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Recovery of Actinides and Lanthanides with Diphenyl[dibutylcarbamoylmethyl]phosphine Oxide from Nitric Acid Solutions by Solventless Extraction

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ABSTRACT

It has been found for the first time that
diphenyl[dibutylcarbamoylmethyl]phosphine oxide (DPDBCMPO) is able to extract
effectively actinides in various oxidation states and lanthanides from acidic solutions
without its preliminary dissolution in organic solvents. The system of DPDBCMPO
– metal – nitric acid has been studied in detail by the methods of physicochemical
analysis. The composition, the structure of complexes forming in this system under
solventless extraction process have been evaluated. The use of inert matrices,
containing DPDBCMPO, for isolation of the actinides and lanthanedes for their
subsequent vitrification is suggested.

Key Words:, CMPO / actinide / lanthanide / nitric acid solutions / radioactive waste management.

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 (lanthanide and actinide elements) from acidic waste solutions of radiochemical practice [1-4]. Therefore, the study of behavior on BNOC as extractants for radionuclides are 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 or LR). For the first time, this phenomenon was found for DPDBCMPO and described earlier[5]. This finding prompted us to study the behavior of DPDBCMPO as LR for extraction of nitric acid and actinides (americium, curium) and lanthanide (praseodymium) from nitric acid solutions[6,7]. The dependence between the weight of solid reagent and the weight of reagent transformed into a LR was established. Determination of the LR composition has shown that its formula can be expressed as follows: $DPDBCMPO \cdot HNO_3 \cdot nH_2O$ for the concentration 3-4 M of HNO_3. The density of this compound has been determined as well.

In this paper, we present the further results of the study of the extraction system of DPDBCMPO – metal – nitric acid.

EXPERIMENTAL

^{237}Np, a mixture of ^{239}Pu and ^{238}Pu- isotopes with an average specific activity of $2.353 \cdot 10^6$ Bq/mg and americium (^{243}Am and ^{241}Am with average specific activity of $9.07 \cdot 10^6$ Bq/mg) were used. Solutions of the radionuclides were prepared in the reagent-grade nitric acid. Praseodymium and neodymium stock solutions were prepared by dissolving weighed portions of $Pr(NO_3)_3 \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$. The DPDBCMPO was synthesized in the laboratory of organophosphorus

compounds of the Institute of Organoelement compounds Russian Academy of Sciences as described in [8]. The techniques, described earlier [9], were used for preparation of Np(IV), Np(V), Np(VI), Pu(III), Pu(IV), Pu(VI) and Am(VI) solutions.

Flow-type methane counter "Protoka" was used for measuring total alpha-activity. Control of Pr(III) and Nd(III) contents, identification of radionuclides' oxidation states and determination of radionuclides' concentrations in various oxidation states were carried out by a SHIMADZU recording spectrophotometer, connected to a PC. The measurement of absorbance infrared spectra were carried out by Fourier spectrometer FTIR PU 9800.

RESULTS AND DISCUSSION

1. Study on the Interaction of DPDBCMPO with Nitric Acid

Weighed portion of the DPDBCMPO powder was introduced into test tube containing the nitric acid solution. The mixture was shaken for 3 minutes and centrifuged for 10 minutes for separation of the phases. The aqueous acid phase was removed from this system and the nitric acid concentration in this solution was determined. These steps were repeated on introducing a new portion of the initial nitric acid solution into the test tube containing DPDBCMPO.

As a result of these operations the reagent was transformed into an oil-like viscous liquid (LR). The data of these experiments are given in Table 1.

