CHEMICAL REVIEWS

REVIEW

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Ionic Liquids-Based Extraction: A Promising Strategy for the Advanced Nuclear Fuel Cycle

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1. INTRODUCTION

Energy is one of the world's most challenging issues.[1] The production of low-carbon energy has considerable global influence on social, economic, and environmental development.[2] Nuclear energy offers high energy density and low greenhouse-gas emissions, unparalleled advantages when compared with other energies.[3] With nuclear energy the world can meet future energy needs without emitting carbon dioxide and the resultant global warming. However, nuclear energy is a double-edged sword, with clean energy on the one hand and safety and environmental concerns on the other. For advanced nuclear energy systems, security and high efficiency are basic goals.

The nuclear fuel cycle (NFC) is the complex process of preparing nuclear fuels for nuclear energy applications. The NFC is often described as having a "front end" and a "back end." The front end includes activities necessary to create nuclear fuels, such as mining, conversion, enrichment, and fuel fabrication. The back end of NFC includes activities necessary after spent nuclear fuels are removed from a reactor, such as storage, reprocessing, and disposal.[4] Nuclear fuel reprocessing technologies, which separate the components of spent fuels, include both aqueous and nonaqueous processes.[5] For decades, the NFC has relied on solvent extraction as the predominant separation technology.[6] Various solvent extraction technologies, for example, PUREX, SREX, TRUEX, DIAMEX and DIDPA, are in use worldwide.[7] The most well-known process, PUREX, was developed at the

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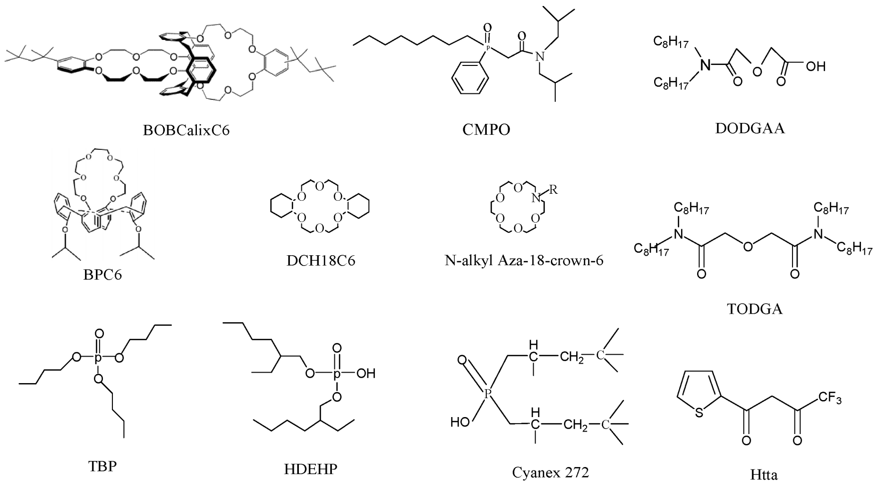


Figure 1. Structures of common extractants used in IL-based extraction.

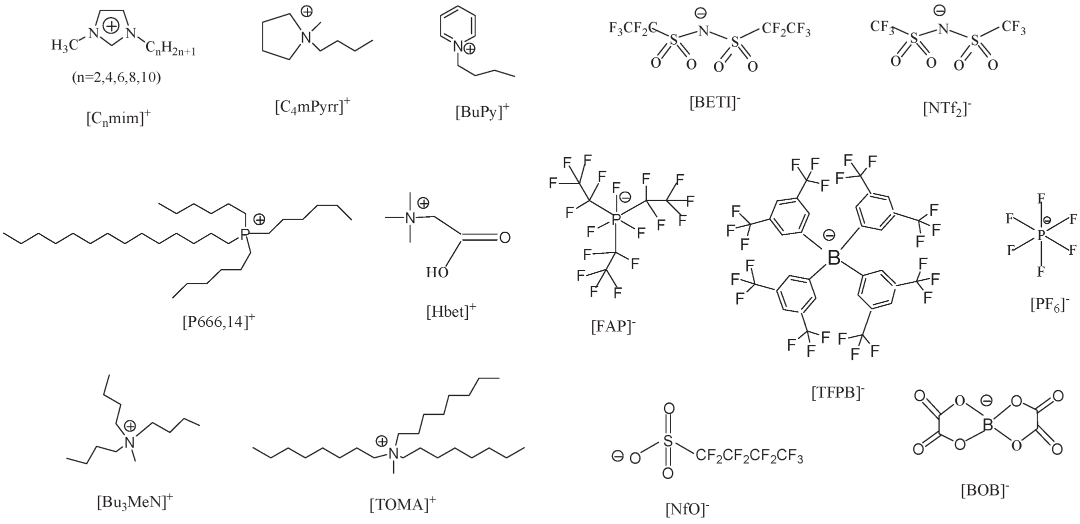


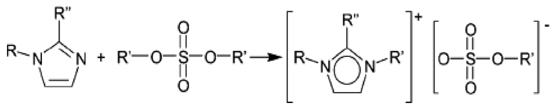
Figure 2. Structures of cations and anions of ILs used as diluents.

Oak Ridge National Laboratory in the 1940s. To meet mounting energy and environmental requirements, major scientific breakthroughs that ameliorate the NFC are needed.[8] The advanced NFC maximizes fuel resource utilization, reduces the volume and toxicity of nuclear waste, facilitates handling and transportation, and saves on geological repository costs.[9] As a separation technology for the advanced nuclear fuel cycle, room-temperature ionic liquids, a novel type of solvent, show promise.[7,10]

Room-temperature ionic liquids (abbreviated herein simply as ILs) are defined as room-temperature molten salts. They are composed of cations and anions, and their melting points are generally below 100 °C.[11] Walden et al.[12] synthesized the first IL, [$C_2H_5NH_3$][NO_3], in 1914 by neutralizing ethylamine with concentrated HNO_3. Such an IL is protic because its synthesis occurs through a proton-transfer reaction. Hurley et al.[13] prepared a second class of ILs in 1951 by using alkylpyridinium chlorides with $AlCl_3$, which is aprotic. In 1992 Wilkes et al.[14] developed water-stable ILs composed of organic cations and inorganic or organic anions. This third class of ILs has been studied widely because of their stability in air and water. ILs are "designer solvents"—their physicochemical properties can be tuned easily through the appropriate combination of cations and anions.[15] It is possible to design an IL composition with specific chemical and physical properties that meet the user's needs.[16] Because ILs have unique properties unmatched by volatile organic compounds (VOCs), ILs have enabled many achievements in the areas of catalysis,[17] carbon dioxide capture,[18] dye-sensitized solar cells,[19] separation,[20] lubricants,[21] electrochemistry,[22] enzymatic reactions,[23] polymerization,[24] and inorganic materials.[25] A further development in the evolution of ILs is the functionalized ILs,[26] which are viewed as tunable, multipurpose materials for a variety of applications other than just as diluents.[27]

Functionalized ionic liquids (FILs) [also referred to as task-specific ionic liquids (TSILs)] incorporate functional groups in their cations[28] and/or anions.[29] They can behave as both the organic phase and extracting agents, suppressing the problems encountered from extractant/diluent miscibility and facilitating species extraction and solvent recovery.[30] IL-based extraction is a novel separation strategy that applies ILs instead of VOCs as diluents and/or extractants. Dai et al. first achieved unprecedentedly large distribution ratios using IL-based extraction for the separation of fission products.[31] ILs have secure and efficient

Scheme 1. General Preparative Route to Alkylimidazolium-Containing ILs[a]



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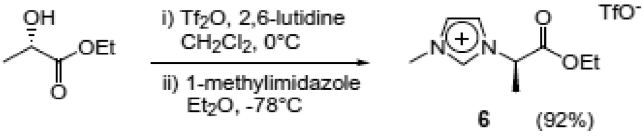
Scheme 2. Preparation of Ester-Imidazolium Salt[a]



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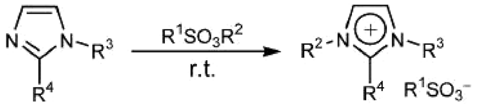
Scheme 3. The Preparation of 1,3-Dialkylimidazolium Alkanesulfonate Salts[a]



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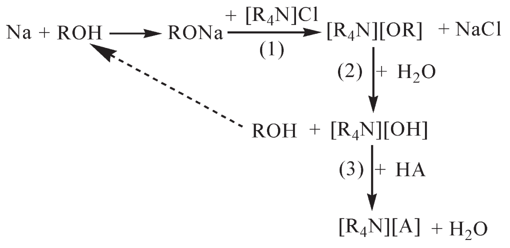
Scheme 4. Synthetic Route to Ammonium IL by Acid−Base Neutralization Reaction: (1) Anion Exchange; (2) Hydrolysis; (3) Acid−Base Neutralization[a]



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properties that make them particularly suitable for use in advanced nuclear fuel separations systems.[10,30a,32] For example, their low volatility and combustibility, wide liquidus range, thermal stability, and enhanced criticality safety can make the IL-based NFC reprocessing safer than that based on VOCs, while IL characteristics such as functional groups, prevention of a third phase formation, high conductivity, and a wide electrochemical window can improve the efficiency of both aqueous and nonaqueous processes such as extraction, adsorption, and electrodeposition. The use of ILs as a substitute for VOCs in the solvent extraction of metal ions increases the complexity of the system chemistry. Moreover, ILs have some disadvantages in this complex system that must be overcome effectively. A great deal of additional work will be required before the potential of ILs in this role can be fully evaluated.[33]

Some applications of ILs in separation science and technology, as well as IL-based extraction in fission products separation have been reviewed before.[33,34] This review attempts to comprehensively summarize ILs for their preparation, purification, physicochemical properties, solvation environment, partitioning behavior, and extraction mechanism, along with strategies for improvement and a forecast of IL-based extraction from the viewpoint of promising technologies for the advanced NFC. The structures of some important extractants, cations, and anions of ILs used as diluents in this review are given in Figures 1 and 2, respectively.

2. PREPARATION OF IONIC LIQUIDS FOR EXTRACTION

2.1. Synthesis Methods

Various synthesis methods have been extensively reviewed before.[35] The emphasis here is placed on the recent advances in preparation of ILs that are relevant to solvent-extraction applications. Holbrey et al.[36] prepared a series of 1,3-dialkylimidazolium alkyl sulfate and 1,2,3-trialkylimidazolium alkyl sulfate salts by alkylation of 1-alkylimidazoles with dimethyl sulfate and diethyl sulfate (Scheme 1). ILs prepared in this manner are intrinsically chloride-free. They can also be used in place of the respective halide salts when preparing other ILs by metathesis.

Jodry et al.[37] transformed *S*-ethyl lactate into its triflate derivative and prepared triflate ([TfO]$^-$) salt by reacting the triflate derivative with 1-methylimidazole (Scheme 2). The [TfO]$^-$ salt so prepared was a white solid, which imparts no color. No trace of halide was present in the products. The [TfO]$^-$ salt can be used to prepare hexafluorophosphate ([PF$_6$]$^-$), bis(trifluoromethylsulfonyl)imide ([NTf$_2$]$^-$), bis(perfluoroethanesulfonyl)imide ([BETI]$^-$), and [N(SO$_2$C$_4$F$_9$)Tf]$^-$ type ILs by anion metathesis.

Cassol et al.[38] prepared some 1,3-dialkylimidazolium alkanesulfonate salts using alkylation of *N*-alkylimidazoles with alkyl sulfonate (Scheme 3). The alkanesulfonate anions can be easily substituted for a series of other anions.

Bradaric et al.[39] reported several direct, solvent-free, halide-free routes to phosphonium ILs via the quaternization of tertiary phosphines with dialkylsulfates (eq 1), trialkylphosphates (eq 2), and alkylphosphonates (eq 3).

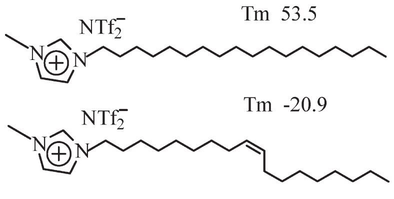
$$\mathrm{SO_2(OR)_2} + \mathrm{P}(n-\mathrm{Bu})_3 \rightarrow \begin{array}{l}[\mathrm{RP}(n-\mathrm{Bu})_3]^+[\mathrm{SO_3(OR)}]^- \\ 1\ (\mathrm{R} = \mathrm{Me, Et}, n-\mathrm{Bu})\end{array} \tag{1}$$

$$\mathrm{O{=}P(OR)_3} + \mathrm{PR'_3} \rightarrow \begin{array}{l}[\mathrm{RPR'_3}]^+[\mathrm{PO_2(OR)_2}]^- \\ 2\ (\mathrm{R} = \mathrm{Me, Et}, n-\mathrm{Bu}; \mathrm{R'} = n-\mathrm{Bu}) \\ 3\ (\mathrm{R} = \mathrm{Me, Bu}; \mathrm{R'} = i-\mathrm{Bu})\end{array} \tag{2}$$

$$\mathrm{O{=}PR(OR)_2} + \mathrm{P}(n-\mathrm{Bu})_3 \rightarrow \begin{array}{l}[\mathrm{RP}(n-\mathrm{Bu})_3]^+[\mathrm{PRO_2(OR)}]^- \\ 4\ (\mathrm{R} = \mathrm{Me}, n-\mathrm{Bu})\end{array} \tag{3}$$

The neutralization reaction based on acid−base chemistry is a widely used method for preparing ILs.[18c,40] Notably, an aqueous solution of [C$_2$mim][OH] was first prepared from 1-ethyl-3-methylimidazolium bromide ([C$_2$mim]Br) using an anion-exchange resin. The [C$_2$mim][OH] aqueous solution was added dropwise to a slightly excess equimolar amino acid aqueous solution to prepare a series of amino acids.[41] Sun et al.[42] proposed a strategy for preparing ammonium-type IL by an acid−base

Scheme 5. Example of the Lipidic ILs[a]



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neutralization reaction (Scheme 4). The method contributes to preparing hydroxide-based ammonium IL and results in functionalized ILs with high purity.

A new strategy to design ILs with low melting points was developed by Davis and his co-workers.[43] Their strategy is based on a model called homeoviscous adaptation (HVA).[44] HVA describes the change in viscosity of membrane lipids in living organisms. By studying the melting points of natural fatty acids, they realized that low-melting fats (oils) often contain a cis-configured double bond in the alkyl chain. This "kink", as they call it, leads to a lower packing efficiency and thus to an increased fluidity — most probably an entropy-dominated effect. They prepared a series of lipid-inspired ILs in a three-step procedure from high-purity fatty-alcohol mesylates, 1-methylimidazole, NaI, and NaNTf$_2$. Indeed, unsaturation leads to a radical decrease in the T_m value with respect to that of the corresponding saturated IL (Scheme 5).

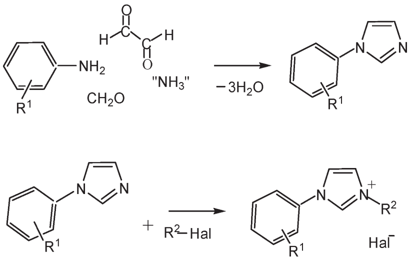
Ahrens et al.[45] proposed another strategy to tune electronic properties of ILs through substitution in appended benzene rings. Electronic interaction between the aromatic substituent and the imidazolium core together with many possible substitution patterns on the aromatic ring offer the opportunities to tune these new ILs far better than is currently possible by inductive interactions (Scheme 6).

2.2. Purification Methods

Some ILs are odorless and colorless. The presence of color in colorless materials is a clear indication of impurities. Earle et al.[46] studied the decolorization of ILs using a special column containing charcoal particles and silica gel. Satisfactory results were obtained for [NTf$_2$]$^-$, tetrafluoroborate ([BF$_4$]$^-$), and [PF$_6$]$^-$ type ILs. They found the best strategy is to decolorize the final IL rather than the halide salt. Burrell et al.[47] described a reliable method for producing large quantities of high quality ILs. They found that high quality ILs can be obtained if the precursors are purified using decolorizing charcoal before the synthesis. Nockemann et al.[48] developed a synthesis method using simple low-temperature processing of 1-methyl-3-alkylimidazolium halides to yield colorless ILs suitable for spectroscopic requirements.

Supercritical CO$_2$ was studied as a means for removing organic impurities and water from ILs. Using scCO$_2$ was efficient for cleaning and drying all the ILs tested, that is, [C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$], and [C$_4$mim][TfO]. Even hygroscopic and water-soluble ILs were dried within a reasonable time.[49] Ren et al.[50] found a method to quickly remove the volatile impurities (including water, ethanol, methanol, acetonitrile, ethyl acetate, and acetone) in ILs using N$_2$. Increasing the temperature and the N$_2$ flow rates can speed the purification process.

Scheme 6. Two-Step Synthesis of Aryl Alkyl ILs[a]



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3. PROPERTIES OF IONIC LIQUIDS FOR EXTRACTION

In the following subsections, IL properties of particular importance to advance NFC applications, that is, radiation stability, volatility, thermal stability, combustibility, density, viscosity, surface tension, solubility, conductivity, electrochemical window, toxicity, and biodegradation, will be discussed in detail.

3.1. Radiation Stability

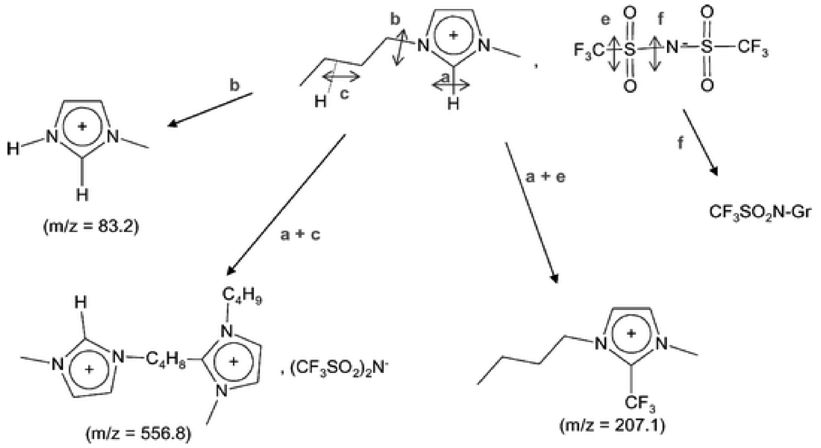
In the NFC, ILs will be exposed to high radiation doses from radioactive actinides and fission products. The radiation stabilities of ILs are crucial factors used to evaluate their potential application in nuclear fuel processing. Harmon et al.[32b] performed critical mass calculations on plutonium metal/IL mixtures and compared the results with similar calculations on aqueous systems. The studied ILs were [C$_2$mim]/[AlCl$_4$] and [C$_2$mim]/[BF$_4$]. The calculations indicate at least an order of magnitude increase in the minimum critical concentration for the IL-plutonium mixtures over aqueous mixtures.

Allen et al.[51] assessed the radiation stability of 1,3-dialkylimidazolium nitrate and 1,3-dialkylimidazolium chloride under α, β, and γ radiation. The results suggest that their stability is similar to that of benzene and they are much more stable than mixtures of tributyl phosphate (TBP) and odorless kerosene under similar irradiation conditions. A TBP-kerosene system is used widely in the NFC, and research by Allen and co-workers reveals the value of potential applications of ILs in NFC.

