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Extraction of Cesium Ions from Aqueous Solutions Using Calix[4]arene-bis(*tert*-octylbenzo-crown-6) in Ionic Liquids

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Solvent extraction of cesium ions from aqueous solution to hydrophobic ionic liquids without the introduction of an organophilic anion in the aqueous phase was demonstrated using calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6) as an extractant. The selectivity of this extraction process toward cesium ions and the use of a sacrificial cation exchanger ($NaBPh_4$) to control loss of imidazolium cation to the aqueous solutions by ion exchange have been investigated.

Ionic liquids (ILs) are attracting increased attention worldwide because of the perceived environmental benefits.[1−3] Ionic liquids have been defined as salts which melt below 100 °C, and many are known that melt below room temperature. The most commonly studied classes of ILs (Figure 1) are cationic N-alkylated nitrogen heterocycles, such as *N*,*N*-dialkylimidazolium or *N*-alkylpyridinium ions.[1−4] These organic cations, which are relatively large and asymmetric, as compared to simple inorganic cations, account for the low melting points of the salts. A variety of anions can be utilized to form ILs, including $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, or other complex anions.[1,2]

Many of these ILs, unlike many conventional molecular solvents currently in use, are nonflammable, chemically tunable, and exert no detectable vapor pressure. These unique features have led to their designation as "designer solvents" for use as potential replacements for noxious volatile organic compounds (VOCs), which can contribute to air pollution and health problems for process workers.[1] The applications of ILs as solvents for various catalytic reactions have been extensively explored,[1−6] as have ILs for membrane-based separation of CO_2,[4,5] sensing volatile organic vapors,[6] and synthesizing novel materials.[7,8] Several reviews and monographs have recently appeared, providing general overviews of the subject.[1−3]

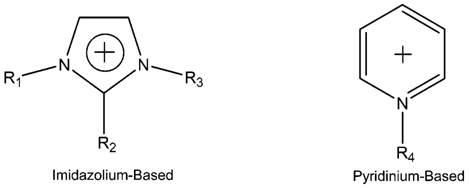

Figure 1. Strctures of two most common ionic liquid cations.

In contrast to higher-temperature inorganic molten salts, examples of ILs are known that are hydrophobic[9] and, thus, form a biphase with aqueous phases yet still retain ionic characteristics.[1] These novel dual properties of hydrophobicity and high ionic character have led to the investigation of ILs as unique separation media for IL/aqueous solvent extractions.[10−14] Large distribution coefficients (D_M) for the extraction of metal ions from aqueous solutions to ILs containing complexing extractants have been observed. For example, whereas conventional solvent extraction

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of Sr^{2+} using *cis*-dicyclohexano-18-crown-6 can deliver practical D_M values of <1, using ILs as extraction solvents delivered values of D_M on the order of 10^4.[13] The enhanced distribution coefficients can be attributed to the unique solvation properties of ILs for ionic species, with synergistic ion-exchange processes playing an important role.[10b,12]

The solvation processes of these ionic complexes by conjugated ions in ILs are much more favorable than those in conventional solvents.[13] The successful extraction of Sr^{2+} by *cis*-dicyclohexano-18-crown-6 also indicates that any interaction between imidazolium cations of the ILs and the crown is limited and weaker than the interaction between Sr^{2+} and the crown ether. Imidazolium compounds have been known to interact with dibenzo-18-crown-6 in the solid state.[15,16]

^{137}Cesium is a major fission product in spent nuclear wastes.[17−21] Its removal from these wastes is a key part of waste remediation strategies.[21] The selective removal of cesium ions from nuclear wastes is essential to the safe and cost-effective production of associated waste forms for superior postclosure performance in a repository. Cesium ion extraction using crown ethers has been investigated by McDowell[17] and Horwitz,[18] as well as many others.[19] McDowell showed that the distribution ratio of cesium ion (D_{Cs}) from 0.1 M nitric acid solutions could be on the order of 10^2 when the crown ether bis(*tert*-butylbenzo)-21-crown-7 was used in combination with the organophilic anion didodecylnaphthalenesulfonic acid (in toluene solution).

