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New method for actinide and rare-earth element recovery by diphenyl[dibutylcarbamoylmethyl]phosphine oxide from nitric acid solutions

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Abstract

It has been found for the first time that diphenyl[dibutylcarbamoylmethyl]phosphine oxide (DPDBCMPO) is able to extract effectively actinide and rare-earth elements from acidic solutions, without its preliminary dissolution in an organic solvent. DPDBCMPO, taken initially as a solid powder, is established to form an oily liquid complex $DPDBCMPO\cdot HNO_3\cdot nH_2O$ (‘liquid reagent’) on contact with 4 M HNO_3. Behavior of Pr(III), Np, Pu and Am in various oxidation states in the process of their extraction by ‘liquid reagent’ is studied. It has been shown that distribution coefficients of the elements extracted by the ‘liquid reagent’ (‘LR’) are greater than are observed in conventional solvent extraction (‘SE’). The use of aluminum phosphate matrix, containing DPDBCMPO, for isolation of the actinide and rare-earth elements and for their subsequent vitrification is suggested.

Keywords: Spectrophotometry; Radiometry; Solventless extraction; CMPO; Actinide; Lanthanide; Nitric acid solutions; Radioactive waste management

1. Introduction

It is known that reagents relating to a class of bidentate neutral organophosphorus compounds (BNOC), in particular diaryl[dialkylcarbamoylmethyl]phosphine oxides (CMPO), are the most promising for the extraction of radionuclides (rare earth and actinide elements) from acidic waste solutions from radiochemical practice [1–4]. Therefore, the study of behavior of BNOC as extractants for radionuclides is of great scientific and practical importance.

Diphenyl[dibutylcarbamoylmethyl]phosphine oxide (DPDBCMPO) is a solid powder compound. On contact with an acidic solution it changes its state of aggregation, undergoing transformation into a liquid oil-like substance unmixed with a water phase (‘liquid reagent’). This phenomenon was described earlier for DPDBCMPO [5]. In this work, the results of a study of the behavior of DPDBCMPO as a ‘liquid reagent’ for extraction of nitric acid and for removal of rare-earths (for example, praseodymium) and actinide elements from nitric acid solutions are presented.

2. Experimental

Np-237, a mixture of Pu-239 and Pu-238 isotopes with average specific activity of $2.353\cdot 10^6$ Bq mg^{-1} and americium (^{243}Am and ^{241}Am) with average specific activity of $9.07.10^6$ Bq mg^{-1} were used. Solutions of the radionuclides were prepared in the reagent-grade nitric acid. Praseodymium solutions were prepared by dissolving weighed portions of $Pr(NO_3)_3\cdot 6H_2O$. The DPDBCMPO was synthesized in the Laboratory of Organophosphorus Compounds of the Institute of Organoelement Compounds, Russian Academy of Sciences, as described in Ref. [6].

Flow-type methane counter ‘Protoka’ was used for measuring total α-activity. Control of Pr(III) content, identification of radionuclide oxidation states, and determination of radionuclide concentrations in various oxidation states, were carried out using a Shimadzu recording spectrophotometer, connected to a PC. The techniques described earlier [7] were used for preparation of Np(IV),

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Np(V), Np(VI), Pu(III), Pu(IV), Pu(VI), and Am(VI) solutions.

3. Results and discussion

3.1. Extraction of praseodymium from nitric acid solutions by 100% DPDBCMPO

A weighed portion of the DPDBCMPO powder was introduced into a praseodymium solution and shaken with this solution for 3 min. The mixture was centrifuged for separation of the phases for 10 min. The appearance of reagent in this solution was controlled. The praseodymium concentration in the aqueous solution was subsequently determined by spectrophotometry. Then, these operations were repeated on introducing new portions of the reagent into tested solution. It was shown that the optical densities of praseodymium solutions in 1 M HNO_3 in a range of concentrations from 0.02 to 0.0004 M at 444 nm obeyed the Lambert–Beer law.

It was established that, on contact with 0.12 M HNO_3, the reagent in the process of metal extraction, followed by centrifugation, remains in the loose powdered form. For the contact time with 1 M HNO_3 the reagent forms a lump of irregular shape, as though covered by an oil film. At an acidity of 2.5 M and above, the reagent is transformed into a yellow oil-like viscous liquid after extraction and centrifugation. With the further increase in acidity the reagent transforms into a liquid state more readily, and a smaller excess of DPDBCMPO is needed for quantitative extraction of the metal. The data obtained on praseodymium extraction are presented in Table 1.