[C$_4$mim][PF$_6$] and [C$_4$mim][NTf$_2$] were studied under ^{137}Cs gamma radiolysis.[52] The density, surface tension, and refraction index of the ILs were unchanged by an absorbed dose of approximately 600 kGy. A comparative study of [C$_4$mim][PF$_6$]/[NTf$_2$] and [Bu$_4$N][NTf$_2$] revealed that the formation of colored products is associated with gamma radiolysis of the [C$_4$mim]$^+$ (Scheme 7). The radiolytic darkening kinetics of the imidazolium-type ILs was influenced by the anions as follows: Cl$^-$ < [NTf$_2$]$^-$ < [PF$_6$]$^-$. The presence of nonvolatile radiolysis products below 1 mol % resulted in an absorbed dose exceeding 1200 kGy. The initial step in [C$_4$mim]$^+$ cation radiolysis is loss of the Bu$^\bullet$ group, the H$^\bullet$ radical from position 2 on the imidazolium ring, and the H$^\bullet$ radical from the butyl chain. Radiolysis of IL anions yields F$^\bullet$ and CF$_3^\bullet$ from [PF$_6$]$^-$ and [NTf$_2$]$^-$, respectively.

The radiochemical stabilities of ILs formed from [C$_4$mim]$^+$ and [NTf$_2$]$^-$, [TfO]$^-$, [PF$_6$]$^-$, and [BF$_4$]$^-$ were investigated under gamma irradiation up to 2.0 MGy.[53] As the results revealed, the anion effect on the degradation order is [NTf$_2$]$^-$ < [TfO]$^-$ < [PF$_6$]$^-$ < [BF$_4$]$^-$. C−H bond dissociation of [C$_4$mim]$^+$ leads to the formation of H$^+$; dissociation of [NTf$_2$]/[TfO] leads to

Scheme 7. Proposed Simplified Degradation Scheme of [C_4mim][NTf_2][a]



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the formation of numerous F$^\bullet$ $^\bullet$CF$_3$, $^\bullet$SO$_2$ radicals and $CF_3SO_2N^{\bullet-}$ radical anion; and dissociation of P—F and B—F in [PF_6]$^-$ and [BF_4]$^-$ leads to the formation of F$^\bullet$ radical.

[$MeBu_3N$][NTf_2] was studied under ^{137}Cs gamma irradiation.[54] [$MeBu_3N$][NTf_2] is stable at high irradiation doses, and its stability does not appear to be affected by the presence of water or air. The many degradation products obtained in small quantities arise mainly from recombination of the primary radiolysis products of the anion $CF_3^\bullet$ or F$^\bullet$ and of the cation. The cation radicals were formed by the loss of a Bu$^\bullet$ group, the Me$^\bullet$ group, or two H$^\bullet$ atoms to form a double bond with the butyl chain. Radiolysis of the anion produced mainly F$^\bullet$ and $CF_3^\bullet$ radicals.

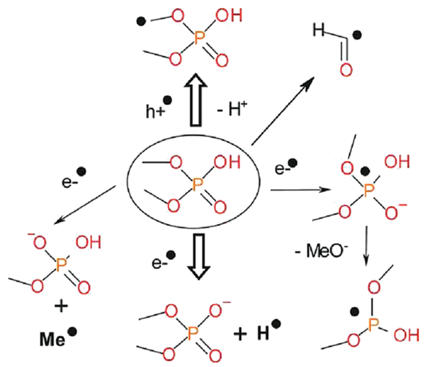
The effects of γ radiation on [C_4mim][BF_4]/[PF_6] were studied. The radiolysis of [C_4mim][BF_4] induces destruction of the alkyl chain and scission of H-atoms of the ring of the imidizolium cation and results in relatively small changes to the [BF_4]$^-$ anion. Radiation caused no change in the viscosity of [C_4mim][BF_4], but the viscosity of [C_4mim][PF_6] decreased by up to 10%. The radiation stability of [C_4mim][BF_4] is higher than that of [C_4mim][PF_6].[55]

The formation of gaseous products during radiolysis of ILs is a significant safety and environmental issue from an engineering viewpoint. Gas products were analyzed after electron beam radiolysis of imidazolium, ammonium, pyridinium, phosphonium, and pyrrolidinium ILs associated with [NTf_2]$^-$ anion. The aromatic ILs incorporating imidazolium and pyridinium cations gave smaller hydrogen gas radiation yields [G(H_2)], while phosphonium ILs gave the largest G(H_2). Nevertheless, this is still about only half of what one would expect from a corresponding mixture of *n*-alkanes.[56] Recently, Yuan et al. investigated the gamma irradiation stabilities of [C_4mim][PF_6] and [C_4mim][NTf_2] during Sr^{2+} extraction. They found that irradiation has significant influence on the DCH18C6/[C_4mim]-[PF_6] and DCH18C6/[C_4mim][NTf_2] system for extraction of Sr^{2+}. The radiation-generated H$^+$ from the ILs decreased the extraction of Sr^{2+} since the reaction with DCH18C6 is competitive between H$^+$ and Sr^{2+}. The extraction efficiency can be recovered by washing irradiated ILs with water for H$^+$ removal.[57] The decrease in Sr^{2+} extraction from a 3 M nitric acid solution added to [C_4mim][NTf_2] is independent of irradiation since the radiation-generated H$^+$ is negligible in highly acidic solutions.[58] Moreover, they indicated that [SO_3]$^{2-}$ is an unambiguous radiolytic product of [C_4mim][NTf_2] in the extraction process.[58]

Irradiation decreased the Cs$^+$ distribution ratio in the bis(2-propyloxy)calix[4]crown-6 (BPC6)/[1-alkyl-3-methylimidazolium] [NTf_2] ([$C_n$mim][NTf_2], $n = 2, 4, 6$) system by 200 times because of the competitive interaction of radiation-generated H$^+$ with BPC6. The decreases in Cs$^+$ extraction were caused mainly by the radiolysis of BPC6.[59] Radical intermediates generated in radiolysis and photoionization of ILs composed of ammonium, phosphonium, pyrrolidinium, imidazolium cations and [NTf_2]$^-$, [N(CN)$_2$]$^-$, and bis(oxalato)borate ([BOB]$^-$) anions were studied. Radiation damage to the cations is unavoidable, and the dissociation of anions is a minor pathway. The addition of 10−40 wt % trialkyl phosphate has little effect on the fragmentation of ILs. Damage to the ILs does not degrade extraction system performance because ILs can protect the extractant from damage, by diverting the damage toward themselves. Moreover, ILs yield no products that interfere with the extraction of metal ions.[60] The radiolysis and photoionization of ILs were studied using magnetic resonance spectroscopy. Large yields of C-centered radicals were observed in the aliphatic chains of phosphonium, ammonium, and pyrrolidinium cations, but not the imidazolium cation. The pattern indicates deprotonation of a hole trapped on the parent cation that competes with rapid electron transfer from a nearby anion. This charge transfer leads to the formation of stable N- or O-centered radicals. The dissociation of parent anions is a minor pathway. As for the radiation stability of IL-based separation systems, some radiation damage to the cation is unavoidable. Low amounts of extractant fragmentation suggest that ILs play a role in protecting the extractant.

Shkrob et al.[61] identified radicals derived from the anions in irradiated ammonium, phosphonium, and imidazolium ILs. Many detrimental reactions are initiated by radiation-induced redox processes involving these anions. Scission of the oxidized anions is indicated to be the main fragmentation pathway. Proton transfer involving the aliphatic arms of the anions is a competing reaction. [CF_3SO_3]$^-$ and [N(CN)$_2$]$^-$ are the most stable among small anions. The derivatives of benzoate and imide anions are relatively stable among larger anions. This stability can be attributed to suppression of oxidative fragmentation. In a subsequent study,[62] they investigated the radiation chemistry of 1,3-dialkyl-substituted imidazolium cations. The rich chemistry was initiated through "ionization of the ions": oxidation and

Scheme 8. Radiolytically Induced Fragmentation of Dimethylphosphoric Acid in ILs[a]



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formation of radical dications in aliphatic arms of the parent cations and reduction of the parent cation, yielding 2-imidazolyl radicals. The subsequent reactions of these radicals depended on the nature of the IL. Product analyses of imidazolium liquids irradiated in the regime of 6.7 MGy revealed several detrimental processes, including volatilization, acidification, and oligomerization. The latter process yielded a polymer, whose radiolytic yield increases with dose. Gradual generation of the polymer accounts for the steady increase in IL viscosity upon irradiation.

The applications of hydrophobic ILs in nuclear separations may put the ILs both in high radiation fields and in contact with aqueous raffinate containing 1−6 M HNO_3. Shkrob et al.[63] investigated the effect of the extracted nitrate and nitric acid on the radiation chemistry of ILs containing 1-alkyl-3-methylimidazolium cations. The nitrate anion was indicated to compete with the IL cation as an electron scavenger, with most of the primary radical species converted to $NO_3^{•2-}$ and $NO_2^{•}$ that initiate a complex sequence of radical reactions. The IL cation damage was not dramatically affected by the presence of nitrate as most of the detrimental radiolytic products were generated via the oxidative pathway. These results were contrasted with the behavior of dialkylphosphoric acids (a class of extractants for trivalent metal ions). They demonstrated that ILs protect these dialkylphosphoric acids against radiation-induced dealkylation (Scheme 8).

3.2. Volatility, Thermal Stability, and Flammability

A major goal of the chemical and nuclear industries today is to search for safer alternatives to VOCs that can minimize solvent loss and air pollution induced by solvent evaporation.[64] Undoubtedly, the low volatility, low combustibility, and high thermal stability of ILs make them ideal candidates as safe and environment-friendly replacements for VOCs in the NFC. One of the key challenges in the advanced NFC lies in development of solvent systems with significantly enhanced thermal stability, reduced flammability, and less environmental impact.

ILs are always regarded as nonvolatile because the vapor pressure of an IL is usually unmeasurable at room temperature.[34c] Interestingly, Earle et al.[65] reported that some aprotic ILs with high thermal stability (i.e., $[C_n\text{mim}][NTf_2]$) can be vaporized at 200−300 °C and low pressure using a Kugelrohr oven and distillation apparatus (Figure 3). However, they did not report direct proof of ions or ion pairs in the vapor phase.[66]

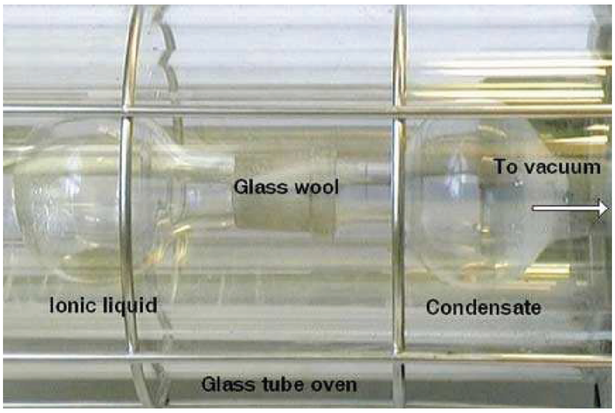


Figure 3. Labeled photograph of the Kugelrohr oven and distillation apparatus. Reprinted with permission from ref 65. Copyright 2006 Nature Publishing Group.

Some imidazolium ILs were indicated to evaporate as ion pairs, with heats of vaporization depending primarily on Coulombic interactions within the liquid-phase and the gas-phase ion pair.[67] The ion pairs indicate clearly that ILs can be distilled without decomposition. The thermal decomposition products from ILs can also cause a rise in vapor pressure.[68] Up to now, the vapor pressures and vaporization enthalpies of ILs have been measured with ultraviolet absorption spectroscopy,[69] mass spectrometry,[70] the integral effusion Knudsen method,[71] the thermogravimetric method,[72] and the transpiration method,[73] to name a few. A recent study indicated that the vapor pressure of ILs remains negligible at near-ambient conditions and that many ILs show no signs of distillation below the temperature of their thermal decomposition.[66]

Many studies have addressed the thermal stability of ILs. The type of anion was thought to have a crucial effect on the thermal stability of ILs;[74] a series of [1-benzyl-3-methylimidazolium][X] show thermal stability decreasing in the order $[NTf_2]^- = [TfO]^- > [TSA]^- > [DCA]^- > [SAC]^- > [TFA]^- > [SCN]^-$.[75] The anion also has a significant impact on the thermal stability of quaternary ammonium salts, the stability order being $[CF_3BF_3]^- < [n\text{−}C_3F_7BF_3]^- \approx [n\text{−}C_4F_9BF_3]^- \approx [C_2F_5BF_3]^- < [BF_4]^- \approx [NTf_2]^-$.[76] The decomposition temperatures of some pyridinium ILs are in the following anion order: $I^- < [SCN]^- < [N(CN)_2]^- < [NTf_2]^- < [TfO]^- < [BF_4]^-$.[77] In addition, Tokuda et al.[78] investigated a series of ILs with $[C_4\text{mim}]^+$, 1-butylpyridinium cation ($[\text{BuPy}]^+$), $[C_4\text{mpyrr}]^+$, and butyltrimethylammonium cation ($[\text{BuMe}_3\text{N}]^+$) associated with the same $[NTf_2]^-$ anion. The comparison of their decomposition onset temperatures indicated that thermal stability of these ILs is in the order of $[C_4\text{mpyrr}]^+ > [C_4\text{mim}]^+ > [\text{BuMe}_3\text{N}]^+ > [\text{BuPy}]^+$.

Fox et al.[79] studied the flammability and thermal stability of 1,2,3-trialkylimidazolium ILs. Flashpoints for the ILs with nucleophilic anions were between 250 and 300 °C, while the ILs with greater fluoride-containing anions were closer to 450 °C. The ILs with nucleophilic anions decomposed about 150 °C lower than ILs with bulky fluoride-containing anions. The alkyl chain length does not have a large effect on the thermal stability of ILs. The decomposition onset temperatures of trialkylimidazolium IL were greater than those of the analogous dialkylimidazolium ILs and were found to be more dependent upon the anion than the cation. The thermal stabilities of imidazolium and pyrrolidinium geminal dicationic ILs were greater than those of traditional monocationic ILs.[80] Luo et al.[72] prepared a new family of low-volatility protic ionic liquids (PILs) following the strategy of pairing organic superbasic proton acceptors with appropriate superacid-based fluorous anions. These new low-volatile PILs exhibit the highest thermal stabilities among known PILs so far.

The thermal stability of ILs is influenced not only by their composition but also by their solute.[81] Smiglak et al.[82] investigated the flammability of 20 imidazolium and phosphonium ILs. The results indicate that although ILs are not flammable themselves, they are not necessarily safe to use near fire and/or heat sources. The decomposition products formed during thermal decomposition of some ILs are sensitive to combustion. Moreover, the impurities in ILs can also result in ignition. Thus, necessary precautions must be maintained when ILs are used. The elements F, Cl, P, S, C, H, N, and O in ammonium, imidazolium, pyridinium, pyrrolidinium, tetrazolium, and aminotetrazole ILs with anions such as $[NO_3]^-$, $[CH_3CO_2]^-$, $[N(CN)_2]^-$, $[C(CN)_3]^-$, $[PF_6]^-$, $[NTf_2]^-$, and $[N(NO_2)_2]^-$ provided ILs with energy and combustibility.[73,83]

Although the vapor pressure and flammability of some ILs can be an issue, the status of ILs as "green" solvents is still unquestionable because their volatility, thermal stability, and combustibility are far superior to those of VOCs under usual conditions. However, the properties of being absolutely nonvolatile and noncombustible are disadvantageous for the purification, regeneration, and disposal of a spent IL-based system. A thorough investigation of these properties is important to the design of an appropriate IL-based separation protocol.

3.3. Density, Viscosity and Surface Tension

The densities of ILs are affected by their structures. The densities of imidazolium ILs decrease slightly as the alkyl chains on the cation increase in length.[84] The density of binary mixtures of $[C_n\text{mim}][BF_4]$ with water and ethanol decreased with an increase of the alkyl chain cation.[84b] When the cation is kept constant, the densities for the counteranions follow the order $[DCA]^- < [SCN]^- < [TFA]^- < [TfO]^- < [SAC]^- < [NTf_2]^-$. The order reveals that IL density increases with an increase in anion bulk and an increase in the number of fluorine atoms.[75] The density of IL always decreases as temperature rises.[85] In the temperature range 293−313 K, the densities of limidazolium ILs and pyridinium ILs decreased linearly with temperature increase.[86] Densities of binary mixtures of 1-butyl-3-methylpyridinium tetrafluoroborate + water, + ethanol and + nitromethane also decreased as the temperature rose.[87] The density of an IL is always about 10% higher than its equimolar physical mixtures; the effect can be well described by the electrostatic contribution among the ionic species involved.[88] The densities of 1.1 M TBP/$[C_8\text{mim}][PF_6]$ and the aqueous phase were found to intersect at an initial nitric acid concentration of 4.1 M. Similarly, for 1.1 M TBP/$[C_4\text{mim}][PF_6]$ phase, a phase reversal occurred at a later stage, at 7.1 M. The decrease of organic phase density with increasing nitric acid concentration can be attributed to the extraction of water by the organic phase.[89]

The viscosity of an IL affects the mass transfer efficiency of IL-based extraction. The viscosity of imidazolium IL always increases as the alkyl chain on the cation is lengthened because of increased van der Waals interactions.[90] The nature of the anion also affects the viscosity of an IL, particularly through relative basicity and the ability to participate in hydrogen bonding.[91] For ILs having a common anion and a similar alkyl chain length on the cation, viscosity increases with cation following the order $[Im]^+ < [Py]^+ < [Pyrr]^+$. Viscosities of ILs with imidazolium-based cations increase in the series $[NTf_2]^- < [CF_3SO_3]^- < [BF_4]^- < [EtSO_4]^- < [MeSO_4]^- < [PF_6]^- < [CH_3COO]^-$.[92]

An almost linear dependence of viscosity as a function of the length of the alkyl group has been observed for $[C_n\text{mim}][NTf_2]$.[93] However, increasing chain length in some ethylene glycol-functionalized imidazolium ILs also has been reported to lead to decreasing viscosities.[94] The viscosity of quaternary ammonium ILs is reduced when the alkyl chain is replaced by an alkoxy chain.[76] In both alkyl and alkoxy ILs, long chains of neighboring cations aggregate within micelle-like structures. However, assembly between alkoxy chains is less than that between alkyl chains and is the reason that alkoxy chains have higher ionic mobility.[95] Temperature has a significant effect on the viscosity of ILs. This temperature effect can be attributed to increased Brownian motion of the constituent molecules of ILs.[75] The viscosities of binary mixtures of $[C_4\text{mim}][SCN]$ and 1-alcohols were indicated to decrease with increasing temperature.[96] An increase in temperature increased viscosity in a non-Arrhenius fashion for the $[C_n\text{mim}][PF_6]$ ILs.[97] Okoturo et al.[98] studied the viscosity-temperature dependence of ILs. The ILs that obeyed the Arrhenius law typically contained asymmetric cations, and the majority did not contain functional groups. The ILs that obeyed the Vogel−Tamman−Fulcher law contained small and symmetrical cations with low molar mass. The ILs that obeyed neither the Arrhenius nor the Vogel−Tamman−Fulcher laws had cations with less symmetry, contained functional groups, and had higher molar mass. The density and viscosity of pure $[C_4\text{mim}][PF_6]$ or its mixture with methyl methacrylate decreased with increasing temperature, and viscosity was more sensitive than density to temperature.[99]

The presence of water[100] and organic solvents[101] can decrease the viscosity of ILs, obviously. The viscosity of $[C_4\text{mim}][PF_6]$ decreased by an order of magnitude by the water molecules dissolved in the IL phase.[102] The viscosity of $[C_2\text{mim}]^+$ type ILs was also found to decrease as the mole fraction of water increased. The behavior was especially critical at low water concentrations, where dramatic variations of viscosity occurred.[103] At the same concentrations, nonpolar solutes lowered the viscosity of $[C_2\text{mim}][NTf_2]$ more than water did.[104] The strong columb interaction between the ions weakens upon mixing with the neutral solvent, leading to higher ion mobility.[105] Chloride impurities always dramatically increase the viscosity of imidazolium ILs. The increased viscosity is related to an increase in the cohesive forces via hydrogen bonding between the chloride and the protons of the imidazolium ring.[100a]

Giridhar et al.[89] investigated the viscosity of the extracting phase as a function of initial acidity. The viscosity of 1.1 M TBP/$[C_8\text{mim}][PF_6]$ decreased from 76 cP to 35 cP when equilibrium aqueous acidity was varied from 0.1 to 8.0 M. As for 1.1 M TBP/$[C_4\text{mim}][PF_6]$, the viscosity remained at 36 cP at all acidities. The presence of water in the organic phase hydrates the ions and reduces the tendency of the IL species to aggregate, which lowers the viscosity of the organic phase. The viscosity of 1.1 M TBP/dodecane decreased marginally, from 3.95 cP to 2.51 cP, when the acidity was adjusted from 0.1 to 3.0 M.

