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Effect of ionic liquids on the extraction of americium by diphenyl (dibutyl) carbamoylmethyl phosphine oxide in dichloroethane from nitric acid solutions

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Abstract The present paper demonstrates that room temperature ionic liquids (RTIL) added at 1–5 wt% to a diphenyl (dibutyl) carbamoylmethylphosphine oxide (Ph_2Bu_2) solution increase the extraction coefficients of americium from nitric acid by more than two orders of magnitude. Moreover, the use of the RTIL—1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide makes the extraction possible even from 8 M HNO_3. This is an important attribute of such extraction system from the point of its possible application for radiochemical analysis of technological samples and environmental solutions, since many methods are based on transferring the solid samples into an 8 M HNO_3 solution. The extraction data obtained revealed that three Ph_2Bu_2 ligands are included into the coordination sphere of americium, two of which represent a compound with the nitrate anion and one with the RTIL anion.

Keywords Liquid–liquid extraction · Actinides · Americium · Room temperature ionic liquids · Diphenyl (dibutyl) carbamoylmethylphosphine oxide

Introduction

Nowadays, experts in radiochemistry pay increasing attention to the modernization of extraction technologies used to treat spent fuel. However, safety concerns of the nuclear fuel cycle include also the development of analytical methods for controlling technological and environmental samples. Methods of radiochemical analysis are distinguished by compactness and low volumes of organic substances used. Therefore, for these purposes the use of rather expensive reagents at present is possible. Room temperature ionic liquids (RTIL) which have acquired considerable interest as diluents for traditional extractants relate to these reagents [1]. RTIL belong to molten salts class because so far as melted salts are consisted of entirely ions, but melt at or below 100 °C. RTIL usually consist of asymmetric organic cations and organic or nonorganic anions. According to the literature, the use of RTIL as polar diluents during solvent extraction significantly increases the distribution coefficients of elements. However, enhanced distribution coefficients are not always desirable because extraction selectivity may be adversely affected. Problems with back extraction may also be the case. As has been shown in our previous paper [2], small additions of RTIL to traditional diluents increase the actinides extraction by bidentate neutral organophosphorus reagents significantly as well. Therefore, the objective of this study was the investigation of the extraction mechanism of americium in the presence of RTIL. This radionuclide is known to be difficultly extracted from mineral acid solutions. Along with this, our aim was to optimize the concentration of various RTIL in an extraction system based on diphenyl (dibutyl) carbamoylmethylphosphine oxide (Ph_2Bu_2) earlier developed for the extraction of actinides in the "Russian" TRUEX process [3].

Experimental

^{241}Am(III) isotope of radiochemical purity was used throughout. Ph_2Bu_2 was synthesized and purified at Nesmeyanov

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Institute of Organoelement Compounds. 1-Butyl-3-methylimidazolium hexafluorophosphate $[C_4mim]^+PF_6^-$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_4mim]^+Tf_2N^-$, and trihexyl (tetradecyl)phosphonium hexafluorophosphate $[P]^+PF_6^-$ were purchased from Merck (Germany) and were used without additional purification.

Equal volumes of an organic phase, containing Ph_2Bu_2, RTIL, and 1,2-dichloroethane, were added to test tubes with diluted HNO_3 containing a trace amount of ^{241}Am ($\approx 10^{-8}$ M). Preliminary experiments have shown that the extraction equilibrium is reached in 5 min after emulsification. Samples were shaken and decanted, then aliquots of both phases were taken to measure α-activity using a Tri-Carb 2700TR (Canberra Packard Inc.) liquid scintillation counter. Although an error of radioactivity measurements did not exceed 2 %, the experimental conditions were selected in such a way that values of distribution coefficients (D_{Am}) would not exceed 10^3.

Results and discussions

The extraction of actinides by dialkyl(diaryl) carbamoylmethylphosphine oxides (CMPO) from diluted mineral acids is studied quite well. It is known that the most active organic compound is a hydrated proton of organic complex ($H_5O_3^+ \cdot$CMPO) [4]. Therefore the distribution coefficients increase with increasing the degree of acid dissociation in the organic phase and, accordingly, with an increase of acid strength and the polarity of the organic phase. Extracted complexes such as $H^+Am(NO_3)_4^-$ nCMPO were shown [5] to form for Am(III), where n may vary from 2 to 3. When HNO_3 is exchanged partly or completely on $HClO_4$ distribution coefficients of Am increase significantly [6].