One can see that the acidity of the solution and the interaction of nitric acid with the reagent are responsible for the physical state of the reagent and for the extraction capacity of the DPDBCMPO. For example, a quantitative extraction of the element can be accomplished even from weakly acidic solutions after preliminary transformation of the reagent into the liquid state on its shaking with nitric acid solution (3 M) (see Table 1).

3.2. Study of the interaction of DPDBCMPO with nitric acid

It was of interest to study the interaction of DPDBCMPO with nitric acid in the absence of an organic solvent, and to determine the relationship between the weight of the dry reagent and the volume of a liquid phase formed on interacting the reagent with the acid. The $[HNO_3]$:[DPDBCMPO] ratio was chosen to be higher than 10, which ensures a maximum of extraction of transplutonium and rare-earth elements by the reagent in organic solvent [1–4].

A dependence between the weight of solid reagent and the reagent transformed into an oily liquid was found using a weighing technique. The results are given in Table 2. One can see that transformation of DPDBCMPO into liquid state is accompanied by its weight gain, with an average coefficient of 1.266±0.015. The density of liquid carbamoyl determined by pycnometry was equal to 1.163 ± 0.012 g cm^{-3}. Thus, the volume of liquid reagent is determined easily from the weight of dry reagent, the weight gain coefficient and density.

An increase of the reagent weight on its contact with a nitric acid solution is due to formation of the reagent compound with a nitric acid. Determination of the compound composition has shown that its formula can be

Table 1
Praseodymium extraction by 100% DPDBCMPO from the nitric acid solutions

$[HNO_3]$ (M)	[DPDBCMPO]^a $\times 10^3$ (M)	D^b	E^b (%)	$[HNO_3]$ (M)	[DPDBCMPO]^a $\times 10^3$ (M)	D^b	E^b (%)
0.12	20	0.098	8.9	4.0	10	0.587	37.0
	60	0.278	21.8				
	120	0.311	23.8		20	5.479	84.6
	300	0.311	23.8				
	300^c		100^c		30		100
1.0	20	0.572	36.4	8.0	5	0.233	18.9
	30	4.690	82.4		10	0.606	37.7
	50	7.91	88.8		15	1.804	64.3
	60		100		20	11.93	92.3
					25		100
2.5	10	0.414	29.3	10.0	5	0.455	31.3
	20	2.780	73.5		10	1.365	57.5
	30	12.56	92.6		15	2.569	72.0
	40		100		20		100

Volume of nitric acid solution, 2 ml; initial concentration of Pr(III) in the nitric acid solution, $4 \times 10-3$ M.

[a] Conditional concentration of DPDBCMPO calculated for the volume of water phase (2 ml).

[b] Calculated by equations: $D = C_{org.}/C_{aq.}$; $E = D/D+1$.

[c] The reagent was transformed into liquid state on preequlibration with 3 M nitric acid.

Table 2
Relationship between the weight of solid reagent and the reagent transformed into a 'liquid reagent'

	Number of experiment					
	1	2	3	4	5	6
Weight of solid DPDBCMPO (g)	0.9396	0.6936	0.5839	0.4159	0.2254	0.1050
Weight of 'liquid reagent' (g)	1.2056	0.8796	0.7398	0.5340	0.3263	0.1290

In experiments 1, 3 and 6, acid concentration is 4.7 M; volume, 8, 4 and 2 ml, respectively. In experiments 2, 4 and 5, acid concentration is 4.18 M; volume, 2 ml.

expressed as follows: DPDBCMPO·HNO_3·nH_2O, where $n=2$–3. This differs from the results obtained in Ref. [8], where the authors applied a solution of DPDBCMPO in an organic solvent. Thus, on the contact of DPDBCMPO with a nitric acid solution the reagent changes the state of aggregation, going into an oil-like viscous liquid as the DPDBCMPO·HNO_3·nH_2O compound. Hereinafter this compound is denoted 'liquid reagent'.

3.3. Extraction of neptunium, plutonium and americium in various oxidation states from nitric acid solutions using the 'liquid reagent'

It was of interest to obtain the characteristics of extraction of Np, Pu and Am using the 'liquid reagent'. For this purpose the weighed amount of the powdered DPDBCMPO was added into aqueous phase containing radionuclide, followed by extraction and centrifugation for separation of phases. After the contact time the liquidization of the reagent and metal recovery were found to be complete. The oxidation state of extracted element in the phase of the 'liquid reagent' was determined by spectrophotometry after preliminary dissolving this phase in dichloroethane.