Interfacial tension, an important physicochemical component in colloid and interface science, plays a role in IL-based extraction for mass-transport efficiency, emulsions, and phase-separation efficiency. The surface tensions of some hydrophobic ILs have been investigated using methods such as the du Noüy ring,[106] pendant drop,[107] capillary rise,[108] molecular dynamics simulations,[109] and dynamic light scattering.[110] The surface tensions of

ILs were shown to decrease with increasing temperature.[106a,107a] As for the surface tensions of some imidazolium, ammonium, and phosphonium ILs, changing anions has a negligible effect on the surface tension of higher alkyl chain phosphonium ILs. Increasing the size of the alkyl chains in ammonium ILs lowers the surface tension due to an increase in the ratio of van der Waals to Coulombic forces, whereas the addition of alkyl chains to the cation increases the surface tensions of ILs due to the orientation of hydrocarbon tails on the surface.[106a] Increasing chain length in $[C_n\text{mim}][\text{NTf}_2]$ ($n = 2-10$) decreased the surface tension because the ionic charge dispersed, reducing the hydrogen bond strength between the anion and cation.[106b] Surface tensions of $[C_4\text{mim}][\text{NTf}_2]$, $[C_6\text{mim}][\text{NTf}_2]$, $[\text{PP}_{13}][\text{NTf}_2]$, $[\text{Tmpa}][\text{NTf}_2]$, $[C_4\text{mim}][\text{PF}_6]$, $[C_6\text{mim}][\text{PF}_6]$, and $[C_8\text{mim}][\text{PF}_6]$ increased systematically with decreasing anion size and alkyl side chain length.[110] Imidazolium-based ILs with longer alkyl chain lengths exhibited lower surface tensions than those with shorter alkyl chain lengths. Once the concentration of IL reached the solubility limit, the surface tension of the aqueous phase leveled off. Adding more IL into the system did not decrease the surface tension further but resulted instead in the formation of a separate IL phase.[84a]

The surface of a hydrophobic IL is more sensitive to the addition of water than is a hydrophilic IL. A hydrophobic IL responds to the addition of water by reorienting its cation to help solvate the water molecule, whereas the orientation in a hydrophilic IL is unaffected.[111] At low water content, the addition of water does not change the surface thickness since water is mainly present in the bulk. As the water content increases, the surface swells before eventually shrinking down close to the solubility limit of water. The nonmonotonic surface thickness can be used to explain the anomalous trend of surface tension in $[C_4\text{mpyrr}][\text{NTf}_2]$-water mixtures.[112] IL partitioning into the aqueous phase was found to be significant enough to change surface tension. An interfacial tension between $[C_4\text{mim}][\text{NTf}_2]$ and water was comparable to that encountered in typical organic−aqueous solvent extractions. Low surface tension and interfacial tension allowed ILs to form emulsions through mechanical agitation, thereby increasing interfacial area and efficiency of extraction.[84a] Interfacial tension at the oil−IL interfaces suggested that ILs were more ordered at the oil-IL interfaces than at the air−IL interfaces. The decrease of entropy resulting from the interfacial orientation of IL was compensated by the increase of entropy resulting from the contact of different chemical species. All the oil phases spread at the air−IL interfaces spontaneously and formed complete wetting films.[113] Surface tension data on the gas−liquid interface of 1,3-dialkylimidazolium alkyl sulfates ($R = C_1-C_4$) showed a decreasing trend as the alkyl chain in the imidazolium cation was varied from the methyl to the butyl chain. A similar trend was observed when the alkyl chain of the anion was modified and the cation was fixed.[114] Interfacial tensions between $[C_4\text{mim}][\text{PF}_6]$ and organic solutes can be correlated to carbon chain length, degree of unsaturation, and functional group. For different organic liquids with the same carbon number, the interfacial tensions change in the sequence alkanes > alkenes > alcohols > aromatic hydrocarbons.[115]

3.4. Solubility

Decreasing the solubility of an IL in water or an organic solvent is important for IL-based extraction. Any measurable solubility will incur significant losses to wastewater from industrial-scale liquid−liquid extraction.[84a] The water−ion interaction strength for miscibility of ILs with water is determined mainly by the size of the ions. Interactions of water with small ions are more favorable because of the localized ionic charge. The second factor that determines water−ion interaction is the magnitude of the charge on the ionic surface atom directly coordinated with water.[116] The activity coefficients of ILs in water are split into cation and anion contributions.[117] The miscibility of an IL with water is determined largely by the associated anion.[111] The anion has the primary effect on water miscibility, with the cation having a secondary effect.[100a] The anions in order of increasing hydrophobicity are Br^-, $\text{Cl}^- < [\text{BF}_4]^- < [\text{PF}_6]^- < [\text{NTf}_2]^- < [\text{BETI}]^-$.[84a] The variations in water content of some imidazolium, pyrrolidinium, ammonium, and phosphonium ILs were mostly due to the identity of anions in the ILs and adhered to the following trend: $[\text{FAP}]^- > [\text{NTf}_2]^- > [\text{PF}_6]^- > [\text{BF}_4]^- > [\text{OTf}]^- >$ halides.[91] The solubilities of $[C_4\text{mim}]^+$ type ILs in water decreased as the hydrophobicities of their anions increased, with the order of hydrophobicity being $[\text{BETI}]^- > [\text{NTf}_2]^- > [\text{PF}_6]^-$.[118] When $[\text{A336}][\text{NO}_3]$ was studied for IL-based extraction in a nitric acid system, the solubilities of $[\text{A336}]^+$ decreased obviously as acidities rose because nitrate ion from HNO_3 can depress the loss of $[\text{A336}]^+$.[119] Solubility decreases as the length of the alkyl chain on the cation increases because of the increased hydrophobicity of IL.[84a,120] The water solubilities of $[C_n\text{mim}][\text{PF}_6]$ decreased monotonically as the 1-alkyl group is lengthened.[121]

The mutual solubilities between water and $[C_4\text{mim}][\text{NTf}_2]$ can be decreased by addition of inorganic salts. At low salt concentrations, a salting-in region was observed. With increasing salt concentration, the IL salted out. The salting-out effect results from the formation of hydration complexes and an increase in cavity surface tension. The salting-in effect results from a direct ionic binding of low-charge-density ions to hydrophobic moieties of the solute.[122] The solubilities of the $[C_2\text{mim}][\text{NTf}_2]$ first increased and then decreased from the addition of NaCl and KCl. The initial increase is caused by ionic interactions in the solution. The $[C_2\text{mim}][\text{NTf}_2]$ eventually began to precipitate when the salt concentration reached a threshold level. This phenomenon, a salting-out effect, will assist the use of ILs in high-ionic-strength applications.[84a] The salting-out effect[123] can be used to enhance the IL in aqueous phase separation. The influence of inorganic salts on the solubility of $[C_4\text{mim}][\text{tricyanomethane}]$ in an aqueous environment further indicates salting-out and salting-in mechanisms. The interactions of the anion of the salt are not only established with the cation of IL but also with its anion. The observed solubility effect is a balance between these two types of interactions.[124]

Understanding the phase behavior of ILs with organic solvents is an important issue for IL-based extraction. An increase in the alkyl chain length of an alcohol or of an alkyl substituent at a benzene ring decreased the solubility of IL.[125] The mutual solubility of $[C_n\text{mim}][\text{NTf}_2]$ with benzene and toluene increased as the alkyl chain in the imidazolium ring lengthened.[117] The ability of ILs to form hydrogen bonds or other possible interactions with potential solvents is an important feature of their solvation behavior.[126] Besides the hydrogen bonding, dipole−dipole, and van der Waals interactions of conventional organic solvents, ILs have ionic interactions, such as mutual electrostatic attraction or repulsion of charged particles. The ionic interactions make ILs prone to miscibility with polar substances.[34j] An increase in the alkyl chain length of aliphatic hydrocarbons decreases the solubility of trihexyl(tetradecyl) phosphonium (P_{66614}) chloride. The shorter alkyl chain of alkanes would favor their better accommodation in the hydrophobic region of the alkyl side chains of IL.[127] Tetra-*n*-butylphosphonium-type ILs with fumarate anion and maleate anion exhibited different solubilities to water in their cis and trans conformations.[128] High pressure influences the melting temperature and the liquidus curve differently for different ILs. The differences in the solubilities of [C_2mim][TOS] and [C_1mim][CH_3SO_4] resulted from their different melting temperatures.[129]

3.5. Conductivity and Electrochemical Window

ILs have advantages over traditional organic solvents in that their conductivities are intrinsic and they do not require the addition of a supporting electrolyte.[91] The IL conductivity is affected by the mobility of the ions, which is inversely proportional to their viscosities, ion sizes, and ion associations.[130] When [TEPP][NTf_2] was compared with [TEPA][NTf_2], [TEPP][NTf_2] showed a large self-diffusion. The large ionic conductivity and low viscosity of [TEPP][NTf_2] are well understood, with the causes of these properties being the large self-diffusion coefficient.[131] For [$C_n$mim][BF_4], electrical conductivity decreased with increasing length of the alkyl chain of the cation.[132]

The effects of high gamma irradiation, equivalent to an expected annual dose in commercial fuel processing (~1.2 MGy), on some imidazolium, pyridinium, and ammonium ILs were studied. All the ILs exhibited an obvious decrease in their conductivity and electrochemical window (at least 1.1 V). Such a decrease can affect the utility of ILs for electrochemical processing.[133]

Water and organic solvents have a crucial effect on the conductivity of ILs. The conductivity of [C_6mim][NTf_2] increased by 40% when wH_2O increased from 1×10^{-5} to 8.98×10^{-3} at 298.15 K.[134] The electrolytic conductivities of aqueous solutions of [C_2mim][C_2N_3] and [C_2mim][$MDEGSO_4$] decreased as their concentrations increased because ionic mobility lessens as the number of IL ions in the solution rises.[135] The conductivity of aqueous [$C_n$mim]Cl solution increased sharply in the water-rich region and decreased in the [$C_n$mim]Cl-rich region. This effect was ascribed to (i) an increase in viscosity and therefore a reduction in the mobility of the charge carriers and (ii) a reduction in the number of charge carriers due to aggregate formation.[136] The conductivity of ([C_6mim][NTf_2] + H_2O) depended strongly on the concentration of water.[134] The conductivity of ILs can be increased by diluting them with polar organic solvents, a phenomenon probably related to decreasing viscosity and separation of ion pairs.[130a] When binary mixtures of polyethyleneglycol with [C_4mim][BF_4] (or [C_4mim][PF_6]) were studied, it was discovered that as more polyethyleneglycol was added, the conductivity of the IL/solvent mixture decreased significantly. Cluster formation decreases the number of conductive free ions; hence, the conductivity of the mixture decreased.[137] Introducing dimethyl carbonate and formamide into ethylammonium nitrate decreased coulomb interactions in ILs and liberated free ions from their associates and aggregates, consequently leading to increased conductivities.[138]

The electrochemical properties of an IL microemulsion composed of [C_4mim][BF_4], Triton X-100, and toluene were studied. The microenvironments of the nonaqueous IL microemulsions not only influence their electrical conductivity but also influence the reversibility of electrochemical reactions. The electrochemical properties of an oil-in-IL microemulsion are better than those of an IL-in-oil microemulsion and a bicontinuous microemulsion.[139] In mixtures of an IL with a solvent having a low dielectric constant, ionic associations play a significant role, leading to low or only moderate values of ionic conductivity. In exchange, the dissociation of ion pairs will be considerably enhanced in the presence of a polar solvent. The conductivities of [C_4mim][BF_4] and [BuMePy][NTf_2] increased much more by adding the polar solvent dimethylformamide than by adding 3-picoline.[140] The conductivities of mixtures of [$C_n$mim]Cl + water and [$C_n$mim]Cl + ethanol increased with temperature, a finding that can be attributed to an increase in the mobility of ILs at higher temperatures.[141] Likewise, the conductivities of {[C_2mim][C_2N_3] + H_2O} and {[C_2mim][$MDEGSO_4$] + H_2O} are greater at higher temperatures,[135] and the conductivities of [C_2mim]$^+$ based ILs increased more than 200 times as temperature increased to 180 K.[142]

The electrochemical window of a substance refers to the voltage range between which the substance becomes neither oxidized nor reduced. The wide electrochemical windows of ILs enable them to overcome the limits imposed by common aqueous or organic media.[22a] The dialkyl-imidazolium ILs were believed to possess a wider electrochemical window than other molten salts described at that time. For example, the electrochemical window of [C_4mim][BF_4] and [C_4mim][PF_6] on tungsten electrod were 6.10 V and >7.10 V, respectively.[143] The combination of a trifluorotris(pentafluoroethyl)phosphate-based IL as the supporting electrolyte in an acetonitrile solution affords a wider anodic window, which is attributed to the high stability of the anionic component.[144]

An increase in water content significantly narrows the electrochemical window of each IL. The electrochemical window decreases in the following order: vacuum-dried > atmospheric > wet at 298 K > 318 K > 338 K.[91] The width of the polarized potential window of interfaces between water and tetraalkylammonium bis(2-ethylhexyl)sulfosuccinate was quantitatively correlated with the solubility of IL in water.[145] Tri-*n*-butylmethylphosphonium fluorohydrogenate was found to have an electrochemical window of 6.0 V, which is the widest among fluorohydrogenate ILs reported to date.[130b]

3.6. Toxicity and Degradation

Because IL-based extraction may result in the release of ILs to the environment, it is critical that the toxicity of ILs be determined in order to prevent a hazardous release and avoid subsequent decontamination. Many systems based on cell,[146] bacteria,[147] algae,[148] fish,[149] and enzyme[150] have been used to assess the toxicity of ILs. The effects of imidazolium ILs on the human tumor cell line HeLa system are lower than the values obtained for conventional organic solvents such as dichloromethane, toluene, or xylene.[146] The acute toxicity of [C_3mim][NTf_2] to *Daphnia magna* compares favorably with the toxicity of some solvents, such as methanol, dichloromethane, acetonitrile, chlorine, ammonia, and phenol.[151] It worth mentioning that some ILs are even more toxic to microorganisms than are VOCs.[152] The toxicities of ILs are closely related to their structures. The toxicity of imidazolium IL correlates directly with the length of the *n*-alkyl substituent in the methyl imidazolium cation. The shorter the chain length of the side chain, the lower is the toxic effect.[153] Some studies have indicated that the cation of an IL has a larger effect on toxicity than the anion.[154]

Varying the anion identity does not significantly alter toxicity. Stolte et al.[155] analyzed 100 Merck KGaA-synthesized ILs with different head groups, side chains, and anions using the WST-1 cytotoxicity assay. With regard to IL cytotoxicity, the head groups are of lesser concern than the side chains because the side chains influence an IL's lipophilicity. The polar ether, hydroxyl, and nitrile in side chains exhibit low cytotoxicity. An appropriate choice of cation and anion structure is important not only in the design of ILs with improved physicochemical properties but also to obtain inherently safer ILs.[156] An increase in alkyl group chain length as well as an increase in the number of alkyl groups substituted on the cation ring of imidazolium and pyridinium corresponded with an increase in toxicity for *Vibrio fischeri*.[152] Introduction of an oxygenated side chain in the imidazolium cation greatly reduced the toxicity of [C_4mim][BF_4].[157] The lower toxicity probably resulted from the reduced permeability of IL cations through the algal cell walls.[158]

Biodegradation pathways for imidazolium IL[159] and pyridinium IL[160] have been reported. In contrast, the (eco)toxicologically more recommendable imidazolium ILs with short alkyl functionalized side chains are difficult to degrade.[161] Docherty et al.[162] investigated the biodegradability of 1-butyl-3-methylpyridinium bromide, 1-hexyl-3-methylpyridinium bromide, and 1-octyl-3-methylpyridinium bromide using activated sludge microbial communities. IL biodegradation products are indicated to be less toxic than the initial compound to a standard aquatic test organism. Biodegradability does not depend significantly on the anion. $[BF_4]^-$ and $[CF_3COO]^-$ in *N*-ethylpyridinium IL did not inhibit the degrading activity of soil microorganisms.[163] The [C_4mim] cation was completely degraded using an electrolysis double cell equipped with electrodes made of iridium oxide, stainless steel, and a boron-doped diamond-coated bipolar electrode.[161] Hydrogen peroxide can be used to degrade alkylimidazolium and pyridinium ILs. The substituent of an imidazolium IL at position 1-N increases resistance to chemical degradation. Replacing the imidazolium headgroup with pyridinium also increases the resistance of IL to degradation.[164] [C_4mim]Cl can be degraded in a Fenton-like system with excess H_2O_2. The mechanism of such degradations indicates that initial $OH^\bullet$ radicals can attack any one of the three carbon atoms on the imidazolium ring.[165]

Photodegradation of [C_4mim][NTf_2] and an iodide solution of [C_4mim][NTf_2] by UV-laser irradiation was studied. Excited state [C_4mim$^+$]* underwent degradation efficiently, and neutral radical [C_4mim]* was relatively stable.[166] The H_2O_2/UV system was found more effective than UV or UV/TiO_2 with regard to the degradation of imidazolium ILs. The H_2O_2-enhanced photodegradation of imidazolium ILs decreased in the order $[C_4mim]^+ < [C_6mim]^+ < [C_8mim]^+ < [Eeim]^+$, which depends on the length of the alkyl chain.[167]

4. SOLVATION ENVIRONMENT

4.1. Dissolution of Metal Ions in Ionic Liquids

To overcome issues related to the solubility of metal ions in ILs, researchers have developed functionalized ILs. Protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][NTf_2], is one example of FILs. [Hbet][NTf_2][168] was found to have a selective dissolving ability for large quantities of metal oxides, including rare earth and uranium oxides, which are of interest for NFC applications. Nockemann found that [Hbet][NTf_2] is able to dissolve stoichiometric amounts of rare earth oxides. The crystal structures of the complexes are dimers, and the cationic dimers decompose into monomers after the dissolution.[168b] Uranium(VI) oxide can be dissolved in carboxyl-functionalized betainium ILs. The dissolution results in the formation of uranyl complexes with zwitterionic carboxylate ligands and $[NTf_2]^-$ counterions. The crystal structure of complexes depends on the cationic core appended to the carboxylate groups (Figure 4).[169]

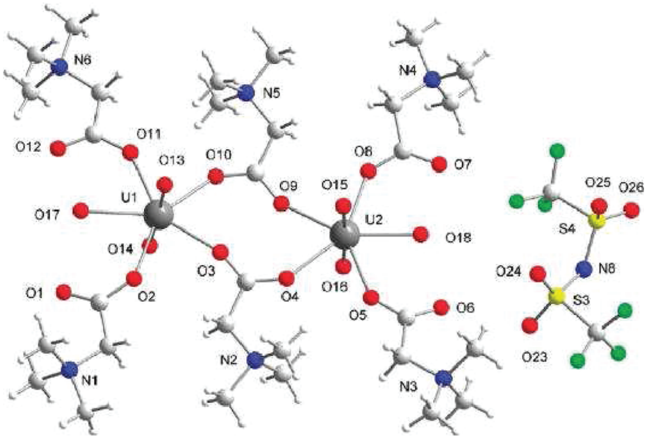


Figure 4. Structure and atom-labeling scheme of the $[(UO_2)_2(bet)_6(H_2O)_2]^{4+}$ dimers and one of the surrounding bistriflimide $[NTf_2]^-$ anions in the crystal structure of $[(UO_2)_2(bet)_6(H_2O)_2][NTf_2]_4$. Reprinted with permission from ref 169. Copyright 2010 American Chemical Society.