In the past decade, mono- and bis-crown-6 derivatives of calix[4]arenes in the 1,3-alternate conformation have been shown to possess both extremely high extractive strength for cesium and excellent (generally exceeding 10^4) selectivity for cesium ion over sodium ion.[20] Without the aid of an organophilic anion, these calixarene crown ethers are capable of extracting cesium from both acidic and alkaline media with distribution ratios generally exceeding unity, and sometimes as high as 100, depending on the concentration of competitive cations (e.g., K^+) in the aqueous solution, the concentration of the calixarene crown, and the polarity of the diluent. By comparison, under the same conditions, the crown ether bis(*tert*-butylbenzo)-21-crown-7 gives D_{Cs} values at least 2 orders of magnitude lower.[20b] A lipophilic derivative of a calix[4]-bis-crown-6, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6), as seen in Figure 2, is currently being investigated for solvent extraction processes for removing cesium ion from alkaline and acidic tank waste.[21,22]

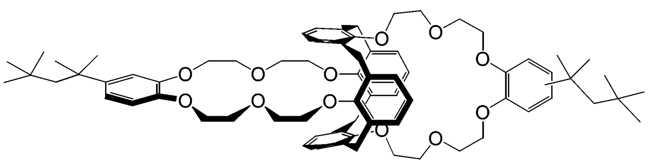

Figure 2. Structure of BOBCalixC6.

The use of calixarene crown ethers for cesium ion extraction in IL media may greatly increase the cesium distribution ratio. Thus, in this report, we extend our investigation of the solvent extraction and ion exchange properties of ILs to the extraction of cesium ions, utilizing the cation receptor BOBCalixC6. These studies are directed primarily toward acquiring an understanding of the mechanism of extraction in the complex IL solvents and secondarily to determining if a Cs-removal technology utilizing ILs is possible.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and solvents were reagent grade and were used without further purification unless noted otherwise. The ILs used in this work were 1-C_n-3-methylimidazolium ($C_n$mim$^+$) bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-), where $C_n = C_2$(ethyl), C_3(*n*-propyl), C_4(*n*-butyl), C_6(*n*-hexyl), or C_8(*n*-octyl). These ILs were synthesized via metathesis reactions as described in the literature.[9,23] The details on synthesis and characterization are given in the Supporting Information Section. Aqueous solutions were prepared using deionized (DI) water with a specific resistance of 18.0 MΩ-cm or greater. BOBCalixC6 was obtained from IBC Advanced Technologies (American Fork, UT) and was used as received (97% stated purity). ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with a Bruker Avance DRX 400 NMR spectrometer. Concentrations of Cs^+ were determined via a Dionex LC20 ion chromatograph equipped with an IonPac CS 12 analytical column. The solubility in water was determined by combining 0.5 mL of IL and 5 mL DI water and shaking for 60 min in a vibrating mixer. A 0.5-mL aliquot of the aqueous phase was removed and diluted to 5 mL with DI water. The absorbance at 211 nm was measured using a Varian UV−vis−NIR spectrometer (model 5000). The solubility of each IL in water was calculated by the comparison of the measured absorbance with that obtained from dissolving a known amount (2−20 mg) of IL in 5 mL of DI water. The water content of the ILs was measured using a Metrohm 652 KF coulometer.

Tracer studies were conducted at The University of Alabama with the use of ^{137}Cs purchased from Amersham (Arlington Heights, IL) as the chloride salt and used as CsCl in 0.6 M HCl. An in-house ^{14}C-labeled 1-butyl-3-methylimidazolium bromide ([C_4mim]Br) was made through the reaction of 1-methylimidazole (Aldrich) with ^{14}C 1-bromobutane (American Radiolabeled Chemicals, St. Louis, MO), where only the β carbon is ^{14}C-labeled. The ^{14}C-labeled [C_4mim]Br was diluted in water and spiked into a sample of [C_4mim][NTf_2]. All gamma counting was conducted on a Packard Cobra II automated gamma counter with a through-bore 3-in. NaI(Tl) crystal, and beta counting was done on a

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Packard 1500 TR liquid scintillation counter with Packard Ultima Gold scintillation cocktail.

Extraction Experiments. The extraction experiments conducted at ORNL were performed in duplicate for each IL by contacting 1 mL of IL containing various concentrations of BOBCalixC6 with 10 mL of Cs^+ aqueous solution (2.5 mM) for 60 min in a vibrating mixer. After centrifugation, the upper aqueous phase was separated, and the concentration of Cs^+ was determined by ion chromatography.

Radiotracer extraction experiments conducted at The University of Alabama were performed in duplicate, and errors between duplicate runs were within 5%. The distributions were conducted in glass vials with 0.5 mL of IL with variable BOBCalixC6 concentrations and 5 mL of 2.5 mM $CsNO_3$. The solutions were vortexed for 90 s, followed by centrifugation of 90 s, and were repeated twice. Equal volumes of both phases were removed, and radiochemical counting was conducted.