The oxidation state of Np(IV) and Pu(IV) on passing into liquid reagent phase does not vary. However, the light absorption band maxima of neptunium (IV) and plutonium (IV) are shifted by 6–10 nm towards longer wavelengths, and their intensities noticeably change as well.

The oxidation state of Np(VI) and Pu(VI) on passing into liquid reagent also does not vary. Changes in Pu(VI) spectrum are characterized by splitting a narrow band of hexavalent plutonium at 830 nm for two bands at 819 and 840 nm, and by a shift of the band positions at 951 and 988 nm by about 10 nm, accompanied by an increase in their intensity.

Changes in the Np(VI), Pu(IV) and Pu(VI) spectra give evidence of the strong bond formation between these actinide cations and 'liquid reagent' as a ligand. A similar interaction probably occurs between neptunium(VI) and 'liquid reagent', but changes in the Np(VI) spectrum are not so marked. The neptunium(VI) complex with 'liquid reagent' exhibits a wide region of monotonously growing absorption below 500 nm.

Plutonium(III) extraction into the reagent phase is accompanied by a change in its oxidation state. It was determined visually that Pu passes into reagent phase as a blue-violet trivalent species. However, after extraction for 3 min the phase of 'liquid reagent' becomes yellow-brown. Absorption bands of plutonium(IV) are only observed in the optical absorption spectrum of the 'liquid reagent'.

Extraction of neptunium(V) is also accompanied by a change of its valent state in the 'liquid reagent' phase. Continuous absorption of neptunium(VI) is only observed in the optical spectrum of the 'liquid reagent'. The low distribution coefficient of Np seems to be indicative of its transfer into the 'liquid reagent' phase, as a pentavalent species, followed by the oxidation of neptunium(V) to neptunium(VI) directly in this phase.

Pentavalent americium, contrary to pentavalent neptunium, is fairly stable in the 'liquid reagent' phase. It reduces slowly to Am(III) at a rate of about 1% per hour.

Americium(VI) disappears on contact with the 'liquid reagent' phase, forming Am(V) and Am(III), which are then distributed between the phases.

Thus, oxidation states of Pu(III), Np(V) and Am(VI) are not stable on contact with the 'liquid reagent' phase. Therefore, the 'liquid reagent' exhibits redox properties. Its potential can be estimated as +1.5 V, based on formal redox potentials of Pu(IV)/Pu(III), Np(VI)/Np(V) and Am(VI)/Am(V), +0.982, +1.37 and +1.60 V, respectively [7].

The results of actinide element extraction in various oxidation states are shown in Table 3. The presented data show a typical tendency of extraction parameters from an oxidation state of recovered elements. The distribution coefficients and extraction efficiency are decreasing depending on the valent state in the following order: $(IV) > (VI) \geq (III) \gg (V)$. The concentration factor varies from 60 to 80.

3.4. Efficiency of metal extraction from nitric acid solutions using 'liquid reagent' and a solution of powdered DPDBCMPO in organic solvent

It was of interest to compare the efficiency of metal extraction from nitric acid solutions using the 'liquid reagent' ('LR', extraction by the reagent) and using the same quantity of DPDBCMPO in organic solvent ('SE', usual solvent extraction). It was shown earlier that the efficiency of praseodymium extraction with 'liquid reagent' is much higher than that for a solution of the same

Table 3
Extraction of Np, Pu and Am from 4 M HNO_3 using 'liquid reagent'

Oxidation state of actinide	[An] in initial solution (M)	[An] in 'liquid reagent' phase (M)	[An] in aqueous phase (M)	D^a	E^a (%)
Np(IV)	1.52×10^{-3}	0.10	6.20×10^{-6}	1.6×10^4	99.6
Np(V)	1.47×10^{-3}	0.05	8.44×10^{-4}	60	43.0
Np(VI)	1.72×10^{-3}	0.113	2.10×10^{-5}	5.4×10^3	98.8
Pu(III)	3.0×10^{-3}	0.132	4.44×10^{-5}	3.0×10^3	98.5
Pu(IV)	3.3×10^{-3}	0.147	8.80×10^{-6}	1.7×10^4	99.7
Pu(VI}	3.59×10^{-3}	0.151	9.90×10^{-5}	1.5×10^3	97.1
Am(III)	0.81×10^{-3}	0.029	1.50×10^{-5}	1.9×10^3	98.2
Am(V)	1.55×10^{-3}	0.030	0.72×10^{-3}	42	54.0

Initial amount of DPDBCMPO in experiments with Pu and Am, 30 mg per volume stock solutions, 1.5 and 1.2 ml, respectively, in experiments: with Np(IV) and Np(VI), 16.3 mg; with Np(V), 13.4 mg. The volume of Np stock solutions is 1.2 ml. The volume of 'liquid reagent' for Pu and Am is 0.033 ml; Np(IV) and Np(VI), 0.018 ml; Np(V), 0.015 ml.