Chernikova et al.[170] studied Cs^+ complexation with 18-crown-6 in some hydrophobic ILs using ^{133}Cs nuclear magnetic resonance spectroscopy. The stability constants correlate well with the crown ether-assisted distribution ratio of Cs^+ from water into ILs, indicating the importance that complex stability has for the extraction process.

The solvation of uranyl salts with different anions ($[NO_3]^-$, $[TfO]^-$, $[ClO_4]^-$, $[SO_4]^{2-}$) in [C_4mim][PF_6]/[NTf_2]/[BF_4] and [Me_3NBu][NTf_2] was studied using spectroscopic simulation. The solubility and coordination properties of U^{6+} in ILs depend on the chemical form of U^{6+}, the IL, and additional anions. The interplay of uranyl ligands (TBP, CMPO, calixarenes) can strongly influence the complexation properties.[171] A molecular dynamics study[172] on the solvation of Ln^{3+} in [C_4mim][SCN] and [$MeBu_3$N][SCN] indicated that the first solvation shell of Ln^{3+} is anionic, with 6−8 N-coordinated ligands. This shell is surrounded by 13−14 $[C_4mim]^+$ or 8−9 $[MeBu_3N]^+$, leading to an "onion type" solvation of Ln^{3+}.

Billard et al.[173] investigated the dissolution of UO_2, UO_3, Nd_2O_3, Eu_2O_3, and Pr_6O_{11} powders in [C_4mim][NTf_2] with the help of small amounts of HNO_3. Using UV−vis and extended X-ray absorption fine structure (EXAFS) spectroscopy, the dissolution of UO_2 was shown to occur with a change in the oxidation state, from U^{4+} to U^{6+} via $[NO_3]^-/[NO_2]^-$ reduction, and with a concomitant complexation with the $[NO_3]^-$ entities to form the rather unusual $[UO_2(NO_3)_3]^-$ moiety. The presence of $[UO_2(NO_3)_3]^-$ moieties in wet [C_4mim][NTf_2] has importance for determining the extraction mechanism and characterizing the extracted complexes through liquid−liquid processes. The differences between the dissolution environments of UO_2 and lanthanides may be useful for their partitioning. This work may open the way to a direct dissolution of fuels in wet ILs, which then could be used as a starting phase for extraction/separation processes with supercritical CO_2.

Stumpf et al.[174] investigated the coordination chemistry and solution reactivity of Eu^{3+} and Cm^{3+} in [C_4mim][NTf_2] using

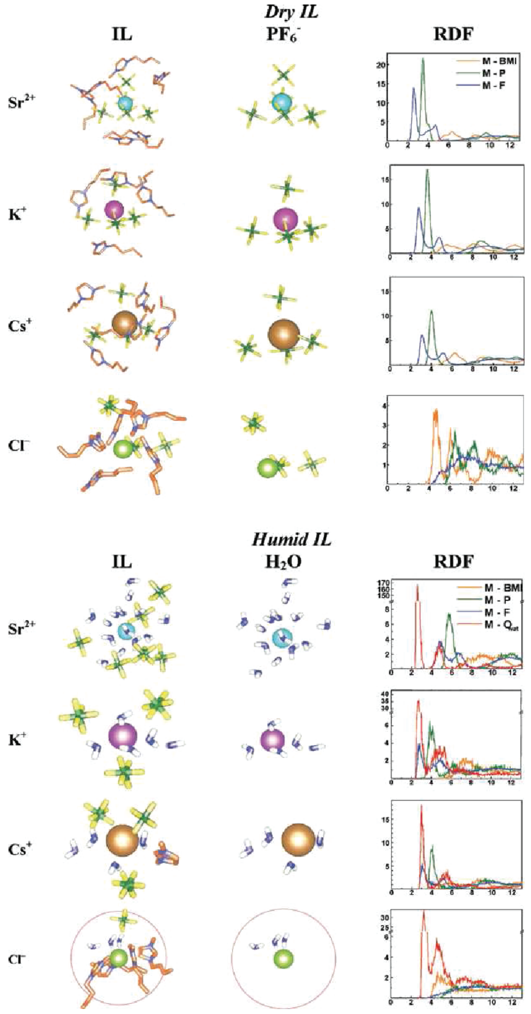


Figure 5. Uncomplexed Sr^{2+}, K^+, Cs^+, and Cl^- ions in the dry versus humid IL at 300 K. Left: snapshot of the first solvation shells, with the contribution of the $[PF_6]^-$ (dry IL) and H_2O (humid IL) molecules shown separately. Right hand side: Solvent RDFs around the ions in the dry versus humid IL at 300 K. Reprinted with Permission from ref 175. Copyright 2005 Royal Society of Chemistry.

time-resolved laser fluorescence spectroscopy. In aqueous systems the chemistry of trivalent lanthanides and actinides are similar; however, in ILs they are dramatically different. A comparison of the influence of copper on the fluorescence emissions of Eu^{3+} and Cm^{3+} in $[C_4mim][NTf_2]$ to the influence in an aqueous system gives evidence that there is a strong correlation between the strength of the ligand field and the reactivity of the trivalent cation. The difference in chemical behavior caused by the use of $[C_4mim][NTf_2]$ as a diluent is important for lanthanides and actinides separation in the NFC reprocessing.

Vayssière et al.[175] reported a molecular dynamics study of the solvation of K^+, Cs^+, and Sr^{2+} with 18-crown-6 (18C6) complexes in $[C_4mim][PF_6]$. Solvent humidity is indicated to be important to the solvation properties. In dry IL, the complexed K^+ and Sr^{2+} cations are locked at the center of the crown by 1 + 1 (for K^+), or by 1 + 2 or 1 + 3 (for Sr^{2+}) $[PF_6]^-$ anions in the facial positions. The Cs^+ cation is perched over the crown, solvated by three $[PF_6]^-$ anions. In humid IL, the complexed K^+ also binds to 1 + 1 $[PF_6]^-$ facial anions only (no water), whereas Sr^{2+} is asymmetrically coordinated to at least three H_2O molecules. According to an energy component analysis, the 18C6, the cations, and their complexes are better solvated by humid than by dry IL (Figure 5).

Servaes et al.[176] studied complex formation between the uranyl ion and nitrate ions in acetonitrile and $[C_4mim][NTf_2]$. The $[UO_2(NO_3)_3]^-$ coordination polyhedron for the uranyl nitrate complex was found to exist in both solvents. Schurhammer et al.[177] investigated the solvation of $[UCl_6]^-$, $[UCl_6]^{2-}$, and $[UCl_6]^{3-}$ complexes in $[C_4mim][NTf_2]$ and $[MeBu_3N][NTf_2]$. They found that $[UCl_6]^{3-}$ was exclusively "coordinated" to $[C_4mim]^+$ or $[MeBu_3N]^+$, which mainly interacted via their CH aromatic protons or their N-Me group, respectively. Around the less charged $[UCl_6]^-$ complex, the cations interacted via the less polar moieties (butyl chains of $[C_4mim]^+$ or $[MeBu_3N]^+$), and the anions displayed nonspecific interactions. $[UCl_6]^{3-}$ interacted more attractively with $[C_4mim][NTf_2]$ than with $[MeBu_3N][NTf_2]$.

Georg et al.[178] studied the complexation of $[UO_2]^{2+}$ with $[NO_3]^-$ in $[C_4mim][NTf_2]$. $[UO_2(NO_3)]^{3-}$ dominates the speciation for a reagent ratio of $[NO_3^-]/[UO_2^{2+}] > 3$. Conditional stability constants of the three successive complexes were calculated. Nishi et al.[179] studied the facilitated transfer of alkali-metal cations by dibenzo-18-crown-6 (DB18C6) across the electrochemically polarizable interface between aqueous solution and [*n*-octadecylisoquinolinium][tetrakis[3,5-bis(trifluoromethyl)phenyl]borate] ($[C_{18}Iq][TFPB]$). The stoichiometry of the complexes in $[C_{18}Iq][TFPB]$ for Li^+, Na^+, K^+, and Rb^+ were found to be 1:1, while for Cs^+ transfer, both 1:1 and 1:2 complexes were likely. The higher selectivity of DB18C6 to K^+ over Na^+ in $[C_{18}Iq][TFPB]$ compared with that in molecular diluents suggests that the IL provides a unique solvation environment for the complexations of DB18C6 with the ions. Attenuated total reflectance−Fourier transform infrared spectrometry was used to characterize the coordination environment of U^{6+} in $[C_4mim][NTf_2]$. In solutions containing nitric acid, only $UO_2(NO_3)_2$ was detected. The $[UO_2(NO_3)_3]^-$ complex did not form, perhaps a result of competition from water.[180]

4.2. Metal Ion-Containing Ionic Liquids and Crystals

The oxalate anion, $[C_2O_4]^{2-}$, can be used as a thermally labile ligand and/or precipitating agent in the nuclear industry. Bradley et al.[181] prepared a dimeric dioxouranium(VI) salt, containing coordinated nitrate and oxalate ligands, in $[C_4mim][NO_3]$. The complex 1-butyl-3-methylimidazolium μ4-(O,O,O′,O′-ethane-1,2-dioato)-bis[bis(nitrato-O,O)dioxouranate(VI)] was indicated to contain four $[C_4mim]^+$ cations and two independent $[\{(UO_2)(NO_3)_2\}_2(\mu 4\text{-}C_2O_4)]^{2-}$ moieties. Moreover, the formation of $[C_nmim]^+$ salts of the dinuclear μ4-(O,O,O′,O′-ethane-1,2-dioato)-bis[bis(nitrato-O,O)dioxouranate(VI)] anion was indicated to be general for a range of alkyl groups, where the 1-alkyl chain is methyl, ethyl, propyl, butyl, pentyl, hexyl, dodecyl, hexadecyl, or octadecyl.[182]

As $[NTf_2]^-$-based ILs are widely used in separation, Babai et al.[183] prepared the alkaline-earth -metal bis(trifluoromethanesulfonyl)imide complexes $[Mppyr]_2[Ca(NTf_2)_4]$, $[Mppyr]_2[Sr(NTf_2)_4]$, and $[Mppyr][Ba(NTf_2)_3]$ using the alkaline-earth-metal iodide and $[Mppyr][NTf_2]$. As for the calcium and strontium compounds, the metal was coordinated by four bidentately chelating $[NTf_2]^-$ ligands separated by $[Mppyr]^+$ cations. The $[Mppyr][Ba(NTf_2)_3]$ formed an extended structure. Ba^{2+} was surrounded by six oxygen atoms belonging to three $[NTf_2]^-$ anions.

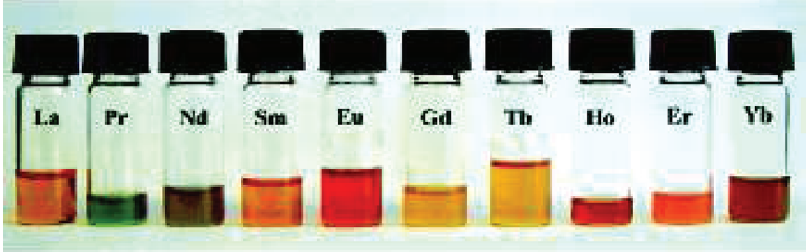


Figure 6. ILs of the type $[C_4mim]_4[Ln(NCS)_7(H_2O)]$ with Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, and Yb. Reprinted with permission from ref 184. Copyright 2006 American Chemical Society.

Table 1. Comparison of the Extraction Results Obtained Using ILs and VOCs[a]

extract phase	D^b (with crown ether in melts)	D (without crown ether in melts)
$BuMe_2lmPF_6$	42	0.67
$BuMelmPF_6$	2.4×10^1	0.89
$EtMeImNTf_2$	4.5×10^3	0.81
$EiMeljuNTf_2$	1.1×10^4	0.64
$PrMe_2ImNTf_2$	5.4×10^3	0.47
$PrMelmNTf_2$	7.6×10^{-1}	0.35
$C_6H_5CH_3$	7.6×10^{-1}	nm[c]
$CHCI_3$	7.7×10^{-1}	nm

[a] Reprinted with permission from ref 31. Copyright 1999 Royal Society of Chemistry. [b] The D value is defined as D = [molten salt concentration of Sr^{2+}]/[aqueous solution concentration of Sr^{2+}]. [c] nm = not measurable.

Three further oxygen atoms of $[NTf_2]^-$ linked the Ba^{2+} cations to infinite chains. Some low-melting lanthanide-containing ILs, $[C_4mim]_{x-3}[Ln(NCS)_x(H_2O)_y]$, also were synthesized (Figure 6). The compounds were transparent liquids at room temperature. In addition, they exhibited good solubility in apolar solvents and ILs. The crystal structures indicate that hydrogen bonding might influence their melting points.[184]

The behaviors of the complex ($[C_4mim]_2[UCl_6]$) in $[C_4mim][NTf_2]$ was studied, and the complex $[C_4mim]_2[UCl_6]$ was characterized in $[C_4mim][NTf_2]$. The octahedral complex $[UCl_6]^{2-}$ is the predominant form of U(IV) in the IL. The existence of hydrogen bonding between $[UCl_6]^{2-}$ and an acidic proton of $[C_4mim]^+$ was confirmed.[185] Hydrophobic ILs are not inert solvents with respect to An^{4+}-hexachloro complexes.[186] The dissolution of $[C_4mim]_2[AnCl_6]$ (An = Np^{4+} and Pu^{4+}) in $[C_4mim][NTf_2]$ yielded solutions of octahedral An^{4+} hexachloro complexes. $[AnCl_6]^{2-}$ was stable to hydrolysis in $[C_4mim][NTf_2]$.[187] Sornein et al.[188] prepared tetrachlorouranium(VI) complex ($[U^{VI}O_2Cl_4]^{2-}$) in $[C_4mim][NTf_2]$ and $[MeBu_3N][NTf_2]$ from a uranium(VI) solution in the presence of a stoichiometric quantity of chloride ions. The reduction potential of $[U^{VI}O_2Cl_4]^{2-}$ is -1.44 V and -1.8 V vs Ag/Ag^+ respectively in $[C_4mim][NTf_2]$ and $[MeBu_3N][NTf_2]$ and does not depend on the chloride concentration. The mechanism proposed for the redox process is a monoelectronic recuction to form the tetrachlorouranium(V) complex ($[U^VO_2Cl_4]^{3-}$), followed by a chemical reaction. The $[U^VO_2Cl_4]^{3-}$ complex seemed more stable in $[C_4mim][NTf_2]$ than in $[MeBu_3N][NTf_2]$. The electrochemical analysis put in evidence specific interactions of the IL cation with the uranium anionic species. Gaillard et al.[189] studied the competitive complexation of uranyl cations with nitrate and chloride ions in $[C_4mim][NTf_2]$. Nitrate and chloride are stronger ligands for uranyl than the $[NTf_2]^-$. When the anions were present simultaneously, neither the limiting complex $[UO_2(NO_3)_3]^-$ nor $[UO_2Cl_4]^{2-}$ alone could be observed. At a $U/NO_3/Cl$ ratio of 1:2:2, the dominant species is likely $[UO_2Cl_3(NO_3)]^{2-}$. When chloride was in excess over uranyl, the solution contained a mixture of $[UO_2Cl_4]^{2-}$ and $[UO_2Cl_3(NO_3)]^{2-}$ species. Chloride ion is always an impurity in prepared ILs. According to the study, the chloride ion can cause interference in complexation studies of ILs even at low concentrations. Aoyagi et al. studied the temperature-dependent yellow-to-red color changes of uranyl thiocyanate complexes with $[C_nmim]^+$. This phenomenon is attributed to changes in the local environment of the uranyl ion, including the coordination number and cation−anion interactions.[190]

5. EXTRACTION BEHAVIORS

In comparison to traditional solvent-extraction behaviors, the metal-ion partitioning in IL-based extraction systems exhibits high complexities. The superior extraction efficiency and enhanced selectivity of some IL-based extraction systems, as compared to those of VOC-based systems, have received considerable attention.

5.1. Alkali Metals and Alkaline-Earth Metals

Both ^{90}Sr and ^{137}Cs are high-heat radionuclides. Dai et al.[31] described the large distribution ratio for Sr^{2+} offered by DCH18C6 in $[R^1R^2\ MeIm][NTf_2]/[PF_6]$ (Table 1). The highest distribution ratio from the DCH18C6-$[EtMeIm][NTf_2]$ ($[C_2mim][NTf_2]$) system was 4 orders of magnitude greater than those from DCH18C6 in toluene and chloroform. The distribution ratios of IL-based extraction systems can be tailored by varying the substituting groups in the imidazolium cation and the counteranions. This pioneering study highlights the vast opportunities in separation applications for ILs with crown ethers.

Xu et al.[191] presented a further study on the extraction of Sr^{2+} using DCH18C6 as extractant and ILs as diluents. They investigated the influences of aqueous phase conditions on the extraction of Sr^{2+}. The study indicates that DCH18C6 achieved higher extraction efficiencies for Sr^{2+} in ILs than in *n*-octanol; the distribution ratio for Sr^{2+} can be more than 10^3 in the case of $[C_2mim][NTf_2]$. The IL effect on Sr^{2+} extraction by DCH18C6 followed the order $[C_2mim][NTf_2] > [C_4mim][NTf_2] > [C_4mim][PF_6] > [C_6mim][NTf_2]$. The extraction efficiency of Sr^{2+} was reduced by increasing nitric acid and Na^+, K^+ in the aqueous phase. Visser et al.[192] studied the extraction of Na^+, Cs^+, and Sr^{2+} using 18C6, DCH18C6, and 4,4′-(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (Dtb18C6) in $[C_n\text{mim}][PF_6]$ (n = 4, 6, 8). Metal ion partitioning was affected by the hydrophobicity of the crown ether and the composition of the aqueous phase. Aqueous solutions of HCl, Na_3citrate, $NaNO_3$, and HNO_3 decreased the metal ion distribution ratios and water content of the IL phase. The highest Cs^+ and Sr^{2+} distribution ratios were observed with the most hydrophobic crown ether, Dtb18C6, at the lowest acidity.

Chun et al.[121] reported an improved preparation of $[C_n\text{mim}][PF_6]$ with the 1-alkyl group from butyl to nonyl for alkali-metal chlorides extraction. The extraction efficiency of the DCH18C6-$[C_n\text{mim}][PF_6]$ system diminished as the length of the 1-alkyl group was increased. The selectivity order for DCH18C6 in the ILs was $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. As the alkyl group was elongated, the K^+/Rb^+ and K^+/Cs^+ selectivities generally increased. Kozonoi et al.[193] studied the extraction behavior of Li^+, Na^+, Cs^+, Ca^{2+}, Sr^{2+}, and La^{3+} from aqueous solution into $[C_n\text{mim}][\text{NfO}]$ (n = 4, 5, 6). The extraction efficiencies of La^{3+} decreased remarkably with an increase in HNO_3 concentration, exhibiting the order $[C_4\text{mim}][\text{NfO}] > [C_5\text{mim}][\text{NfO}] > [C_6\text{mim}][\text{NfO}]$ (i.e., the extraction efficiencies decrease as the IL becomes more hydrophobic). The extraction of metal species using $[C_4\text{mim}][\text{NfO}]$, $[C_5\text{mim}][\text{NfO}]$, and $[C_6\text{mim}][\text{NfO}]$ proceeded mainly through cation exchange with the partial transfer of noncharged species.