Table 1. Nitric Acid Extraction by DPDBCMPO in the Course of the First (Δ_1) and the Second (Δ_2) Contacts with Initial Solutions of HNO_3. (The volume of HNO_3 is 3 ml)

Amount of solid DPDBCMPO, g-mol	[HNO₃], M			Total amount of HNO₃ extracted, g-mol	Ratio of LR : HNO₃
	Initial	Extracted after			
		1st contact (Δ_1)	2nd contact (Δ_2)		
7.26×10^{-4}	1.937	0.171	0.014	5.57×10^{-4}	1:0.76
7.14×10^{-4}	3.176	0.249	0.008	7.69×10^{-4}	1:1.08
8.11×10^{-4}	3.947	0.225	0.008	6.99×10^{-4}	1:0.86
7.85×10^{-4}	5.190	0.288	0.031	9.56×10^{-4}	1:1.21
8.54×10^{-4}	6.464	0.201	0.093	8.82×10^{-4}	1:1.03
10.35×10^{-4}	7.233	0.359	0.052	12.35×10^{-4}	1:1.19
10.98×10^{-4}	8.143	0.340	0.050	11.69×10^{-4}	1:1.06

One can see from the data obtained that the average ratio of extracted quantity of nitric acid to the taken quantity of DPDBCMPO is equal 1.03 ± 0.12 over the range of nitric acid concentration from 2M to 8M.

Thus on the contact of DPDBCMPO with nitric acid solution the reagent changes its state of aggregation going into an oil-like viscous liquid compound of composition DPDBCMPO•HNO₃•nH₂O (LR). This differs from the results obtained in the work[10], were the authors applied solution of DPDBCMPO in the organic solvent.

2. Study on the Interaction of Lanthanides with DPDBCMPO·HNO₃·nH₂O as LR

It is known that americium(III) is extracted forming di- and threesolvates with reagent on extraction with CMPO solution in organic solvent [11]. It was of interest to establish the composition of the complex formed on a metal solventless extraction, for example neodymium, with LR.

The first evaluation of the composition of an extracted compound of praseodymium with LR has been accomplished by the authors earlier [12]. The ratio of the metal extracted to the reagent taken on praseodymium extraction by 100% DPDBCMPO from nitric acid solutions has been found to be equal to 6.0 ± 0.8; 5.7 ± 0.5 and 4.4 ± 0.4 for solutions acidity 4M, 8M and 10M, respectively. These data were obtained under conditions when the reagent concentration did not exceeded the metal one more than five times because otherwise the metal quantitative extraction would be observed.

More detailed study of the neodymium extraction by LR under these conditions has shown that the complex extracted is a solid compound. The melting point of this compound is found to be about 65-70°C. Therefore extraction was carried out on a thermostatically controlled conditions (about 80°C). The heated phases were separated by centrifugation after «thermoextraction». The of aqueous phase was analyzed to determine the neodymium residual concentration (at ambient temperature). After that the aqueous phase was discarded. The complex obtained staying in the test tube was put into the contact with a new portion of initial neodymium solution in nitric acid. The extraction process was finished when the neodymium concentration have been remained constant in aqueous phase after a number of «thermoextraction» cycles. The total quantity of neodymium extracted from a few portions of the aqueous phase was determined and the molar ratio of LR to metal in the complex formed has been calculated. The results of these experiments are shown in Table 2.

Table 2. Determination of the Composition of the Complex Forming on Extraction of Neodymium by LR from Nitric Acid Solutions

[HNO₃], M (initial)	Taken in initial solution, g-mol		Amount of Nd, g-mol		Ratio of LR : Nd	[HNO₃], M (after extraction)
	LR	Nd	in solution	in extract		
2.82	1.68×10⁻⁴	0.441×10⁻⁴	0.053×10⁻⁴	0.429×10⁻⁴	3.92	2.82
		0.470×10⁻⁴	0.429×10⁻⁴			2.85
		0.470×10⁻⁴	0.470×10⁻⁴			2.80
7.22	1.97×10⁻⁴	1.356×10⁻⁴	0.860×10⁻⁴	0.500×10⁻⁴	3.94	7.20
		0.682×10⁻⁴	0.678×10⁻⁴			7.13
		0.682×10⁻⁴	0.682×10⁻⁴			7.25

One can see that the ratio of the components in the resulting complex is close to 4 over the range of nitric acid concentrations from 3M to 7M. Thus, the composition of the complex extracted on solventless extraction differs from that found for conventional solvent extraction conditions [11] (di- and threesolvates).

