, Sarah L. Garvey, and Mark L. Dietz. "Evaluation of Hydroxylalkyl-functionalized Imidazolium-based Ionic Liquids as Solvents for the Extraction of Metal Ions", 17th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN (October 2011). {oral presentation}
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