Synergistic extraction is an effective method for improving extraction efficiency and selectivity in VOC-based solvent extraction. Stepinski et al.[194] reported the synergistic effect of extractants in ILs. They observed that the addition of TBP can markedly increase the extraction of Sr^{2+} from acidic nitrate media into $[C_n\text{mim}][NTf_2]$ by DCH18C6. The alkyl chain length of the IL cation has important effects on the magnitude of the synergistic enhancement, which contributes to the design of IL-based synergistic systems.

Mono- and bis-crown-6 derivatives of calix-[4]arenes in the 1,3-alternate conformation possess high extractive strength and excellent selectivity for cesium ion in VOC-based extraction. Luo et al.[195] studied a calix[4]arenebis(*tert*-octylbenzo-crown-6) (BOBCalixC6)/$[C_n\text{mim}][NTf_2]$ (n = 2, 3, 4, 6, 8) system for Cs^+ extraction. BOBCalixC6 revealed higher distribution ratios for Cs^+ in the ILs than in chloroform. The selectivity of the IL-based system for extracting Cs^+ over Na^+ and Sr^{2+} was high. The concomitant extraction of K^+ along with Cs^+ also was observed. The shorter-alkyl-chain ILs have higher distribution ratios; however, the solubilities of BOBCalixC6 in the longer-alkyl-chain ILs were greater. Therefore, a compromise must be made in determining the optimum IL. The large distribution ratios for fission products using IL-based extraction processes make it difficult to strip extracted metal ions.

Luo et al.[196] synthesized eight *N*-alkyl aza-18-crown-6 ethers for Sr^{2+}, K^+, Na^+, and Cs^+ extraction. The pH-sensitive complexation capability of these aza-based ligands allowed a facile stripping process to be developed so that the IL-based extraction system could be reused. These ligands had a lower extraction efficiency for Cs^+ than DCH18C6. *N*-Octyl aza-18-crown-6 had an extraction efficiency for Sr^{2+} comparable to that of DCH18C6. The optimization of both ligands and ILs can lead to an extraction system that is highly selective toward Sr^{2+}. Xu et al.[59] demonstrated that BPC6 in $[C_n\text{mim}][NTf_2]$ (n = 2, 4, 6) exhibits an extremely high extraction efficiency for Cs^+ in aqueous solutions. The BPC6 showed a higher distribution ratio for Cs^+ than BOBCalixC6 in $[C_n\text{mim}][NTf_2]$. The low-acidity extraction behavior of the system provides an alternative method for Cs^+ extraction under low-acidity conditions relevant to high-level liquid wastes (HLLWs). Both Na^+ and Al^{3+} are usually prevalent ions in HLLWs. In the case of the IL-based systems, Na^+ and Al^{3+} show a competition effect on the extraction of Cs^+ because of competitive complexation of Na^+ and Al^{3+} with BPC_6. Luo et al.[118] studied the extraction of Sr^{2+} and Cs^+ using DCH18C6 in $[C_2\text{mim}][PF_6]$, $[C_2\text{mim}][NTf_2]$, $[C_4\text{mim}][PF_6]$, $[C_4\text{mim}][NTf_2]$, and $[C_4\text{mim}][\text{BETI}]$. The distribution ratios for both Sr^{2+} and Cs^+ increased markedly with the hydrophobicity of IL anions for the same IL cation. Such effects of IL anions can be explained using ion-exchange (see section 6.2), mass-action, and solvation principles. Moreover, the hydrophobic IL anions enhanced the selectivity of DCH18C6 for Sr^{2+} over Na^+, K^+, and Cs^+.

5.2. Rare Earths and Actinides

Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) is a highly effective actinide extractant in traditional organic diluents. Visser et al.[197] investigated CMPO in IL-based extraction for Am^{3+}, Pu^{4+}, Th^{4+}, and $[UO_2]^{2+}$ extraction. Distribution ratios of CMPO (CMPO and TBP) were at least an order of magnitude higher in $[C_4\text{mim}][PF_6]$ than in *n*-dodecane. Nakashima et al.[198] studied the extraction behavior of Ce^{3+}, Eu^{3+}, and Y^{3+} using CMPO in $[C_4\text{mim}][PF_6]$ and *n*-dodecane. The extraction efficiency of CMPO in $[C_4\text{mim}][PF_6]$ was exceedingly high compared to that in *n*-dodecane. They presumed that the dielectric constant of the ILs is high enough to achieve higher extractability as compared with that of *n*-dodecane. The high extraction efficiency would drastically increase cost efficiency in industrial separations applications. In addition, the selectivity of CMPO for lanthanide ions in $[C_4\text{mim}][PF_6]$ was found to be better than in *n*-dodecane. The extractability of Ce^{3+} using CMPO in $[C_4\text{mim}][NTf_2]$ was higher than that in $[C_4\text{mim}][PF_6]$. Such anionic effects can be attributed to the metal coordination environment in the ILs, which can be affected by the hydrogen bond basicity and/or dipolarity of the extracting IL phase. The metal ions can be effectively stripped using acetohydroxamic acid (AHA), ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), and citric acid, which form a water-soluble complex with metal ions. An aqueous solution of $[C_4\text{mim}]$Cl with high concentrations of $[C_4\text{mim}]^+$ can also strip metal ions sufficiently due to the cation exchange mechanism. They also observed that after repeated extraction and stripping processes four times, no appreciable decline in the extraction efficiency and no extraction hindrance by the complexing agent were observed.

Zuo et al.[199] studied the extraction and separation of Th^{4+} using ILs. They found that pure $[C_8\text{mim}][PF_6]$ can be used for separating Ce^{4+} from Th^{4+}, and Ln^{3+} in nitric acid medium. $[C_8\text{mim}][PF_6]$ showed a good distribution ratio for Ce^{4+}, whereas the distribution ratio was small for Th^{4+} and negligible for Ln^{3+}. The extraction behavior of Ce^{4+} by $[C_8\text{mim}][PF_6]$ can be attributed to the formation of $[Ce(NO_3)_6]^{2-}$, and the anion can form new IL with the $[C_8\text{mim}]^+$ cation. The extraction of Th^{4+} sulfate using primary amine N1923 in $[C_8\text{mim}][PF_6]$ was studied.[200] The extraction behavior was quite different from that using *n*-heptane or dichloromethane as a diluent. A slope analysis method revealed that the extraction mechanism was reverse micellar solubilization, which was confirmed by polarized optical microscopy/transmission electron microscopy. The Th^{4+} was

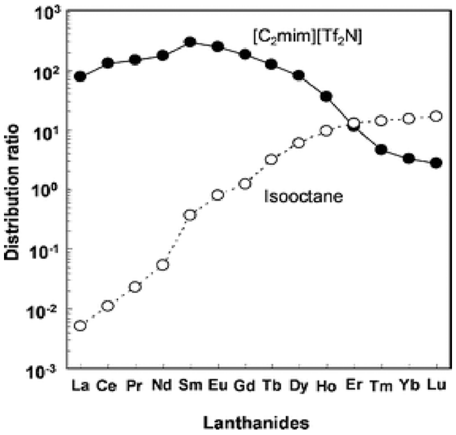


Figure 7. Selectivity of TODGA for lanthanides in $[C_2mim][Tf_2N]$ or in isooctane. Reprinted with permission from ref 202. Copyright 2008 Royal Society of Chemistry.

well separated from La^{3+}, Ce^{3+}, Nd^{3+}, Gd^{3+}, Er^{3+} by N1923/$[C_8mim][PF_6]$ at low acidity, and a satisfactory stripping ratio was achieved using mixed strippants of citric acid, formic acid, and hydrazine hydrate. Yoon et al.[201] studied the extraction of Ce^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} using bis-(2-ethylhexyl)-phosphoric acid (HDEHP) in $[C_nmim][PF_6]$ (n = 2, 4) or $[C_4mPy][PF_6]$. They found that the IL system showed more than three times greater extractability for lanthanide than when hexane was used as a diluent. Moreover, the imidazolium-type IL system generally offered a higher distribution ratio than the pyridinium-type IL system. The $[C_4mPy][PF_6]$ system gave much higher selectivity to heavy lanthanide, Yb than the other systems.

Shimojo et al.[202] studied the extraction behavior of all lanthanides except for Pm^{3+} using tetraoctyldiglycolamide (TODGA) in $[C_nmim][NTf_2]$ (n = 2, 4, 6). Application of ILs as the extracting phase provided unprecedented enhancement of the extraction performance of TODGA for lanthanides compared with that of an isooctane system. TODGA gave higher selectivity for middle lanthanides in the IL systems, but provided higher selectivity for heavier lanthanides in the isooctane system (Figure 7). In addition, TODGA exhibited outstanding extraction ability for $^{241}Am^{3+}$ as well as for lanthanides. Shen et al. studied the extraction of $[UO_2]^{2+}$ in aqueous solution using diglycolamide as an extractant in $[C_nmim][PF_6]$ (n = 4, 6, 8). The extraction capability of diglycolamides was indicated to be remarkably higher in ILs than in chloroform, particularly at low HNO_3 concentration.[203]

To assess the performance of TBP in IL for nuclear fuels reprocessing, the extraction behavior of U^{6+} by TBP dissolved in $[C_4mim][PF_6]$ was compared with that by a TBP/dodecane system. The extraction of U^{6+} by a 1.1 M TBP/$[C_4mim][PF_6]$ system was similar to the behavior by a traditional TBP/dodecane system when the concentration of nitric acid was less than 4.0 M. Increased U^{6+} extraction was observed from high nitric acid (>4 M) concentrations using the TBP/$[C_4mim][PF_6]$ system. The increased extraction may be attributed to ion exchange between $[PF_6]^-$ and anionic uranyl nitrate complexes, $[UO_2(NO_3)_3]^-$.[204]

Rout et al.[205] observed much larger distribution ratios of $^{241}Am^{3+}$ using TBP and CMPO in $[C_4mim][NTf_2]$ than in *n*-dodecane. Comparable extraction behavior can be achieved by 0.05 M CMPO in IL media instead of 0.2 M CMPO in TRUEX solution. By using $[C_4mim][NTf_2]$ as diluents, the amount of CMPO needed for Am^{3+} extraction from HLLWs (3−4 M in HNO_3) can be minimized by a factor of 4.

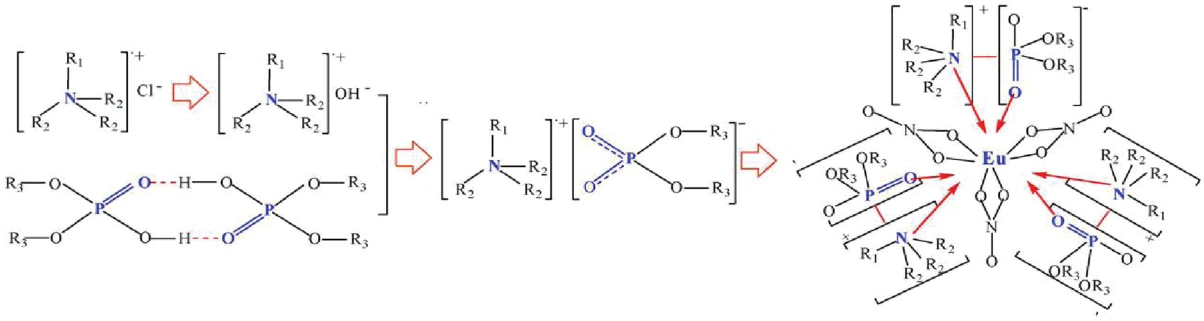
Okamura et al.[206] investigated the synergistic effect of 18-crown-6 derivatives, such as 18C6, DCH18C6, and DB18C6 on extraction of trivalent lanthanids into $[C_4mim][NTf_2]$ with 2-thenoyltifluoroacetone (Htta). The 18C6 and DCH18C6 revealed a synergistic effect for light Ln^{3+}, wherase no enhancement of extractability was observed when DB18C6 was used. The synergistic effect by crown ether (CE) increased as the atomic number of the lanthanide decreased. Light Ln^{3+} showed a remarkable synergistic effect; however, the extraction behavior of the heavy lanthanides hardly changed. The synergistic effect depended on the size-fitting ability of Ln^{3+} into the cavity of crown ether.

Trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous komplexes (TALSPEAK), which was originally developed in the 1960s at Oak Ridge National Laboratory,[207] is a well-documented method for the separation of actinides from fission product and rare-earth elements.[208] This separation process relies on the use of diethylenetriamine pentaacetic acid (DTPA) as an aqueous complexing agent to selectively retain actinides, while lanthanides are extracted into the organic phase by di(2-ethylhexyl)phosphoric acid (HDEHP). Sun et al.[209] very recently reported excellent extraction efficiencies and selectivities using HDEHP as an extractant for some rare earth elements (REEs) in $[C_nmim][Tf_2N]$/[BETI] than in diisopropyl benzene (DIPB), an organic solvent used as a diluent for the conventional TALSEAK process. Both cations and anions of ILs exhibited obvious effects on the extraction processes, which are mainly considered to be a cation-exchange mechanism. The distribution ratios of applying ILs to the TALSPEAK process are quite attractive. The strategy to enhance selectivities of REE ions using addition of complexants in aqueous phases opens up an alternative avenue for REEs separation via ILs.

Functionalized ILs (FILs) contain complexing substructures in their cations and/or anions. They can behave both as the organic phase and the extracting agent. Ouadi et al.[30b] reported the application of FILs based on quaternary ammonium cations bearing phosphoryl moieties in the liquid−liquid extraction of U^{6+}. Some FILs achieved 2 orders of magnitude higher distribution ratios for U^{6+} than TBP in $[Me_3BuN][NTf_2]$ under the conditions of the PUREX process. A high distribution ratio (D > 1000) was obtained with [A336][TS] for the extraction of ^{238}U from natural water, with high selectivity compared to divalent magnesium and calcium ions, which showed no affinity to this IL.[210] Rout et al. synthesized the FIL, [diethyl-2-(3-methylimidazolium)ethylphosphonate]$[NTf_2]$ ($[ImP][NTf_2]$). Extraction of Pu^{4+}, U^{6+}, and Am^{3+} from nitric acid medium by a solution of $[ImP][NTf_2]$ in $[C_nmim][NTf_2]$ (n = 4, 8) was studied as a function of nitric acid concentrations. The distribution ratios of Am^{3+} and U^{6+} in $[ImP][NTf_2]$/$[C_nmim][NTf_2]$ and $[C_nmim][NTf_2]$ were significantly low at all nitric acid concentrations, which led to unusually high separation factors for Pu^{4+} from other actinides.[211] Odinets et al. synthesized some CMPO-modified FILs. The results show that high separation of Pu^{4+}, Am^{3+}, Eu^{3+}, and U^{6+} can be achieved using these FILs as active agents of solid phase sorbents based on carbon nanotubes.[212]

Some bifunctional IL extractants prepared using $[A336]^+$ cation with an organicphosphonic acid group or organiccarboxylic

Scheme 9. The Proposed Structure of [A336][P204] and Its Coordination Environment with Eu(III)[a]



[a] Reprinted with permission from ref 213. Copyright 2010 Elsevier Ltd.

acid group as anions revealed an obvious synergistic effect vs their mixed precursors for Eu^{3+} extraction.[213] Moreover, saponification wastewater from application of industrial acidic extractants can be avoided by using bifunctional IL extractants. Sun et al.[213,214] were the first to report the inner synergistic effect of FILs. The effect is similar to the traditional synergistic effect produced by two extractants. It is called an "inner synergistic effect" because it comes from the cation and anion of the same bifunctional IL (Scheme 9).

5.3. Other Fission Products

Not only hydrophobic ILs can be used in IL-based extraction, some hydrophilic ILs such as $[C_4mim]Cl$ can also form biphasic systems for metal ions separation. The aqueous biphasic systems can be formed from a wide range of ILs including imidazolium-, pyridinium-, phosphonium-, and ammonium-based salts, and a variety of inorganic salts including phosphates, carbonates, hydroxides, and sulfates. Many of the inorganic salts are largely present in nuclear tank wastes. Cocalia et al.[16] reported that distribution ratios for $[TcO_4]^-$ from a concentrated K_3PO_4 solution to the IL-rich phase without extractant exceeded 700. The study offers the potential to remove $[TcO_4]^-$ from tank waste using IL. The extraction of $[TcO_4]^-$ and related tetra-oxo anions from aqueous solutions into IL-based solvents incorporating $[P_{66614}][NTf_2]$ and DCH18C6 was studied. The solvents exhibited high distribution ratios (100−500 for $[TcO_4]^-$), significant electrical conductivity (>100 μS/cm), and a wide (4 V) electrochemical window. The results suggest that these solvents may provide the basis for improved approaches to the extraction and recovery of anions.[215]

6. EXTRACTION MECHANISMS

Because of the unique structure of ILs, the mechanisms of IL-based extraction are quite different from those of VOC-based extraction. For different combinations of IL, extractant, and metal ion, different mechanisms may apply. A thorough understanding of the mechanisms will benefit the development of high-efficient IL-based extraction systems for NFC application. Currently, the possible mechanisms involving IL-based extraction are anion-exchange, cation-exchange, solvation, and multiple mechanism. Table 2 lists some examples that are described in the following subsections.

6.1. Anion-Exchange Mechanism

Extended X-ray absorption fine structure (EXAFS) is an experimental technique that provides direct clues about behavior in liquids or solutions, which can provide key information about the primary coordination environment of metal complexes in ILs.[34g] Jensen et al.[216] investigated the structure of Ln^{3+}-2-Htta complexes in $[C_4mim][NTf_2]$ using EXAFS, equilibrium thermodynamics, optical absorption and luminescence spectroscopies, high-energy X-ray scattering, and molecular dynamics simulations. Their studies indicate the formation of anionic $[Nd(tta)_4]^-$ or $[Eu(tta)_4]^-$ complexes with no water coordinated to the metal center in $[C_4mim][NTf_2]$. The presence of anionic lanthanide complexes in $[C_4mim][NTf_2]$ was made possible by the exchange of IL anions into the aqueous phase for the lanthanide complex. The resulting complexes in the IL phase were thought to be weak $[C_4mim][Ln(tta)_4]$ ion pairs that exert little influence on the structure of the IL phase. The acid dependence of $[Ln(tta)_4]^-$ partitioning provides a realistic mechanism for recovering the lanthanide from the IL phase through treatment with the acidic form of the anion, $H(NTf_2)$.

Ouadi et al.[30a] synthesized two imidazolium type FILs containing 2-hydroxybenzylamine entities for Am^{3+} extraction. The authors presented a possible anion-exchange mechanism for Am^{3+} partitioning. In the mechanism, the negative charge of the extracting complex in the IL phase is balanced by the transfer of $[NTf_2]^-$ from the $[C_4mim][NTf_2]$ phase into the aqueous phase.

6.2. Cation-Exchange Mechanism

Dietz and Dzielawa[217] observed that the extraction behavior of DCH18C6 for Sr^{2+} differed between 1-octanol and $[C_nmim][NTf_2]$. In 1-octanol the distribution ratio for Sr^{2+} shows a nitric acid dependency characterized by increasing Sr^{2+} partitioning with increasing acidity. In contrast, in $[C_nmim]^+$ systems the distribution ratio for Sr^{2+} shows a nitric acid dependency characterized by a significant decrease in Sr^{2+} partitioning with increasing acidity. That is, Sr^{2+} partitioning in the IL systems does not involve nitrate ion coextraction. They further indicated that increasing $Sr(NO_3)_2$ extraction would be accompanied by increasing transfer of the $[C_5mim]^+$ from $[C_5mim][NTf_2]$ to the aqueous phase. Thus, a cation-exchange mechanism seems reasonable.