[a]Calculated by equations: $D=C_{\text{org.}}/C_{\text{aq.}}$; $E=(D/D+V_{\text{aq.}}/V_{\text{org.}})\times100$.

quantity of DPDBCMPO in fluoropol or dichloroethane [9], for the case when the DPDBCMPO was deficienct for maximum metal extraction (ratio between concentrations of metal and reagent is equal to 1:3).

The same result is observed when the quantity of DPDBCMPO is sufficient for complete metal extraction (Table 4, ratio between concentrations of metal and reagent is equal to 1:20). The efficiency of Np(IV) and Np(VI) extraction by 'liquid reagent' from nitric acid solution is also higher, compared with solutions of DPDBCMPO in organic solvent.

3.5. Isolation of praseodymium into DPDBCMPO immobilized on powder-like matrix of aluminum phosphate glass

The use of 'liquid reagent' immobilized on a powdered matrix of aluminum phosphate glass is one of the alternatives for isolation of actinide and rare-earth elements from wastes, for their subsequent underground disposal.

A solution of praseodymium (0.01 M) in 3 M HNO_3 was used in the experiment. The sample of molten aluminum phosphate glass was powdered. Immobilization of the reagent on the glass powder was done as follows. A weighed quantity of DPDBCMPO was dissolved in acetone and this solution was mixed with weighed portion of the glass powder. Then acetone was evaporated carefully with stirring and the product was dried at ambient temperature. The matrix of aluminum phosphate glass (2.5 g) contained 0.3 g DPDBCMPO. The prepared powder-like mass (1.73 g), containing 5.0×10^{-4} mol of the reagent, was placed into a chromatographic column (5 mm i.d. and 40 mm height). At the first stage, 1 ml of 3 M HNO_3 was passed through the column to transform DPDBCMPO into 'liquid reagent'. Subsequently, 5 ml of nitric acid solution, containing 5×10^{-5} mol of praseodymium passed through the column, followed by 2 ml of 1 M HNO_3 at a rate of about 0.18 ml min^{-1} for washing. The concentration of Pr(III) was measured spectrophotometrically.

Table 4
Extraction of 1.51×10^{-3} M Np(IV) and 1.72×10^{-3} M Np(VI) from 4 M HNO_3 (1.2 ml) using the 'LR' and 'SE' methods

Oxidation state of NP	Extraction method	D^a	$E^a_{\text{Pr(III)}}$ (%)
IV	LR	242	99.6
	SE with DCE	20	95.2
VI	LR	81	98.8
	SE with DCE	8	88.4

Initial quantities of DPDBCMP used in the both methods equal 16.3 mg.
*a*Calculated by equations: $D=C_{\text{org.}}/C_{\text{aq.}}$; $E=D/D+1$.

Residual concentration of Pr(III) in the collected volume of solution after sorption and washing was 3×10^{-4} M. Thus, as much as 99% of the initial amount of praseodymium was isolated from the solution. The column content was transferred quantitatively into a glass graphite test-tube. This test-tube was placed into a muffle, where praseodymium adsorbate with glass powder was melted at 1100°C for 4–5 h. The final weight of the vitrified matrix was 1.3 g. Weight loss compared to initial matrix weight (1.73 g) can be explained by partial dissolution of ground matrix in nitric acid.

4. Conclusions

The data obtained show that, on contact with nitric acid solutions, the DPDBCMPO powder changes its state of aggregation, being transformed into a liquid colorless viscous substance unmixed with aqueous phase. The solution acidity, and interaction of the reagent with nitric acid, are the factors determining the physical state of the product of their interaction and the extraction capacity of the compound formed. The use of the compound of reagent with nitric acid ($\text{DPDBCMPO}\cdot HNO_3\cdot nH_2O$, where $n=2$–3) permits extraction of the metals in question more effectively in comparison with extraction by the DPDBCMPO solutions in organic solvents. This is promising for the processing of acidic highly radioactive wastes, because the use of toxic and environmentally hazardous organic solvents can be avoided.

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