The use of UV spectra could not confirm the mass balance of the imidazolium cation and the distribution of $[C_4mim]$ between the IL and aqueous phases. Thus, the ^{14}C-labeled $[C_4mim]Br$ was used to confirm the UV data. Through the use of the radio-labeled IL, the mass balance of the system was also confirmed.

RESULTS AND DISCUSSION

Extraction Results: The distribution of cesium at various concentrations of BOBCalixC6 (Table 1 and Figure 3) in the ILs used here are high. The only exception is for $[C_2mim][NTf_2]$ at high BOBCalixC6 concentration, for which the solubility of BOBCalixC6 is limited to $\sim 10^{-2}$ M. This difference in solubility of BOBCalixC6 can be attributed to the hydrophobic interaction (or lack thereof) between the alkyl groups of the imidazolium cations and the BOBCalixC6. The longer alkyl groups interact more favorably with the hydrophobic BOBCalixC6, leading to higher solubilities.

The distribution coefficients when using ion chromatography for extraction of Cs^+ are defined in eq 1 as

$$D_{\mathrm{Cs}} = \frac{(C_{\mathrm{i}} - C_{\mathrm{f}})}{C_{\mathrm{f}}} \frac{\text{volume of aqueous phase}}{\text{volume of IL phase}} \tag{1}$$

where C_i and C_f represent the initial and final concentrations of Cs^+ in the aqueous phase. The distribution ratio is calculated by the above equation, since only the aqueous phase is measured and a volume ratio is needed in the calculation to account for the difference in volume between the two phases. Thus, a distribution ratio for Cs^+ greater than 1 ($D_{Cs} > 1$) represents an overall preference of Cs^+ to the IL phase. The values of D_M were measured in duplicate with uncertainty within 5%.

Radiotracer distribution ratios were calculated using eq 2.

$$D_{\mathrm{Cs}} = \frac{[\mathrm{CPM}]_{\mathrm{IL}}}{[\mathrm{CPM}]_{\mathrm{aq}}} \tag{2}$$

Both phases were counted radiochemically using equal volumes.

Table 1. Distribution Ratios (D_{Cs}) between the ILs and 2.5 mM $CsNO_3$

[BOBCalixC6] (mM)	C_n in $[C_nmim][NTf_2]$						
	ethyl C_2[a]	propyl C_3	butyl C_4	butyl[b] C_4	hexyl C_6[c]	octyl C_8[c]	$CHCl_3$[c]
0	0.084	0.055	0.024	0.19	ud	ud	ud
1.00	1.61	1.36	0.77	0.95	0.56	0.45	ud
3.40	4.68	3.90	3.67	2.92	3.20	2.50	ud
7.71	15.3	14.6	13.8	11.7	11.5	8.10	ud
13.6	nm	137	131	63.8	57.4	17.9	0.034

[a] nm: not measured because concentration of BOBCalixC6 could not be reached. [b] Work conducted using radiotracer technique. Although there are differences between the data obtained via ion chromatography and radiotracer, the general trends are identical. [c] ud: undetectable via ion chromatography.

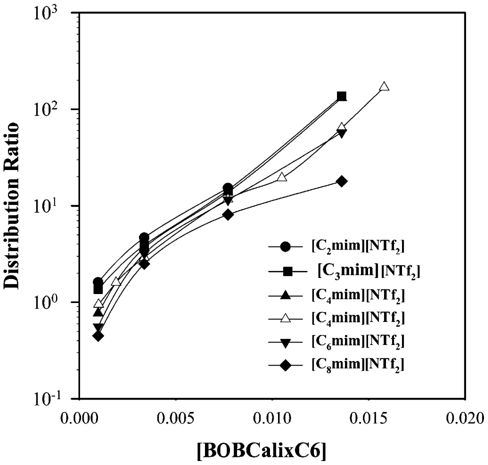

Figure 3. Dependence of D_{Cs} on the concentration of BOBCalixC6 in the IL phase. The data labeled in the closed symbols are from ORNL, and those in the open symbol are from UA.