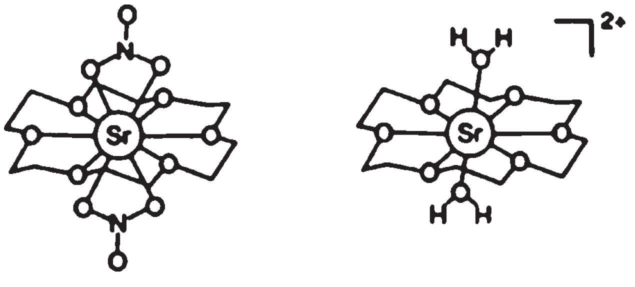
Visser et al.[223] studied $[UO_2]^{2+}$ extraction by CMPO, TBP in $[C_4mim][PF_6]$ and $[C_8mim][NTf_2]$. UV−visible spectra demonstrate that the uranyl-CMPO complexes in dodecane and $[C_4mim][PF_6]$ were not equivalent. EXAFS measurements reveal that the uranyl complexes in dodecane solutions were of the stoichiometry $UO_2(NO_3)_2(CMPO)_2$. In contrast, the extraction of uranyl in both ILs indicates a net stoichiometry of $UO_2(NO_3)(CMPO)_2$. The concentration of IL cation in aqueous phase increased in proportion to the amount of

Table 2. Comparison of Typical Mechanisms of VOC-Based and IL-Based Extraction

Mechanism	VOC-Based extraction	IL-Based Extraction	Ref.
Anion Exchange	$[Ln(H_2O)_n]^{3+}_{aq} + 3Htta_{org}$ $\rightleftharpoons [Ln(tta)_3(H_2O)_{n-6}]_{org} + 3H^+_{aq} + 6H_2O_{aq}$ $[Ln(H_2O)_n]^{3+}_{aq} + 4Htta_{org}$ $\rightleftharpoons [Ln(tta)_3(Htta)]_{org} + 3H^+_{aq} + nH_2O_{aq}$	$Ln^{3+}_{aq} + 4Htta_{IL} + [C_4mim][NTf_2]_{IL}$ $\rightleftharpoons [C_4mim][Ln(tta)_4]_{IL} + 4H^+_{aq} + [NTf_2]^-_{aq}$	216
		$[AmOH]^{2+}_{aq} + [ClO_4]^-_{aq} + [C_4mim][NTf_2]_{IL} + 2[LH_2]_{IL}$ $\rightleftharpoons [(AmOH)(LH)_2(ClO_4)]_{IL} + [C_4mim]^+_{IL} + 2H^+_{aq} + [NTf_2]^-_{aq}$	30a
Cation Exchange		$M^{3+}_{aq} + 3CMPO_{IL} + 3[C_4mim]^+_{IL}$ $\rightleftharpoons [M(CMPO)_3]^{3+}_{IL} + 3[C_4mim]^+_{aq}$	198
	$Ln^{3+}{}_{aq} + (3\text{ or }4)TODGA_{org} + 3[NO_3]^-_{aq}$ $\rightleftharpoons [Ln(TODGA)_{(3\text{ or }4)}(NO_3)_3]_{org}$	$Ln^{3+}_{aq} + 3TODGA_{IL} + 3[C_nmim]^+_{IL}$ $\rightleftharpoons [Ln(TODGA)_3]^{3+}_{IL} + 3[C_nmim]^+_{aq}$	202
		$Ln^{3+}_{aq} + Htta_{IL} + CE_{IL} + 2[C_4mim]^+_{IL}$ $\rightleftharpoons [Ln(tta)(CE)]^{2+}_{IL} + H^+_{aq} + 2[C_4mim]^+_{aq}$	206
	$[Sr(CE)]^{2+}_{org} + 2NO^-_{3\,aq}$ $\rightleftharpoons [Sr(NO_3)_2(CE)]_{org}$	$[Sr(CE)]^{2+}_{IL} + 2[C_nmim]^+_{IL}$ $\rightleftharpoons [Sr(CE)]^{2+}_{IL} + 2[C_nmim]^+_{aq}$	217
	$Sc^{3+}_{aq} + 2Cyanex925_{org} + 1.5[SO_4]^{2-}_{aq}$ $\rightleftharpoons [Sc(SO_4)_{1.5}(Cyanex925)_2]_{org}$	$Sc^{3+}_{aq} + 3Cyanex925_{IL} + 3[C_8mim]^+_{IL}$ $\rightleftharpoons [Sc(Cyanex925)_3]^{3+}_{IL} + 3[C_8mim]^+_{aq}$	218
		$Pu^{4+}_{aq} + [NO_3]^-_{aq} + 2CMPO_{IL} + 3[C_8mim]^+_{IL} \leftrightarrow$ $[Pu(NO_3)(CMPO)_2]^{3+}_{IL} + 3[C_8mim]^+_{aq}$ (1M Aqueous acidity) $Pu^{4+}_{aq} + [NO_3]^-_{aq} + CMPO_{IL} + 3[C_8mim]_{IL}{}^+ \leftrightarrow$ $[Pu(NO_3)(CMPO)]^{3+}_{IL} + 3[C_8mim]^+_{aq}$ (2M Aqueous acidity)	219
Solvation Mechanism	$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2TBP_{org}$ $\rightleftharpoons [UO_2(NO_3)_2(2TBP)]_{org}$	$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2TBP_{IL}$ $\rightleftharpoons [UO_2(NO_3)_2(2TBP)]_{IL}$	204
		$Na^+_{aq} + [TcO_4]^-{}_{aq} + CE_{IL}$ $\rightleftharpoons [Na(CE)(TcO_4)]_{IL}$	215
		$Sc^{3+}_{aq} + 2\ Cyanex\ 925_{IL} + [(R_3N^+CH_3)NO_3]^-_{IL} + 3[NO_3]^-_{aq}$ $\rightleftharpoons [(R_3NCH_3)\ Sc\ (NO_3)_4\ (Cyanex\ 925)_2]_{IL}$	119
Multiple Mechanism		$$\begin{tikzcd} {[CsBPC6]^+_{aq} + [C_nmim]^+_{IL}} \arrow[r, shift left] \arrow[d, shift left, "-\ BPC6"] & {[CsBPC6]^+_{IL} + [C_nmim]^+_{aq}} \arrow[l, shift left] \arrow[d, shift left, "-\ BPC6"] \\ {Cs^+_{aq} + [C_nmim]^+_{IL}} \arrow[r, shift left] \arrow[u, shift left, "+\ BPC6"] & {Cs^+_{IL} + [C_nmim]^+_{aq}} \arrow[l, shift left] \arrow[u, shift left, "+\ BPC6"] \end{tikzcd}$$	59
	$Na(DCH18C6)^+ + [NO_3]^-_{aq}$ $\rightleftharpoons [Na(NO_3)(DCH18C6)]_{org}$	$[Na(DCH18C6)]^+ + [C_nmim][NTf_2]_{IL}$ $\rightleftharpoons [Na(DCH18C6)(NTf_2)]_{IL} + [C_nmim]^+_{aq}$ $Na^+_{aq} + [(H_3O)(DCH18C6)]^+_{IL}$ $\rightleftharpoons [Na(DCH18C6)]^+_{IL} + [H_3O]^+_{aq}$ $[(H_3O)(DCH18C6)]^+_{IL} + [C_nmim][NTf_2]_{IL}$ $\rightleftharpoons [(H_3O)(DCH18C6)(Tf_2N)]_{IL} + [C_nmim]^+_{aq}$	220
	$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2TBP_{org}$ $\rightleftharpoons [UO_2(NO_3)_2(TBP)]_{org}$	$[(UO_2)(TBP)_2]^{2+}_{IL} + 2[C_nmim][Tf_2N]_{IL}$ $\rightleftharpoons [UO_2(TBP)_2(Tf_2N)_2]_{IL} + 2[C_nmim]^+_{aq}$	221

Table 2. Continued

Mechanism	VOC-Based extraction	IL-Based Extraction	Ref.
		$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2TBP_{IL} \rightleftharpoons [UO_2(NO_3)_2(TBP)]_{IL}$	
	$[UO_2]^{2+}_{aq} + 2[(HA)_2]_{org} \rightleftharpoons [UO_2(HA_2)_2]_{org} + 2H^+_{aq}$	$[UO_2]^{2+}_{aq} + 2[(HA)_2]_{IL} \rightleftharpoons [UO_2(HA_2)_2]_{IL} + 2H^+_{aq}$	222
	$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2[(HA)_2]_{org} \rightleftharpoons [UO_2(NO_3)_2 2(HA)_2]_{org}$	$[UO_2]^{2+}_{aq} + 2[NO_3]^-_{aq} + 2[(HA)_2]_{IL} \rightleftharpoons [UO_2(NO_3)_2 2(HA)_2]_{IL}$	



(a) (b)

Figure 8. Coordination environments of (a) $Sr(NO_3)_2(DCH18C_6)$ in 1-octanol and (b) the $[Sr(DCH18C6)(H_2O)_2]^{2+}$ cation present in $[C_5mim][NTf_2]$. Reprinted with permission from ref 224. Copyright 2002 American Chemical Society.

$UO_2(NO_3)(CMPO)_2$ in the IL phase, supporting a predominantly cation-exchange mechanism for the partitioning. Since $[C_8mim][NTf_2]$ is more hydrophobic than $[C_4mim][PF_6]$, less of the $[C_8mim]^+$ cation leached into the aqueous phase and a smaller amount of $[UO_2]^{2+}$ complex partitioned to the IL phase, resulting in a lower distribution ratio. The distribution of Cs^+ to the BOBCalixC6/$[C_n mim][NTf_2]$ ($n = 2, 3, 4, 6, 8$) system was observed to decrease with increasing chain length of the substituted alkyl group in the IL cation. This effect is consistent with a cation-exchange mechanism. The higher distribution ratios for the shorter-alkyl-chain ILs can be attributed to the ion-exchange capability of the less hydrophobic imidazolium cations.[195]

Jensen et al.[224] investigated the extracting complexes formed by Sr^{2+} together with DCH18C6 in $[C_5mim][NTf_2]$ and 1-octanol. The EXAFS shows that little nitrate was coordinated to the $[Sr(DCH18C6)]^{2+}$ cation in $[C_5mim][NTf_2]$ and that the coordination sites left vacant by the nitrate were occupied by water molecules. ^{15}N NMR and ion chromatography further confirm that the amounts of anion coextracted into the IL were vastly insufficient to produce neutral strontium complexes. The cationic $[Sr(DCH18C6)]^{2+}$ complex became a component of the IL, with its positive charge being balanced by two noncoordinated $[NTf_2]^-$ anions. As revealed in Figure 8, the coordination compounds formed in 1-octanol and in $[C_5mim][NTf_2]$ are different. The extraction mechanism of DCH18C6/$[C_5mim][NTf_2]$ for Sr^{2+} is a cation-exchange mechanism.

Nakashima et al.[198] investigated the extraction of Ce^{3+}, Eu^{3+}, and Y^{3+} into $[C_4mim][PF_6]$ from aqueous solutions using CMPO as an extractant. The extraction does not seem to be influenced by anionic species because extraction efficiency was not affected by HNO_3 concentration in the IL system. They examined the effect of the $[C_4mim]^+$ concentration in the aqueous phase on the extraction in the IL-based system by adding $[C_4mim]Cl$ to aqueous phase as a source of $[C_4mim]^+$. The extraction efficiency of the IL system indeed decreased with increasing $[C_4mim]^+$ concentration. These results support a cation-exchange mechanism.

Shimojo et al.[202] found that the extraction behavior of lanthanides using TODGA in $[C_2mim][NTf_2]$ contrasted markedly with that in isooctane. In the isooctane system, the extractability of lanthanides improved with increasing HNO_3 concentration. In the IL system, the extraction efficiency of lanthanides declined with increasing HNO_3 concentration. To reveal the anionic species effect, influences of H_2SO_4 and HNO_3 on extractability were compared. The anionic species had a great influence on the isooctane system but no obvious influence on the IL system. As for the isooctane system, the extracted complex accompanied a counteranion to form an ion pair. However, the anionic species were not involved in the transfer of lanthanides into ILs. Thus, the cation-exchange mechanism emerges as a convincing extraction mechanism for the IL-based system.

Cyanex 925 (branched trialkylphosphine oxides) is an industrial extractant for rare earths separation. The Sc^{3+} extraction using Cyanex 925 in hexane is following a solvation mechanism. Sun et al.[218] studied the extraction mechanisms of Cyanex 925 for Sc^{3+} in $[C_8mim][PF_6]$. The extraction efficiency of a Cyanex 925/$[C_8mim][PF_6]$ system for Sc^{3+} decreased gradually as $[C_8mim]Cl$ aqueous-phase concentration increased. To investigate whether the chloride ion influences extraction, sodium chloride was used in this study. The result reveals that sodium chloride had little effect on extraction. It is $[C_8mim]^+$ rather than Cl^- in the aqueous phase that restrains extraction; thus, the extraction mechanism of the Cyanex 925/$[C_8mim][PF_6]$ system for Sc^{3+} is a cation-exchange mechanism.

The extraction of La^{3+}, Nd^{3+}, and Eu^{3+} into $[C_4mim][NTf_2]$ using Htta and DCH18C6 was also indicated to be a cation-exchange mechanism.[206] The relationships between logD for Ln^{3+} and the logarithmic initial Htta (DCH18C6) concentration in $[C_4mim][NTf_2]$ reveal that cationic $[Ln(tta)(DCH18C6)]^{2+}$ and $[Ln(tta)_2(DCH18C6)]^+$ can be extracted competitively as ternary complexes. The complexation of tta^- to $[Ln(CE)]^{3+}$ enhanced extraction efficiency, which can be attributed to low-charged and/or hydrophobic complexes; they were preferentially extracted into IL since the mechanism is by cation exchange. The extraction mode of $^{241}Am^{3+}$ from HNO_3 (1.0−3.0 M) medium into the CMPO-TBP/$[C_4mim][NTf_2]$ phase resembles the stoichiometries (i.e., Am/CMPO = 1:3−1:2.4) observed for

TRUEX solvent. However, $^{241}Am^{3+}$ extraction in the IL-based system was followed by obvious IL solubility. The unique solvation ability of IL seems to be responsible for extraordinary extraction of the IL-based system. Because the distribution ratio of $^{241}Am^{3+}$ decreased with an increase in the concentration of $[C_4mim]^+$ in the aqueous phase, the extraction process cannot rule out the possibility of a cation-exchange mechanism.[205]

The extraction of Pu^{4+} from nitric aqueous phase by CMPO in $[C_8mim][PF_6]$ was indicated to be a cation-exchange mechanism. The stoichiometries of extracting complexes were $[Pu(NO_3)(CMPO)]^{3+}$ and $[Pu(NO_3)(CMPO)_2]^{3+}$ when the aqueous acidity was 2 and 1 M, respectively.[219] Similarly, the Pu^{4+} extraction by DCH18C6 in $[C_4mim][PF_6]$ was also indicated to be cation-exchange. The stoichiometry of the extracted cationic complex can be written as $[Pu(CE)_n(NO_3)_2]^{2+}$, where n can be 1 or 2 depending on the acidity of extraction (1 or 2 M HNO_3).[225]

6.3. Solvation Mechanism

The extraction of $[TcO_4]^-$ into $[P_{66614}][NTf_2]$-based solvent systems proceeded via partitioning of a sodium (or ammonium) crown-ether pertechnetate ion pair. The extracted species was stabilized by strong interactions with the constituent ions in the IL solvent, resulting in high distribution ratios for the extracted ions.[215] In contrast to various previously studied IL-based cation extraction systems, facile anion extraction without significant transfer of the IL ions to the aqueous phase was observed.

As mentioned above, the extraction mechanism of the Cyanex 925/$[C_8mim][PF_6]$ system for scandium is indicated to be cation exchange.[218] Unlike $[C_8mim][PF_6]$, $[A336][NO_3]$ behaves not only as diluent but also as extractant for Sc^{3+} extraction. The effect of increasing nitrate ion concentration contributing to an enhanced distribution ratio clearly indicates that extraction in the $[A336][NO_3]$-based system was achieved by a solvation mechanism.[119]

6.4. Multiple Mechanism

In some IL-based extractions, more than two mechanisms operate in the system under different extraction conditions. The mixed extraction mechanism is called a multiple mechanism. As the chain length of the substituted alkyl group in $[C_nmim]^+$ increases, the hydrophobicity of the cation likewise increases. Thus, exchange between the cation and cationic strontium—crown ether complex will be difficult. Using a combination of radiometric, chromatographic, and EXAFS methods, Dietz et al.[226] found that the extraction mechanism of Sr^{2+} transfer from acidic nitrate media into a DCH18C6/$[C_nmim][NTf_2]$ ($n = 5, 6, 8, 10$) system shifted from cation exchange to strontium nitrato-crown ether complex partitioning as the hydrophobicity of the IL cation increased. As for $[C_5mim][NTf_2]$ and $[C_6mim][NTf_2]$, the extraction mechanism was cation exchange. As the alkyl chain length increased, nitrate coextraction became increasingly significant. The extraction mechanism of $[C_8mim][NTf_2]$ revealed a shift from cation exchange to extraction of the neutral complex. For $[C_{10}mim][NTf_2]$, the amount of nitrate extracted was exactly that expected if extraction of the neutral complex is the sole mode of strontium ion partitioning. To determine the generality of the mutiple mechanism mentioned above, Dietz et al.[220] subsequently studied the partitioning of Na^+ between aqueous nitrate media and $[C_nmim][NTf_2]$ containing DCH18C6. The extraction mechanism of the partitioning is believed to take place via as many as three pathways: conventional nitrato complex extraction and/or either or both of two ion-exchange processes. The study reveals that increasing the alkyl chain length of the IL cation (from $[C_5mim]^+$ to $[C_{10}mim]^+$) was insufficient to eliminate the possibility of ion exchange as a mode of metal ion partitioning between the two phases. Dietz et al.[221] also studied the extraction of uranium from nitric acid using TBP into $[C_nmim][NTf_2]$ (n = 5−10). The shape of the acid dependency of uranium extraction into $[C_nmim][NTf_2]$ varied considerably as the alkyl chain length of $[C_nmim]^+$ changed from $[C_5mim]^+$ to $[C_{10}mim]^+$. Shapes of acid dependency and TBP concentration revealed uranium extraction into the $[C_{10}mim][NTf_2]$ involving partitioning of the neutral uranyl—TBP—nitrato complex. As for $[C_5mim][NTf_2]$ and $[C_8mim][NTf_2]$, the partioning changed from a cation-exchange process to a neutral uranyl—TBP—nitrato complex extraction as the aqueous acidity increased.

Xu et al.[59] studied the extraction mechanism of the BPC6/$[C_nmim][NTf_2]$ (n = 2, 4, 6) system for Cs^+ using UV—vis spectroscopy. There was a linear increase of $[C_4mim]^+$ in the aqueous phase with the extraction of Cs^+, which implies some $[C_4mim]^+$ are exchanged from the IL phase to the aqueous phase by Cs^+ or $[BPC6 \cdot Cs]^+$ complexes. In addition, the pure ILs can also extract Cs^+ from aqueous solutions. The extraction of Cs^+ by pure ILs was achieved by exchange between $[C_4mim]^+$ and Cs^+. Accordingly, they proposed a dual extraction mechanism for extracting Cs^+ by the BPC6/$[C_nmim][NTf_2]$ system, that is, via exchange of $[BPC6 \cdot Cs]^+$ complex or Cs^+ by imidazolium ions of ILs.