Tetrasolvate complex of neodymium with LR was obtained on ambient temperature as well. The LR immobilized on an inert matrix of silica oxide was used for this purpose. Extraction experiments were carried out under static conditions. A weighed portion of silica oxide containing the specified quantity of LR as well as a solution of neodymium in nitric acid were introduced into a glass test. Then the extraction process was carried out. After that the residual concentration of neodymium was determined in aqueous phase by spectrophotometry. It was shown that 3 minutes of extraction time

and 10 minutes centrifugation for separation of phases was sufficient for the complete saturation of LR phase by the metal extracted under these conditions. Apparently a thickness of LR layer coating the inert matrix surface provides a complete contact of all amount of LR with metal extracted. Therefore a resulting solidified complex does not prevent the extraction process. The results obtained are given in Table 3.

Table 3. Determination of the composition of the complex formed on Nd extraction by LR immobilized on an inert matrix of silica oxide from 3 M HNO₃ solutions

(SiO₂, mg) LR in SiO₂, g-mol	Nd in initial solution, g-mol	Nd in solution after extraction, g-mol	Nd extracted, g-mol	LR : Nd
(150) 2.45×10⁻⁵	2.45×10⁻⁵	1.81×10⁻⁵	0.64×10⁻⁵	3.8
(502) 8.2×10⁻⁵502	4.40×10⁻⁵	2.16×10⁻⁵	2.24×10⁻⁵	3.7

One can see that the ratio of components in resulting complex is close to 4 under these conditions as well.

3. The effect of organic solvent on the complex of neodymium with LR

The violet solid complex of neodymium with LR(tetrasolvate) dissolves well in organic solutions: dichloroethane, chloroform, acetonitrile, acetone. The absorption band maximum of neodymium at 795 nm (aqueous nitric acid solutions) is shifted by 4 nm toward longer wavelengths in dichloroethane, but its intensity does not change noticeably (10.2 ± 0.8 $mol^{-1}1cm^{-1}$).
If to dissolve the complex of neodymium with LR resulting under solventless extraction conditions into dichloroethane and to mix this solution with an aqueous nitric acid ($[H^+] \geq 2M$) solution of the same volume then 40% quantity of metal goes into aqueous phase from organic phase. If to mix the obtained aqueous phase with equal portion of pure dichloroethane, then after extraction the neodymium concentration in the aqueous phase does not change. Therefore, the tetrasolvate complex is decomposed under dissolving in an organic solvent due to solvation effect of the latter. It is the reason of the more efficient extraction of the metals by LR in comparison with the metals extraction by solution of powdered DPDBCMPO in organic solvent from nitric acid solutions reported earlier[6,7].

4. Infrared study of compounds forming in the system of DPDBCMPO – nitric acid – metal

The bond coordination manner (mono-, semi- or bidentate) of reagent with HNO₃ and lanthanides (III) on extraction of those by solutions of CMPO in organic solvent was discussed earlier[13-16]. It was of interest to obtain the same information for the HNO₃-DPDBCMPO complex (LR) and for the lanthanides - LR complex under conditions of solventless extraction.

Fig.1 shows IR spectra for free DPDBCMPO (1), LR(2) and tetrasolvate complex of neodymium with LR(3). Spectrum of DPDBCMPO was recorded using KBr. The spectra 2 and 3 were recorded when liquid compounds studied have been placed between two thin silicon plates with the thickness of liquid layer a same micron.