Data on the equilibrium distribution of americium in a system 0.05 M Ph_2Bu_2-RTIL-dichloroethane—HNO_3 are given in Table 1.

As one can infer from Table 1, the distribution coefficients of Am experience an increase by a factor of more than 10, when using every RTIL regardless of the acidity of the aqueous phase. The most effective additive was $[C_4mim]^+Tf_2N^-$, allowing at 1–5 wt% in the organic phase an increase in D_{Am} by two orders of magnitude. Moreover, this RTIL is more resistant to the influence of nitric acid and has lower viscosity. It has been demonstrated [7] that upon mixing $[C_4mim]^+PF_6^-$ with 8 M HNO_3 PF_6^- is converted into PO_4^{3-} and becomes hydrophilic.

As shown in Fig. 1, the D_{Am} values increase in a linear fashion in all cases with the concentration of RTIL containing the hexafluorophosphate anion. However, for $[C_4mim]^+Tf_2N^-$, this relationship has a more complicated character, with a larger increase in D_{Am} observed at lower

Table 1 Distribution coefficients of Am(III) in the 0.05 M Ph_2Bu_2-RTIL-dichloroethane—HNO_3 system

IL	Aquious phase	[IL] (wt%)	D_{Am}
$[P]^+PF_6^-$	1 M HNO_3	0	0.70
		1	1.6
		5	3.8
		10	6.9
		25	14.4
		50	38.8
	2 M HNO_3	0	1.1
		1	2.2
		5	4.4
		10	7.3
		25	15.5
		50	38.8
$[C_4mim]^+PF_6^-$	1 M HNO_3	0	0.70
		1	27.0
		5	90.1
		10	232
		25	363
		50	458
	2 M HNO_3	0	1.1
		1	28.2
		5	101
		10	155
		25	342
		50	793
$[C_4mim]^+Tf_2N^-$	1 M HNO_3	0	1.1
		1	119
		5	224
		10	459
		25	468
		50	764
	2 M HNO_3	0	0.70
		1	92.2
		5	204
		10	347
		25	431
		50	748
	4 M HNO_3	0	1.5
		1	41.1
		5	185
		10	292
		25	305
		50	647
	8 M HNO_3	0	0.37
		1	1.1
		5	2.9
		10	5.8
		25	11.9
		50	56.8

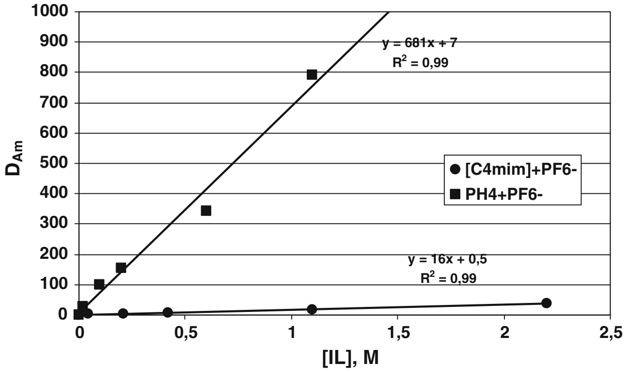

Fig. 1 Dependence of two Am distribution coefficients on the molar concentrations of $[P]^+PF_6^-$ or $[C_4mim]^+PF_6^-$ in the organic phase. The americium is extracted by dichloroethane containing 0.05 M Ph_2Bu_2 from an aqueous solution of 2 M nitric acid

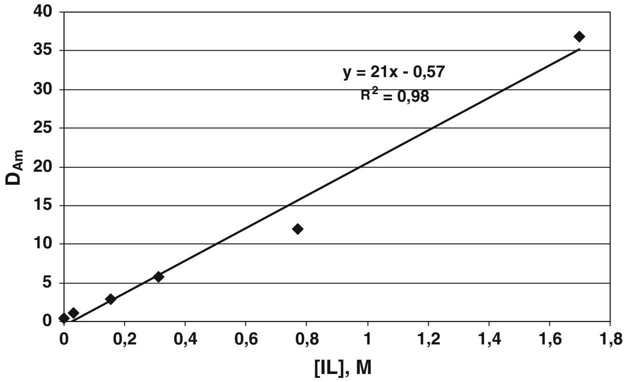

Fig. 2 Dependence of an Am distribution coefficient on the molar concentration of $[C_4mim]^+Tf_2N^-$ in the organic phase. The aqueous phase is a solution of 8 M nitric acid. The Am is extracted from this phase into dichloroethane containing 0.05 M Ph_2Bu_2