Chaumont et al. studied the extraction mechanism of Sr^{2+} by 18C6 in $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$ using molecular dynamics.[227] In binary IL—water solutions, the charged complexes $[Sr(18C6)]^{2+}$ mostly partitioned to the aqueous phase, whereas the neutral complexes $[Sr(18C6)(NO_3)_2]$ were more concentrated in the interfacial domain. The aqueous solutions in contact with the ILs contained $[C_4mim]^+$ but almost no $[C_8mim]^+$ ions. The results support a classical extraction mechanism to $[C_8mim][PF_6]$ and an ion-exchange mechanism to $[C_4mim][PF_6]$.

Cocalia et al.[222] studied the extraction of $[UO_2]^{2+}$, Am^{3+}, Nd^{3+}, and Eu^{3+} using dialkylphosphoric or dialkylphosphinic acids from aqueous solutions into $[C_{10}mim][NTf_2]$ and dodecane. The dependence of distribution ratios on the aqueous phase acidity and the extractant concentration showed similar trends for both the $[C_{10}mim][NTf_2]$-based system and the dodecane-based system. Moreover, the metal ion coordination environments in the IL and dodecane were indicated to be identical by EXAFS (Figure 9) and UV—vis spectroscopy measurements. This work reveals a system in which both the biphasic extraction equilibria and the metal coordination environment can be identical in IL and VOC.

The extraction behavior of U^{6+} by a 1.1 M TBP/$[C_4mim][PF_6]$ system was found to be similar to the behavior by a TBP/dodecane system at acidities less than 4.0 M. Distribution ratios for U^{6+} by the TBP/$[C_4mim][PF_6]$ system significantly increased as sodium nitrate was added. A similar trend was also observed for the extraction of U^{6+} by a TBP/dodecane system. Moreover, the stoichiometry of U^{6+} extraction by TBP in IL resembles that by TBP in dodecane, wherein two molecules of TBP are associated with one molecule of uranyl nitrate in the organic phase. As a result, the two systems have the same solvating mechanism.[204]

7. IMPROVEMENT STRATEGY

The perception that all ILs are "green" solvents may lead to inappropriate experimental design and utilization of these chemicals.[228]

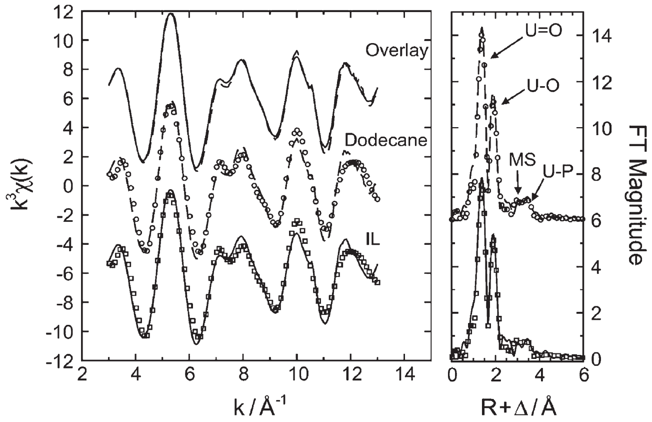


Figure 9. k^3-Weighted uranium L_3-edge EXAFS of the $[UO_2]^{2+}$ $-$HDEHP complex extracted into $[C_{10}mim][NTf_2]$ and dodecane. Adapted with permission from ref 222. Copyright 2005 Royal Society of Chemistry.

The imidazolium ILs, that is, $[C_nmim][PF_6]/[NTf_2]$, have been widely used in IL-based extractions; however, unfortunately work in several research groups has indicated that imidazolium-based ILs had certain characteristics that could adversely impact their utilization in metal ion extractions. Decompositions of ILs at acidic aqueous phases, such as $[PF_6]^-$ hydrolyzing into toxic and corrosive $[PO_4]^{3-}$, HF, POF_3, H_2PO_3F, and HPO_2F_2,[192,197,228] and leaching of $[C_nmim]^+$ to the aqueous phase,[192] are two major obstacles. Moreover, most mechanisms of imidazolium IL-based extraction concern ion-exchange processes.[30a,58,198,202,206,216,218,220,221] The mechanisms release ILs to the aqueous phase as metal ions are extracted. Obviously, the ion-exchange processes result in the loss of the IL phase and contaminate the aqueous phase. To address problems associated with IL-based extractions, various improved methods have been developed and reported.

7.1. Increasing Carbon Chain Length of Ionic Liquid Cation

The imidazolium-type IL with the longer alkyl chains contributes to higher solubility of extractant and lower loss of imidazolium cation to the aqueous phase because of its higher hydrophobicity. However, extraction efficiency is always observed to decrease with increasing carbon chain length of the substituted alkyl group. This observation is consistent with the cation-exchange mechanism. The longer the alkyl chain is, the more hydrophobic the organic cation becomes, and accordingly, the less IL will partition to aqueous phase.[195] The extraction efficiencies of Li^+, Na^+, K^+, Rb^+, and Cs^+ by the DCH18C6$-$$[C_nmim][PF_6]$ (n = 4, 5, 6, 7, 8, 9) system decreased as the 1-alkyl group in the ILs elongated. With the exception of the $[C_6mim][PF_6]$-based system, both the K^+/Cs^+ and the K^+/Rb^+ selectivities increased as the 1-alkyl group of $[C_nmim][PF_6]$ elongated.[121] Luo et al.[196] reported that the distribution ratios for Na^+, K^+, Sr^{2+}, and Cs^+ decreased with an increase of the alkyl chain length of ILs in the DCH18C6$-$$[C_nmim][NTf_2]$ (n = 2, 4, 6, 8) system. Moreover, the Sr^{2+}/Na^+, Sr^{2+}/Cs^+, and Sr^{2+}/K^+ selectivities decreased as the 1-alkyl group of ILs lengthened. Such dependence can be attributed to the ion-exchange capability of the corresponding cations of a specific IL.

7.2. Addition of Sacrificial Cation Exchanger

Because of the cation-exchange mechanism, $[C_4mim]^+$ is lost from the BOBCalixC6$-$$[C_4mim][NTf_2]$ system to the aqueous phase during Cs^+ extraction. When $NaBPh_4$ was added as a sacrificial cationic exchanger in the IL phase, tetraphenylborate anion ($[BPh_4]^-$) formed insoluble compounds with Cs^+ and enhanced extraction of Cs^+. Because Na^+ is very hydrophilic, its transport to aqueous phases from ILs is highly thermodynamically favorable. The addition of $NaBPh_4$ decreased the loss of $[C_4mim][NTf_2]$ by about 24%, and UV spectra of $[C_4mim]^+$ in aqueous phases confirm the substitution of $[C_4mim]^+$ by Na^+ in the ion-exchange process.[195]

7.3. Synergistic Extraction

TBP addition is shown to markedly increase the extraction of Sr^{2+} from acidic nitrate media into $[C_nmim][NTf_2]$ (n = 5, 6, 8, 10) by DCH18C6. This effect can be attributed to the formation of a synergistic adduct between the $Sr^{2+}$$-$DCH18C6 complex and TBP. The magnitude of the synergistic enhancement was shown to depend on the alkyl chain length of the IL cation. As the cation hydrophobicity increased, the synergistic extraction effect diminished. Thus, synergistic effects arising from combinations of neutral extractants are unlikely to be useful as a means of overcoming the decrease in metal ion extraction efficiency that accompanies increased IL cation hydrophobicity.[194]

7.4. Fluorous Ionic Liquid

Incorporation of fluorine atoms into the IL cation is an alternative approach to increase the hydrophobicity of the imidazolium-type IL cation. Heitzman et al.[229] compared the extraction behavior of DCH18C6 for Sr^{2+} in $[F-C_nmim][NTf_2]$ (n = 5, 8, 10) and $[C_nmim][NTf_2]$ (n = 5, 8, 10). The predominant mode of strontium ion transfer from aqueous nitrate media into $[F-C_nmim][NTf_2]$ containing DCH18C6 shifted from cation exchange to strontium nitrato-crown ether complex partitioning as the length of the fluoroalkyl substituent increased. Fluoroalkyl substituents are shown to be only slightly more effective than their nonfluorous analogues at inducing this shift. At the same time, the fluorinated ILs yielded strontium distribution ratios as much as 1 order of magnitude lower than the corresponding $[C_nmim]^+$ salts. Therefore, fluorous ILs appear to offer no compelling advantages over $[C_nmim]^+$ ILs as extraction diluents.

7.5. Addition of Complexing Agent

Adjusting aqueous acidity is a common method for achieving rare earth separation in traditional VOC-based extraction systems. However, the method is unsuitable for imidazolium IL-based extraction because of the loss of IL and the decrease of extraction efficiency at acidic media. Sun et al.[230] reported the selective extraction of Y^{3+} from $Y^{3+}/Er^{3+}/Tm^{3+}/Yb^{3+}$ mixtures into Cyanex923/$[C_8mim][PF_6]$ by adding EDTA to the aqueous phase. Because of the different complexing abilities from EDTA, extractabilities for Yb^{3+}, Tm^{3+}, and Er^{3+} were more suppressed than that for Y^{3+}. Accordingly, the extraction efficiency and selectivity for Y^{3+} could be enhanced in this IL-based system. $[C_8mim]^+$ concentration in the aqueous phase was not affected by the added EDTA. In addition, they[231] used the complexing method with the Cyanex923/$[C_8mim][PF_6]$ system to separate Y^{3+} from Sc^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+} by solid$-$liquid extraction. The lower $[C_8mim]^+$ concentration obtained by solid$-$liquid extraction with the complexing method had two causes: First, the IL loss of solid$-$liquid extraction was lower than that of liquid$-$liquid extraction because of the immobilization effect. Second, the lower extraction efficiencies for other REEs except Y^{3+} resulted in the loss of less $[C_8mim]^+$ because of the cation-exchange mechanism.

7.6. Sustainable Ionic Liquid-Based System

The sustainability of IL is strongly dependent on the purpose of the applied technical processes.[232] Some processes may not concern the release of cation or anion from IL to aqueous phase; thus, an IL-based system can be regarded as sustainable IL-based systems for these particular processes. The partitioning equilibria and coordination environment of $[UO_2]^{2+}$, Am^{3+}, Nd^{3+}, Eu^{3+} by dialkylphosphoric or dialkylphosphinic acids in $[C_{10}mim][NTf_2]$ and dodecane are indicated to be identical. The ability to control metal coordination and partitioning equilibria offers significant opportunities to develop separation systems that overcome the limitations and mechanistic complexity previously found for IL-aqueous systems by the selection of appropriate complexants and ILs.[222]

The extraction of $[TcO_4]^-$ and related tetra-oxo anions from aqueous solutions into $[P_{66614}][NTf_2]$ containing DCH18C6 was indicated to be an ion-pair extraction mechanism. The extracted species was stabilized by strong interactions with the constituent ions in the IL solvent, resulting in high distribution ratios for the extracted ions. These solvents thus combine the favorable solvation properties of the IL component with the propensity for molecular solvents to move toward extraction of neutral species.[215]

The extraction behavior of U^{6+} by a 1.1 M TBP/$[C_4mim]$-$[PF_6]$ system was found to be similar to the behavior by a TBP/dodecane system at acidities less than 4.0 M. Distribution ratios for U^{6+} by the TBP/$[C_4mim][PF_6]$ system increased significantly as sodium nitrate was added. A similar trend has also been observed for the extraction of U^{6+} by a TBP/dodecane system. Moreover, the stoichiometry of U^{6+} extraction by TBP in IL resembled that by TBP in dodecane, wherein two molecules of TBP are associated with one molecule of uranyl nitrate in the organic phase.[204]

To aid in the design of a sustainable IL-based system, the Cyanex 925-$[A336][NO_3]$ system was studied for separating scandium from yttrium and lanthanides. $[A336][NO_3]$ is a functionalized IL. Its cation is an ammonium group; its functional group contributes toward higher extraction efficiency and selectivity. Its anion is a nitrate ion, which improves the stability of $[A336][NO_3]$ in a nitric acid extraction system. Moreover, a solvation mechanism in the system contributed to avoid loss of the IL phase. The Cyanex 925-$[A336][NO_3]$ system was easy to strip, regenerate, and recycle.[119]

8. OTHER SEPARATION METHODS RELATED TO IL-BASED EXTRACTION

8.1. Solid−Liquid Extraction

Dai et al.[233] synthesized silica aerogel using IL as the reaction solvent. They developed sol−gel silica glass materials containing $[C_2mim][NTf_2]$ and DCH18C6 for selective extraction of Sr^{2+}. The partition coefficient of such materials with IL was indicated to be higher than that without IL because the diffusion of crown ether in IL is much faster than in solid silica.[234] $[C_8mim][PF_6]$ was used as the solvent medium and pore templating material during preparation of separation materials using a sol−gel method for Y^{3+} uptake. IL doped into the silica gel matrix provided a diffusion medium for the extractant. The methods resulted in higher removal efficiencies and excellent stability for metal ions separation.[235] To ameliorate mass transfer efficiency of IL base extraction, $[C_8mim][PF_6]$ containing Cyanex923[231] and [A336][CA-100][236] were immobilized on XAD-7 resin for solid−liquid extraction of REEs.

8.2. Microextraction

The goal of microextraction lies in miniaturizing the sample preparation process to simplify laboratory operations, reduce solvent waste, and improve sample utilization. The simultaneous preconcentration of Sm, Eu, Gd, and Dy in uranium dioxide powders with IL solvents using a 1-hydroxy-2,5-pyrrolidinedione (HYD) ligand was studied. HYD showed a significant increase in the preconcentration factor of Sm, Gd, and Dy ions in $[C_6mim][PF_6]$ as compared with CCl_4.[237] In addition, the ligands 1-(2-pyridylazo)-2-naphthol and HYD revealed a synergestic effect for Sm, Eu, Gd, and Dy ions in $[C_6mim][PF_6]$, which contributed to the REEs simultaneous preconcentration using the liquid−liquid microextraction method.[238]

8.3. Supported Liquid Membranes

Supported liquid membranes (SLMs) have attracted attention as a tool to efficiently separate and/or preconcentrate targeted species; however, the commercializations of SLMs are limited due to the instability of the membrane.[239] Kubota et al.[240] recently developed a stable IL-based SLMs using $[C_nmim][NTf_2]$ (n = 4, 8, 12) containing *N*,*N*-dioctyldiglycol amic acid (DODGAA) as the mobile carrier for separation of Y^{3+} and Eu^{3+} from Zn^{2+}. Their research indicated that the extractability of DODGAA for Y^{3+} and Eu^{3+} in IL was higher than that in *n*-dodecane. The quantitative transport of Y^{3+} and Eu^{3+} through the membrane was successfully attained. The membrane can be used to separate Y^{3+} and Eu^{3+} from Zn^{2+}. This was the first application of IL-based SLMs to the separation of metal ions.

8.4. Electrolytic Extraction

Spent nuclear fuel is a valuable source for noble metals. Solvent extractions are important processes used to separate the metals. Electrochemical deposition from the stripping aqueous solutions of solvent extraction is the final step in obtaining pure metal. The electrochemical method is critical to research on ILs in nonaqueous nuclear fuel reprocessing. ILs have been shown to be effective media for electrodepositing metals because of their potentially wide electrochemical windows, high conductivity, and the high solubility of metal ions.[22a,241]

8.4.1. Alkali Metal and Alkaline-Earth Metal. Chen et al.[242] investigated the electrochemistry of cesium in tributylmethylammonium bis(trifluoromethylsulfonyl)amide ($[Bu_3MeN][NTf_2]$). Bulk deposition experiments conducted at a rotating mercury film electrode gave an average recovery of 97% of the electrodeposited cesium. The method can be used to strip the extracted Cs^+ from the IL. The deposition of Cs^+ and Sr^{2+} extracted by BOBCalixC6 and DCH18C6 in $[Bu_3MeN][NTf_2]$ was indicated to be about 90%. Stoichiometries of Cs^+ and Sr^{2+} extracted by BOBCalixC6 and DCH18C6 in $[Bu_3MeN][NTf_2]$ were determined using cyclic staircase voltammetry.[243]

Tsuda et al.[244] investigated the effects of water and oxygen on the electrochemical processing step for the recovery of Cs^+ extracted into $[Bu_3MeN][NTf_2]$ or $[MePrPip][NTf_2]$ containing BOBCalixC6 from simulated aqueous tank waste. The entire treatment cycle for the removal of Cs^+ from tank waste using a hydrophobic IL can be carried out in an open cell, provided that the cell is sparged with dry N_2 (Figure 10).

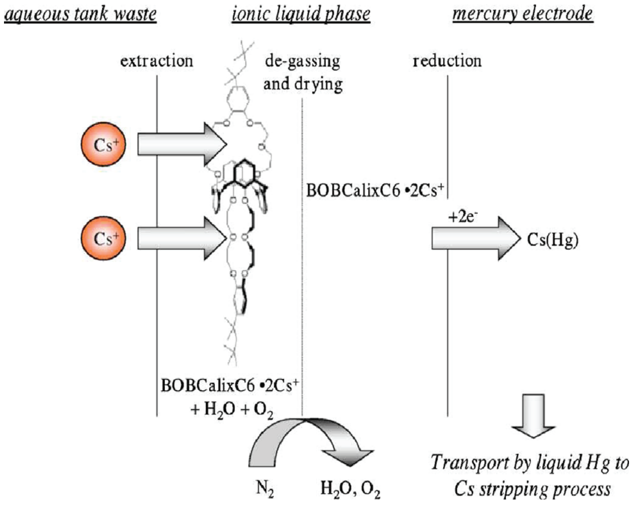


Figure 10. Overall cesium extraction and recovery cycle in [Bu_3MeN]-[NTf_2] + BOBCalixC6. Reprinted with permission from ref 244. Copyright 2006 The Electrochemical Society.

Chen et al.[245] studied the extraction and electrodeposition of Sr^{2+} and Cs^+ from aqueous solutions using DCH18C6 and BOBCalixC6 in ILs (i.e., [C_3mim][NTf_2], [C_4mim][NTf_2], [Bu_3MeN][NTf_2], and [BuMePy][NTf_2]). [Bu_3MeN][NTf_2] was the best choice among the studied ILs because it can provide a sufficiently negative limit of potential for electrodepositing coordinated Sr^{2+} and Cs^+ ions. To obtain successful electrodeposition, the anions contained in the aqueous solutions should be exchanged with halide ions because some particular reducible anions such as nitrate may interfere with the electrodeposition. Moreover, the dissolved oxygen and moisture in IL from the extraction step should be removed. Otherwise, the electrodeposition process will be inhibited because both oxygen and water reduce at a more positive potential than the coordinated Cs^+ and Sr^{2+} ions, respectively.