As seen in Table 1, the D_{Cs} values to the ILs in the absence of an extractant are very low. The small amount of Cs^+, which does partition into the ILs, correlates with the observed hydrophobicities of the IL organic cations.[10] The hydrophobicity is also inversely related to the solubility of the corresponding 1-alkyl-3-methylimidazolium cation ($[C_nmim]^+$) in the aqueous phase and, thus, its ion-exchange capability. Because $[C_2mim]^+$ is the most hydrophilic cation studied here and is exchangeable with metal ions, the distribution coefficient of Cs^+ to $[C_2mim][NTf_2]$ is the largest for the ILs in the series tested. Accordingly, the selectivity of this solvent is dominated by the hydrophobicity of the metal ions extracted (i.e., their Hofmeister selectivity).[24,25]

As seen in Table 1, the distribution coefficients (D_{Cs}) of Cs^+ from water to ILs with BOBCalixC6 strongly depend on the concentration of BOBCalixC6 in the ILs and increase with the concentration of the extractant. This observation is very similar to that noted in the extraction of Sr^{2+} with *cis*-dicyclohexano-18-crown-6 (DCH18C6) in ILs, indicating that the complexation of Cs^+ plays a key role in the partitioning processes.[14]

From infinite dilution distribution studies as a function of nitric acid concentrations in the aqueous phase, at $[HNO_3] \leq 0.1$ M, BOBCalixC6 shows virtually quantitative extraction of cesium. At acid concentrations >0.1 M, an acid dependency occurs, lowering the distribution ratio, as shown in Figure 4. A ligand dependency from 1 M HNO_3 of 1:1 was calculated as illustrated in Figure 5. It

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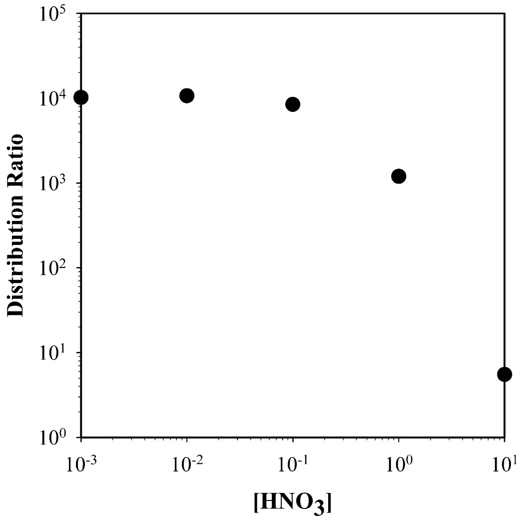

Figure 4. Extraction of cesium at trace level concentrations (“infinite dilution”) into $[C_4mim][NTf_2]$ containing BOBCalixC6 at 7.71 mM as a function of nitric acid concentration.

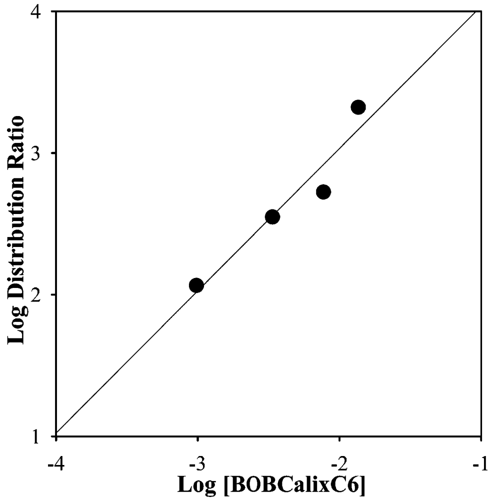

Figure 5. Ligand dependency of BOBCalixC6 in $[C_4mim][NTf_2]$ from 1 M HNO_3. Slope = 1.004; $R^2 = 0.928$.

is known that one cesium in each crown cavity can complex two cesium atoms per BOBCalixC6,[27] but at infinite dilution (that is, with cesium concentrations below picomolar), the 1:1 monocomplexed BOBCalixC6 is favored.

The distribution of Cs^+ to the IL phase was observed to decrease with increasing chain length of the substituted alkyl group (R) in the organic cation of the IL. This observation is consistent with a mechanism that includes ion-exchange during the extraction. The longer the alkyl chain is, the more hydrophobic the organic cation becomes, and accordingly, the less the IL will partition to the aqueous phase.[26]

Selectivity. The selectivity for Cs^+ was investigated from aqueous solutions containing competitive Na^+, K^+, and Sr^{2+} ions in contact with BOBCalixC6-loaded $[C_4mim][NTf_2]$. The selectivity coefficient for Cs^+ in the presence of competitor cations can be obtained from the ratios of the D_{Cs} values to the corresponding distribution coefficients of the competitive ions.