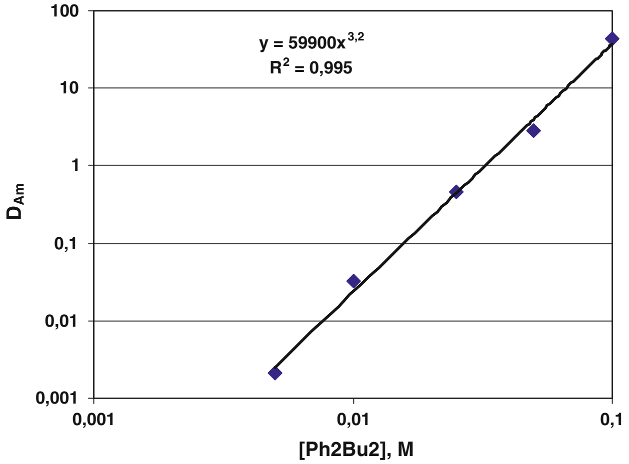

Fig. 3 Dependence of the extraction coefficient D_{Am} on the Ph_2Bu_2 concentration in the organic phase. The Am is extracted from 8 M nitric acid as the aqueous phase into dichloroethane containing increasing concentration of the extracting agent Ph_2Bu_2 and 5 % $[C_4mim]^+Tf_2N^-$

contents of RTIL (Table 1). Furthermore, the dependence of D_{Am} on the $[C_4mim]^+Tf_2N^-$ concentration becomes almost linear only in case of 8 M HNO_3 (Fig. 2). This may be explained by the fact that water activity and hence its solubility in the organic phase decreases upon increasing acid concentration [8]. In this case, activity coefficients of the extractable compound approach unity, and the dependence of D_{Am} versus RTIL concentration close to linearity [9].

Studies on the effect of the Ph_2Bu_2 concentration on the extraction efficiency revealed that an extracted complex with a Am-to-Ph_2Bu_2 ratio of 1:3 is formed (Fig. 3), both in the presence (this work) and the absence [5] of RTIL. As shown in Fig. 3 a slope of the dependence of D_{Am} on Ph_2Bu_2 content in logarithmical coordinates is about 3.2. However, this conclusion could be made after taking into consideration the following assumptions:

(1) When introducing RTIL into the organic phase, a dissociated organic complex $([C_4mim]^+\cdot CMPO)PF_6^-$ is formed, also under circumstances when strong acids, e.g., chloric acid or chlorinated cobalt dicarbollide, are added [10].

(2) The extraction ability of this complex significantly exceeds the extraction ability of free Ph_2Bu_2 and the complex of Ph_2Bu_2 with nitric acid.

(3) Physical properties of solvent (polarity, dielectric constant) do not change significantly under the influence of RTIL. This is possible only in the case when RTIL occurs at the level of several weight percentages.

These assumptions are important not only for the explanation of the RTIL effect on the extraction balance, but also for the calculation of the content of complexes being formed. However, it must be admitted that the calculation of activity coefficients of organic compounds formed in such complicated extraction systems is rather difficult. Smirnov [4] used IR spectrometry for the determination of the extraction complexes composition (taking into calculations the spectra of free extractant). However, spectra become much more complicated, when the RTIL is introduced into the organic solution, and the calculation for two free reagents (Ph_2Bu_2 and RTIL) introduced simultaneously is not possible.

Americium distribution coefficients decrease with the increase of the nitric acid concentration in aqueous phase at the extraction by the mixture of Ph_2Bu_2 and RTIL (Table 1). At high contents of the extraction agent (Ph_2Bu_2), this dependence while monotonic bears an exponential character which does not allow one to make conclusion on the content of the extracted complexes. At lower concentrations of the extracting agent (Ph_2Bu_2), D_{Am} values vary inversely with the nitric acid concentration (Table 2).