Giridhar et al.[246] developed an extraction-cum-electrodeposition method for decontaminating palladium from other fission products using an [A336]Cl/chloroform system. Controlled potential electrolysis of the organic phase loaded with palladium resulted in palladium metal, which does not entrap fission products such as ^{137}Cs, ^{90}Sr, and ^{154}Eu. The method was also studied for U^{6+} extraction and recovery using a TBP/[C_4mim]-[NTf_2] system. The [C_4mim][NTf_2] performs both as diluent for TBP and as electrolytic medium for deposition of uranium oxide. The clean organic phase can be recycled after electrodeposition. The method is believed to reveal some advantages: it eliminates several complex processing steps involved in the fabrication of UO_2, minimizes the generation of secondary wastes, and lowers the risk in handling radioactive raffinate.[247]

8.4.2. Rare Earths and Actinides. The absorption spectra of [C_4mim]$_2$[UCl_6] and [$MeBu_3N$]$_2$[UCl_6] in [C_4mim][NTf_2] and [$MeBu_3N$][NTf_2] indicate that the octahedral complex $UCl_6{}^{2-}$ is the predominant chemical form of U^{4+} in [NTf_2]$^-$-based ILs. Hexachloro complexes of U^{4+} are stable to hydrolysis in the ILs. Voltammograms of [UCl_6]$^{2-}$ in both ILs reveal several electrochemical systems attributed to the following processes (eqs 4−6):

$$[UCl_6]^{2-} \rightarrow [UCl_6]^{-} + e^{-} \quad (4)$$

$$[UCl_6]^{2-} + e^{-} \rightarrow [UCl_6]^{3-} \quad (5)$$

$$[UCl_6]^{2-} + e^{-} + x[NTf_2]^{-} \rightarrow [UCl_6(NTf_2)_x]^{(3+x)-} \quad (6)$$

Uranium redox potential values depend strongly on the IL cation. The ILs cannot be considered as inert solvents with respect to An^{4+}-hexachloro complexes.[186] Bhatt et al.[248] reported the electrochemical properties of group 15 quaternary alkyl bistriflimide salts, [$(Me)_4X$][NTf_2] (where X = N, P, or As) for electrodeposition of europium. They studied the voltammetric behavior of [$Th(NTf_2)_4(HNTf_2)$]·$2H_2O$ in [Me_3BuN][NTf_2]. The results indicate that Th^{4+} was reduced to Th(0) in the IL in a single reduction step. An insoluble product was being formed at the electrode surface, which was attributed to the formation of ThO_2 by reaction with water. A comparison of the E^0 value with those obtained for Th^{4+} reduction in a LiCl-KCl eutectic salt (400 °C), water, and nonaqueous solvents showed that the reduction in [Me_3BuN][NTf_2] was easier to accomplish than that in these other solvents.[249] Electrochemical behavior of U^{6+} in [C_4mim]Cl was studied using cyclic voltammetry, chronopotentiometry, and square wave voltammetry.[250] U^{6+} in [C_4mim]Cl underwent a single-step two-electron-transfer reduction to uranium oxide (UO_2), depositing at a glassy carbon working electrode. Thermal analysis of the uranium oxide deposit obtained by the electrolysis of U^{6+} from [C_4mim]Cl revealed the entrapment of nearly 5% [C_4mim]Cl during electrodeposition.

Ohashi[251] investigated the solubility of UF_4 in ILs and the electrochemical properties of uranium species dissolved into ILs. UF_4 dissolved completely in [C_4mim]Cl by heating at 100 °C in air. The dissolved UF_4 oxidized to U^{6+} species and formed U^{6+} species with mixed ligands of F^- and Cl^-. In the cyclic voltammogram of [C_4mim]Cl solution containing dissolved UF_4, uncoupled reduction and oxidation peaks were observed. The reduction peak corresponded to the reduction of $U^{6+} + e^- \rightarrow U^{5+}$ followed by further reduction to UO_2.

Ikeda et al.[252] reported that the uranyl species $Cs_2UO_2Cl_4$ or $UO_2Cl_2 \cdot nH_2O$ in [C_4mim]Cl exists as [UO_2Cl_4]$^{2-}$. Cyclic voltammograms revealed that [UO_2Cl_4]$^{2-}$ in [C_4mim]Cl reduced quasireversibly to [UO_2Cl_4]$^{3-}$.

Rao et al.[253] studied the dissolution of UO_3, UO_2, and U_3O_8 in protonated [Hbet][NTf_2]. Dissolution of UO_3 in [Hbet][NTf_2] was very rapid, and the saturation solubility of uranium was found to be 15 wt % at 373 K. In contrast, dissolution of UO_2 was sluggish, and it was facilitated only by the oxidation of UO_2 to [UO_2]$^{2+}$. U_3O_8 is insoluble up to 453 K. The differences in solubilities can be used to separate the uranium oxides. The cyclic voltammetry of U^{6+} in the resultant solution indicates a surge in the cathodic peak current from the reduction of U^{6+} to U^{5+}, and the corresponding anodic peak current is observed. Increasing the potential sweeping rate increases the peak current and shifts the peak potential negatively, indicating the irreversible electroreduction of U^{6+} in [Hbet][NTf_2].

Rao et al.[254] revealed the possibility of dissolving tissue paper and other cellulose-based materials containing soluble U^{6+} and Pd^{2+} in [C_4mim]Cl. U^{6+} and Pd^{2+} in the IL solution can be deposited into uranium oxide (UO_2) and metallic palladium. They[255] studied the electrodeposition of Eu_2O_3 in [BuMePy][NTf_2]. The IL was indicated to possess an adequate electrochemical window and extended cathodic stability for the electrodepositing of lanthanides and actinides in metallic form. The electrochemical behavior of Eu^{3+}, Sm^{3+}, and Ce^{3+} in [C_4mim]Cl at a platinum working electrode was studied. The Sm^{3+} and Ce^{3+} underwent a single-step one-electron quasireversible transfer to divalent ion. However, Eu^{3+} reduction resulted in the adsorption of the reduced product Eu^{2+}_{ads} on the electrode.[256]

Bhatt et al.[257] studied the reduction of La^{3+}, Sm^{3+}, or Eu^{3+} to the zerovalent state in $[Me_3BuN][NTf_2]$. The lanthanide cations can be introduced to the IL as the $[NTf_2]^-$ hydrate complexes $[Ln(NTf_2)_3(H_2O)_3]$. The lanthanide in the complexes was shown to be reducible to the metallic state in the IL.

Alkali-metal uranyl chloride ($M_2UO_2Cl_4$, M = Na or Cs) was dissolved in $[C_4mim]Cl$, and the redox behavior of uranyl ion in the IL solution was investigated. Controlled potential electrolysis of U^{6+}-loaded $[C_4mim]Cl$ gave a black deposit, which was characterized to be uranium oxide.[258] Extraction of U^{6+} from nitric acid medium by TOMAC in chloroform was studied. Controlled potential electrolysis of U^{6+}-loaded TOMAC at −1.0 V also gave a black uranium oxide deposit. The results indicate that uranyl ion in the organic phase underwent a single-step, two-electron quasireversible reduction at the working electrode. The system can be exploited for the direct recovery of uranium from spent fuel or from HLLW.[258] Legeai et al.[259] studied lanthanum electrodeposition in ambient atmosphere using $[OMP][NTf_2]$. The IL is indicated to present good properties for lanthanum electrodeposition (i.e., great cathodic stability, low hygroscopy, and low viscosity).

8.4.3. Platinum Group Metals.

Platinum group metals are major fission products. Jayakumar et al.[260] studied the electrochemical behavior of $RhCl_3$ in $[C_4mim]Cl$. Electrodeposition of Pd from coexisting Rh was studied, and a separation factor of 10 was achieved when the deposition was carried out at Pd peak potential. The study indicated that codeposition of Rh seemed to be inevitable during electroseparation of Pd in $[C_4mim]Cl$. Electrochemical behavior of Ru^{3+}, Rh^{3+}, and Pd^{2+} in $[C_4mim][Cl]$ was studied using glassy carbon and stainless steel as working electrodes. The study established the feasibility of using $[C_4mim]Cl$ for the electrochemical recovery of fission platinoids at 373 K.[261]

8.5. Conjugated Ionic Liquid and Supercritical Carbon Dioxide Extraction

Mekki et al.[262] developed a three-step extraction system of water-$[C_4mim][NTf_2]$-$scCO_2$ for extraction of trivalent La^{3+} and Eu^{3+}. The lanthanides were quantitatively extracted from the water phase to $[C_4mim][NTf_2]$ containing fluorinated β-diketones. No synergistic moiety (TBP) or modifier (MeOH) from IL phase to $scCO_2$ phase was needed to reach high extraction efficiencies. A depressurization of $scCO_2$ phase allowed the ligands to be dissolved again in the IL phase for recycle.

Wang et al. showed that uranyl ions in solution in nitric acid can be effectively extracted by $[C_4mim][NTf_2]$ with TBP (Figure 11). Spectroscopic information suggested that the uranyl complex in the IL phase was $[UO_2(NO_3)_2(TBP)_2]$.[263] This uranyl nitrate-TBP complex can be effectively transferred to the $scCO_2$. The results suggest that $[C_4mim][NTf_2]$ may be used to preconcentrate uranium and other actinides from liquids or solids, and back-extract them into $scCO_2$. The IL can be recycled for use after the stripping. The advantage of this approach is that radioactive materials may be removed from a large volume of water into a smaller volume of IL. Then the concentrated radioactive materials can be transferred from IL to $scCO_2$. This would greatly reduce the volume of radioactive materials to be treated by a supercritical fluid process.

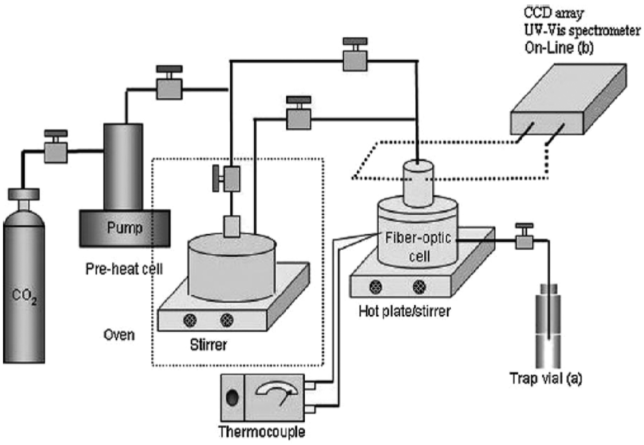


Figure 11. Apparatus for the extraction of $[UO_2(NO)_2(TBP)_2]$ from the IL to $scCO_2$. Products were analyzed either by trapping in hexane for UV/vis and fluorescence spectroscopy (bypass fiber-optic cell, arrangement a) or by an in situ spectroscopic method (arrangement b). Reprinted with permission from ref 263. Copyright 2009 WILEY-VCH Verlag GmbH & Co.

Uranium dioxide can be dissolved in $[C_4mim][NTf_2]$ containing TBP-HNO_3 with a molar ratio of UO_2^{2+}/TBP = 1:2. The dissolved uranyl species can be transferred to the sc-CO_2 phase. The extracted uranyl species in sc-CO_2 were indicated to be $UO_2(TBP)_2(NO_3)_2$ and $UO_2(TBP)_2(NO_3)_2 \cdot HNO_3$. The IL-sc-$CO_2$ coupled dissolution/extraction process may provide a new “green” technique for treating uranium-containing wastes.[264]

9. CONCLUSIONS AND OUTLOOK

Research on the nuclear fuel cycle is essential to the development of advanced nuclear energy. Recent studies show that the application of ILs to the advanced nuclear fuel cycle is full of opportunities and challenges. Applying ILs is not a matter of simply replacing VOCs with ILs. Current work in separation chemistry[265] and radiation chemistry[266] have revealed that solvent systems containing ILs, with their unique properties, show some intriguing differences over conventional systems. These differences are contributing to the designs of highly efficient and radiolytically robust separations systems for the advanced nuclear fuel cycle. Although the status of ILs as “green” solvents has been questioned, their designability makes them full of potential. Not only can they be used as diluents, ILs can be highly efficient extractants. Excluding binary, ternary, and higher order mixtures, more than 10^{18} ILs can be prepared through different combinations of substitution patterns and ion choices.[267] Every year, many papers and patents on ILs are published and the numbers of commercial available ILs are increasing. The immensity of the fundamental research provides powerful support for a potential IL-based separation technology for the advanced nuclear fuel cycle. The following are the next steps to separation technology success.

ILs as related to the NFC must be thoroughly understood. To meet the technology requirement, the following IL factors need to be considered comprehensively: cost, purity, acidity stability, radiation stability, viscosity, solubility, density, electrical conductivity, electrochemical windows, extraction efficiency, selectivity, extraction mechanism, stripping ratio, and recycling.

Because IL types are so numerous and influenced by so many factors when used for extraction, experimentally measuring all ILs for extraction is unfeasible. Chemoinformatics methods seem to be the most effective strategy for dealing with these thorny issues and should be pursued.[268] Methods important for the design of IL-based separations processing include quantitative structure−property relationships,[154,269] molecular dynamics simulations,[270] database,[271] combinatorial chemistry,[272,273] and computer-aided molecular design.[274]

As IL-based extraction methods have developed, functionalized ILs have become the focus, and work on functionalized ILs needs to continue. The functional groups in both cations and anions of functionalized ILs not only enhance their extractability and selectivity but also provide them with excellent physicochemical properties for extraction. Although FILs based on incorporation of functional groups into the cation structure of ILs have been extensively investigated, synthesizing FILs through functionalization of the anion structure of ILs is less investigated. Using IL anions as a vehicle to introduce functional groups has an advantage in development of highly efficient extractants for metal ions from the perspective of Coulombic interactions.

Recent progress in dynamic combinatorial chemistry has resulted in a number of powerful methodologies for synthesis of highly effective receptors for small molecules.[275] Morrow and her co-workers have successfully applied this ligand synthesis strategy to searching of selective extractants in traditional solvent extraction.[276] The application of the dynamic combinatorial chemistry in tailoring IL-based extraction systems may lead to further enhancement of both extraction efficiencies and extraction selectivities for ILs.

More protocols should be designed for novel, highly efficient, environmentally friendly separations based on the advantages of ILs. One of the key properties associated with ILs is their wide electrochemical windows. There are enormous potentials in utilizing ILs for separation of fission products based on electrorefining or electrochemical deposition.[34f] Furthermore, coupling traditional solvent extraction with electrochemical separation and stripping is possible with ILs. These hybrid processes could considerably enhance separation efficiencies and reduce footprints associated with separation processes.

So far most of the work on IL-based extraction involves extraction thermodynamics. Extraction kinetics and interfacial activity studies are important means for developing IL-based extraction. Extraction kinetics affords the possibilities for quantitative separation of metal ions that cannot be separated when at equilibrium. The investigation of extractant interfacial activities can offer important parameters for controlling extraction reactions and mass transport kinetics and will improve our understanding of IL-based extractions.

Small-scale industrial tests of IL-based extraction should be undertaken. Such tests will reveal more challenges, deepening our understanding and directing us in the design of rational IL-based separation systems for the advanced NFC.

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Huimin Luo was born in Shanghai, China, in 1962. She obtained her B.S. degree (1982) and M.S. degree (1986) in Chemistry at Zhejiang University, Hangzhou, China. In 1988, she moved to the United States and obtained her Ph.D. (1992) in organic chemistry at the University of Tennessee, Knoxville, under the direction of Prof. J. L. Adcock. She was the recipient of U.S. DOE Alexander Hollaender Distinguished Postdoctoral Fellowship (1993). She worked as a postdoc with Dr. F. F. (Russ) Knapp in Nuclear Medicine Program at Oak Ridge National Laboratory (ORNL) before she joined Rhone-Poulenc-Rorer (RPR, now Sanorfi Aventis) Pharmaceutical company as a Research Scientist. In 1999, she moved back to ORNL and has worked as a Senior Research Staff Member. She has published 2 book chapters, over 70 peer-reviewed journal papers, and holds

3 U.S. patents. Her present research interests focus on ionic liquids, solvent extraction, organic synthesis, and nuclear chemistry.

Sheng Dai was born in Wenzhou, China (1963). He obtained his B.S. degree (1984) and M.S. degree (1986) in Chemistry at Zhejiang University, Hangzhou, China. He moved to the United States in 1986 and obtained his Ph.D. (1990) in physical chemistry at University of Tennessee, Knoxville, under the direction of Prof. T. F. Williams. He started his research career at Oak Ridge National Laboratory (ORNL) as a Postdoctoral Fellow under the joint supervision of the late Dr. J. P. Young and late Prof. G. Mamantov in the field of molten salts and high-temperature spectroscopy. He is currently a Corporate Fellow and Group Leader in Chemical Sciences Division at ORNL and Professor of Chemistry at the University of Tennessee. He has published over 300 peer-reviewed journal papers and holds 13 U.S. patents. His current research interests include ionic liquids, porous carbon and oxide materials, nanoparticles, advanced materials and their applications for energy storage as well as catalysis by nanomaterials.

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ABBREVIATIONS

[A336]$^+$	tricaprylmethylammonium cation
An	actinide
[BETI]$^-$	bis(perfluoroethanesulfonyl)imide anion
[BF$_4$]$^-$	tetrafluoroborate anion
[BOB]$^-$	bis(oxalato)borate anion
BOBCalixC6	calix[4]arenebis(*tert*-octylbenzo-crown-6)
BPC6	bis(2-propyloxy)calix[4]crown-6
[BPh$_4$]$^-$	tetraphenylborate anion
[Bu$_3$MeN]$^+$	tributylmethylammonium cation
[BuMe$_3$N]$^+$	butyltrimethylammonium cation
[BuPy]$^+$	1-butylpyridinium cation
[C18Iq]$^+$	*n*-octadecylisoquinolinium cation
CE	crown ether
[C$_n$mim]$^+$	1-alkyl-3-methylimidazolium cation
[C$_n$mPyrr]$^+$	*N*-alkyl-*N*-methylpyrrolidinium cation
Cyanex 925	branched trialkylphosphine oxides
18C6	18-crown-6
DB18C6	dibenzo-18-crown-6
DIAMEX	diamide extraction
DIDPA	diisodecylphosphoric acid
Dtb18C6	4,4′-(5′)-di-(*tert*-butylcyclohexano)-18-crown-6
DTPA	diethylene triamine pentaacetic acid
EDTA	ethylenediaminetetraacetic acid
[Eeim]$^+$	1-ethyl-3-ethylimidazolium cation
EXAFS	extended X-ray absorption fine structure
[FAP]$^-$	tris(perfluoroetheyl) trifluorophosphate anion
HBET	protonated betaine
HDEHP	bis(2-ethylhexyl) phosphoric acid
HLLWs	high level liquid wastes
HYD	1-hydroxy-2,5-pyrrolidinedione
Im	imidazolium
[ImP]$^+$	diethyl-2-(3-methylimidazolium)ethyl-phosphonate cation
Ln	lanthanide
[MDEGSO$_4$]$^-$	2-(2-methoxyethoxy)ethyl sulfate anion
[MePrPip]$^+$	*n*-methyl-*n*-propylpiperidinium cation
[Mppyr]$^+$	*N*-methyl-*N*-propylpyrrolidinium cation
NFC	nuclear fuel cycle
[N(CN)$_2$]$^-$	dicyanamide anion
[NfO]$^-$	nonafluorobutanesulfonate anion
[NTf$_2$]$^-$	bis(trifluoromethylsulfonyl)amide anion
[P$_{66614}$]$^+$	trihexyl(tetradecyl)phosphonium cation
[PF$_6$]$^-$	hexafluorophosphate anion
[PP$_{13}$]$^+$	*N*-methyl-*N*-propylpiperidinium cation
PUREX	plutonium−uranium extraction
REEs	rare earth elements
[R^{1}R^2 MeIm]$^+$	1-R^1-2-R^2-3-methylimidazolium cation
[SCN]$^-$	thiocyanate anion
scCO$_2$	supercritical CO$_2$
SLMs	Supported liquid membranes
SREX	strontium extraction
TALSPEAK	trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous komplexes
TBP	tributyl phosphate
[TEPP]$^+$	triethyl-*n*-pentylphosphonium cation
[TEPA]$^+$	*N,N,N*-triethyl-*N*-pentylammonium cation
[TfO]$^-$	trifluoromethansulfonate anion
[Tmpa]$^+$	*N,N,N*-trimethyl-*N*-propylammonium cation
TOMAC	*N,N,N*-trioctyl-*N*-methylammonium chloride
[TOS]$^-$	tosylate anion
[TFPB]$^-$	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion
TRUEX	transuranic extraction
[TS]$^-$	thiosalicylate anion
TSILs	task-specific ionic liquids
FILs	functionalized ionic liquids
VOCs	volatile organic compounds

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