Table 2. Selectivity of $[C_4mim][NTf_2]$ Extraction Phases Containing BOBCalixC6

[BOBCalixC6] (mM)	aqueous phase[a]	D_{Cs}	D_K	D_{Na}	D_{Sr}	D_{Cs}/D_K
1.06	$Cs^+ + K^+ + Na^+$	3.60	0.239	~0		15.1
	$Cs^+ + K^+$	3.51	0.890			3.94
	$Cs^+ + K^+ + Sr^{2+}$	4.67	1.05		~0	4.45
7.96	$Cs^+ + K^+ + Na^+$	371	7.00	~0		53.0
	$Cs^+ + K^+$	228	8.08			28.2
	$Cs^+ + K^+ + Sr^{2+}$	576	8.39	~0	~0	68.7
14.1	$Cs^+ + K^+ + Na^+$	572	37.7	~0		15.2
	$Cs^+ + K^+$	289	48.1			5.98
	$Cs^+ + K^+ + Sr^{2+}$	1138	43.1		~0	26.4

[a] The initial concentration of each ion in aqueous phase was 0.77 mM.

Table 2 shows the competitive extraction results for Cs^+ in the presence of Na^+, K^+, and Sr^{2+}. The distribution coefficients for Na^+ and Sr^{2+} using BOBCalixC6 in $[C_4mim][NTf_2]$ were too small to be detected by ion chromatography. This observation is consistent with what has previously been observed for BOBCalixC6 and related calixarene-crown ethers in conventional solvents.[20b,22,27]

Coextraction of K^+ along with Cs^+ has been observed, however, using BOBCalixC6 in conventional solvents.[21] The concomitant extraction of K^+ along with Cs^+ is also observed in the studies reported here (Table 2). The selectivity coefficients determined under various conditions range from ~3.94 to ~68.7, which are lower than the selectivities of ~220 seen in organic solvents, such as 1,2-dichloroethane.[27] The lower selectivity of cesium over potassium may be attributable to the greater polarity of the ionic liquid than 1,2-dichloroethane (dielectric constant 10.19 at 25 °C).

Effects of Extractable Counteranions and Addition of the Sacrificial Ion Exchanger $NaBPh_4$. Table 3 shows the D_{Cs} values as a function of the type of counteranion present for Cs^+. From these data, it is clear that the distribution coefficients do not change significantly with different anions at low concentrations of BOBCalixC6. At BOBCalixC6 concentrations of 13.8 mM, the D_{Cs} values for $CsNO_3$ and CsOAc (OAc = acetate) are greater than that for CsCl. However, the distribution coefficient for CsCl is the greatest at 20.0 mM BOBCalixC6.

This negligible dependence of the D_{Cs} values on a counteranion can be partially rationalized by two models: (1) ion-exchange or (2) similar anion solubilities in the ILs. On the basis of the ion-exchange model, only cations are involved in the extraction process. Accordingly, the counteranions have little effect on the D_{Cs} values. The second model requires similar solvation properties of Cl^-, NO_3^-, and OAc^- in ILs. From the present experiments, it is not yet clear which is the dominant factor.

Using an ion-exchange model, imidazolium cations are lost from the IL to the aqueous phase during partitioning of metal cations from the aqueous phase to the IL. Thus, the addition of a sacrificial cationic species (e.g., Na^+, H^+) to the IL phase that will preferentially transfer to the aqueous phase should reduce the loss of imidazolium cations. A sacrificial cation in the IL that has no affinity toward BOBCalixC6 and that is more hydrophilic than the IL's imidazolium cation should result in an enhancement of D_{Cs}.

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Table 3. The Effects of Extractable Counteranion on the Distribution Ratios (D_{Cs}) from $[C_4mim][NTf_2]$ Phases Containing BOBCalixC6 with and without $NaBPh_4$[a]

	[BOBCalixC6] (mM)							
	7.71		10.0		13.8		20.0	
anion	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M
NO_3^-	10.9	9.76	22.4	21.9	97.6	92.7	629	608
Cl^-	12.2	11.4	22.6	22.6	75.3	66.6	956	940
OAc^-	12.8	13.4	24.9	22.6	120	85.4	925	798

[a] The initial aqueous concentration of Cs^+ was 2.5 mM with the specified anion. The solubility of $NaBPh_4$ is also dependent on the water contents of the original ILs.