Table 2 Distribution coefficients of Am(III) between 0.01 M Ph_2Bu_2 in dichloroethane in the presence of varying concentrations of $[C_4mim]^+Tf_2N^-$, and HNO_3

$[HNO_3]$ (M)	$[C_4mim]^+Tf_2N^-$ (%)				
	1	5	10	25	50
0.01	76.0	213	269	421	637
1.0	13.2	56.6	72.8	117	311
2.0	5.3	27.2	38.9	72.7	136
4.0	0.37	1.77	2.56	6.15	14.5
6.0	0.10	0.31	0.42	1.53	2.07
8.0	0.035	0.076	0.089	0.10	0.28

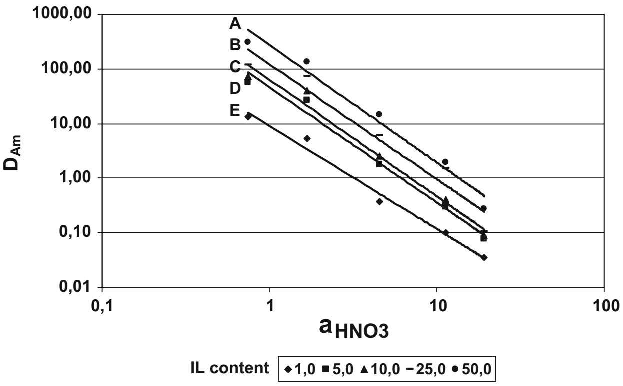

Fig. 4 Distribution coefficients of Am from aqueous solutions of HNO_3 into dichloroethane containing 0.01 M Ph_2Bu_2 and $[C_4mim]^+Tf_2N^-$. The *straight lines* represent the computed Am distributions coefficients versus the nitric acid concentration in the aqueous phase. From *bottom* to *top*, the five *straight lines* reflect increased concentrations of $[C_4mim]^+Tf_2N^-$ in the organic phases

The entries in Tables 1 and 2 indicate that D_{Am} decreases with increasing the concentration of nitric acid. That is true in the entire concentration range of the RTIL. But there is a difference in the character of D_{Am} versus C_{HNO3} dependences. To explain this effect it is necessary to account for the activity coefficients of the metal–ligand complexes in the dichloroethane phase. This is a challenge because the activity coefficients depend on the concentration of water in the dichloroethane. This problem is currently under investigation.

Dependences of D_{Am} on the nitric acid activity in the aqueous phase at extraction using 0.01 M Ph_2Bu_2 solutions in dichloroethane containing the RTIL are given in Fig. 4. The nitric acid activity values were determined as described in [11]. As can be seen from the data obtained, the slope of the log D_{Am} versus log (a_{HNO3}) dependences varies from 1.9 to 2.4 depending on the RTIL concentration (Table 3).

Table 3 Parameters of the lines on Fig. 4

Line	Notation	IL content (wt%)	D_{Am} equation	R^2
A	●	50	$y = kx^{-2.14}$	0.97
B	▬	25	$y = kx^{-2.10}$	0.94
C	▲	10	$y = kx^{-2.13}$	0.98
D	■	5	$y = kx^{-2.10}$	0.98
C	◆	1	$y = kx^{-1.89}$	0.99

Thus, the extraction data acquired show that three molecules of Ph_2Bu_2 are included into the americium coordination environment, two of which represent compound with NO_3^- and one—with RTIL anion. This mechanism is inherently differs from the one suggested previously [12] for the extraction of uranyl nitrate by CMPO in 100 % RTIL. According to [12] RTIL forms an outer-sphere complex by the cation-exchange mechanism. But simplifying the composition of extracted complexes may be the same in the both cases. Therefore, further work in the frames of these studies will be focused on the determination of water and nitric acid content in extracts, as well as on separate examination of the influence of cation and anion content of RTIL in the organic phase on the americium distribution.

Conclusions

The present study demonstrated that the introduction of RTIL (1–5 % by weight) increases americium distribution coefficients in a Ph_2Bu_2 system by more than order of magnitude. The extraction data showed that three ligands of Ph_2Bu_2 are included into the americium coordination environment, two of which represent compound with NO_3^- and one—with RTIL anion. The use of $[C_4mim]^+Tf_2N^-$ makes the extraction of Am possible even from 8 M HNO_3. The latter finding is important for eventual application of this extraction system in radiochemical analysis of technological and environmental samples, since many methods are based on transferring the solid samples into 8 M HNO_3 solution [13]. In this case, the extraction selectivity and its enhancement are also important. Studies carried out earlier have shown [2] that even though plutonium and uranium are extracted better from highly concentrated solutions of nitric acid than americium, the ratios of the distribution coefficients of plutonium and uranium to the distribution coefficient of americium do not increase upon addition of an RTIL. It is necessary to take into consideration here that uranium, neptunium, and plutonium are extracted at initial stages of the radiochemical analysis, and main difficulties concern, therefore, the extraction of americium with a high-degree yield.

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