Table 4. Loss of RTIL Calculated from UV Spectra[a]

	[BOBCalixC6] (mM)							
	7.71		10.0		13.8		20.0	
RTIL loss (mM)	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M	$NaBPh_4$ 0.0 M	$NaBPh_4$ 0.12 M
CsCl	20.7	15.6	20.5	15.7	21.2	15.8	21.0	15.7
CsOAc	20.9	15.6	20.7	15.6	20.7	15.8	21.1	16.0

[a] The initial aqueous concentration of Cs^+ was 2.5 mM with the specified anion.

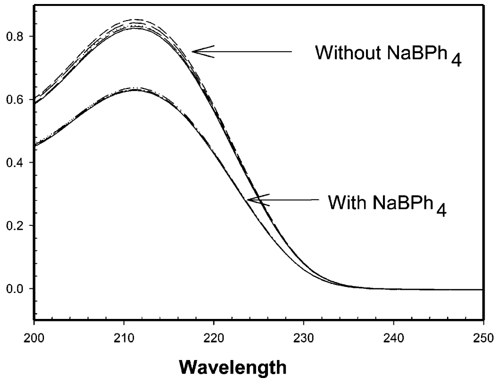

Figure 6. UV spectra of imidazolium (C_4mim) cation in the aqueous phase with and without the use of $NaBPh_4$.

Sodium tetraphenylborate ($NaBPh_4$) was added in our experiments as such a sacrificial hydrophilic cationic exchanger. It is known that in aqueous solutions, the BPh_4^- anion forms insoluble compounds with large cations[28] such as Cs^+ and imidazolium cations and also enhances extraction of cesium. Therefore, the release of the BPh_4^- anion from the imidazolium-based ILs to aqueous solutions should be negligible in the presence of the organic cations in aqueous phases. Furthermore, Na^+ is very hydrophilic so that its transport to aqueous phases from ILs is highly thermodynamically favorable. In addition, our experiments indicated that $NaBPh_4$ could be readily dissolved in the studied ILs.

Table 3 compares the extraction results obtained using $[C_4mim][NTf_2]$ containing various concentrations of BOBCalixC6 with and without 0.12 M $NaBPh_4$. As seen in Table 3, no significant changes of the corresponding D_{Cs} values with the addition of $NaBPh_4$ were observed. The small changes that were observed in D_{Cs} with the addition of $NaBPh_4$ imply that high concentrations of Na^+ may compete with Cs^+ for the coordination with BOBCalixC6 or that the extraction of Cs^+ is not totally through the ion-exchange process.

Support for the substitution of $[C_4mim]^+$ by Na^+ in the ion-exchange process proposed above comes from the analysis of the concentration of $[C_4mim]^+$ released to the corresponding aqueous phases during extraction. As seen in Table 4 and Figure 6, the addition of $NaBPh_4$ decreases the loss of ILs by about 24%, as determined by measuring the UV spectra of $[C_4mim]^+$ in the corresponding aqueous phases.

CONCLUSIONS

The work reported here demonstrates that ILs can be effective media for liquid−liquid extraction, though care must be exercised in developing a mechanistic understanding of the entire process. Solutions of BOBCalixC6 in these ILs provide efficient extraction of Cs^+ cation from aqueous solutions under conditions that give negligible extraction with traditional organic solvents (e.g., 1,2-dichloroethane).[20b,29] The selectivity for extracting Cs^+ over Na^+ and Sr^{2+} is quite high; however, the concomitant extraction of K^+ along with Cs^+ has been observed, and the selectivity is less than in traditional organic solvents. Although the shorter-alkyl-chain ILs have higher distribution coefficients, the solubilities of BOBCalixC6 in the corresponding ILs are less. The higher distribution coefficients for the shorter-alkyl-chain ILs can be attributed to the ion-exchange capability of the less hydrophobic imidazolium cations. Because BOBCalixC6 is very hydrophobic, its solubilities in the longer-alkyl-chain ILs (more hydrophobic) are greater. Therefore, a compromise has to be made in determining the optimum IL.

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Unlike traditional organic solvent extraction, the efficiency of cesium-cation extraction from aqueous solutions into IL solutions of BOBCalixC6 does not change significantly with different counteranions (e.g., from nitrate to chloride to acetate). The addition of $NaBPh_4$ can decrease the loss of ILs by 24%, thus indicating at least a partial role for ion exchange in the observed results. Further study of these ILs continues in our laboratories.

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SUPPORTING INFORMATION AVAILABLE

The details on synthesis and characterization of ILs are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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