IR spectrum of DPDBCMPO exhibits absorption bands at 1639 cm⁻¹ and 1200 cm⁻¹, which would been assigned to free carbonyl and phosphoryl stretching modes, respectively. The free carbonyl and phosphoryl stretching frequencies of DPDBCMPO change as result of complexation.
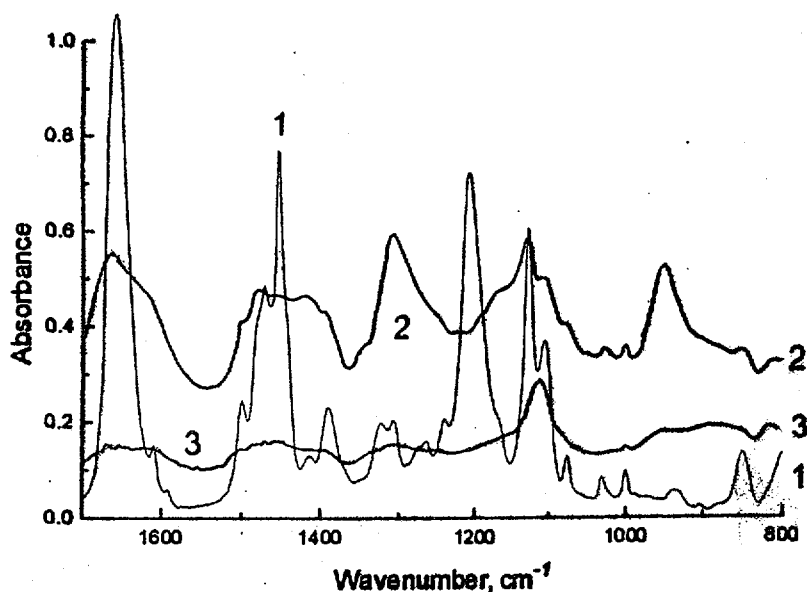
Fig.1. Infrared spectra of DPDBCMPO (1), LR (2) and complex of Nd with LR (3)

In IR spectrum (2) of LR the absorption band position of free C=O group at 1639 cm^{-1} is retained But this band expands and exhibit an arm at 1594 cm^{-1}, which should be classified as a slight interaction between the carbonyl oxygen and the proton of nitric acid. The absorption band of free P=O group at 1200 cm^{-1} disappears transforming to the absorption band at 1125 cm^{-1} indicating that the H^+ ion is bound to phosphoryl oxygen. Moreover, the spectrum of LR exhibits absorption bands at 1298 cm^{-1} and 949 cm^{-1}, which one can assign to vibrations of coordinating nitrate ion [15].

In the range characteristic for the carbonyl stretching frequencies of spectrum 3 the absorption bands at 1639 cm^{-1} and 1594 cm^{-1} are observed. The intensity of the latter increases compared with the same band of the spectrum 2. It indicates, that the bond between the carbonyl oxygen and Nd^{3+} ion is more strong than that between the carbonyl oxygen and the proton of nitric acid. The absorption band of free P=O group at 1200 cm^{-1} disappears completely. This spectrum exhibits absorption band at 1107 cm^{-1}, which should be assign to P=O groups bound with Nd^{3+} ion.

Therefore, we can accept that in structure of LR the proton is bound monodentate with phosphoryl oxygen and in complex of metal-LR the Nd^{3+} ion is bound bidentate with both phosphoryl and carbonyl oxygens.

5. Extraction of Np, Pu and Am in various oxidation states from nitric acid solutions by LR

It was of interest to obtain the characteristics of extraction of Np, Pu and Am by LR. 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 phase of LR was determined by spectrophotometry after preliminary dissolving this phase in dichloroethane.

Oxidation state of Np(IV) and Pu(IV) on passing into liquid reagent phase doesn't vary. However, the light absorption band maxima of Np(IV) and Pu(IV) are shifted by 6-10 nm toward longer wavelengths and their intensities noticeably change as well.

Oxidation state of Np(VI) and Pu(VI) on passing into liquid reagent doesn't vary also. Changes in Pu(VI) spectrum are characterized by splitting a narrow band of Pu(VI) at 830 nm onto two bands at

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819 and 840 nm and by shift of the bands 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 LR as a ligand. A similar interaction probably occurs between Np(VI) and LR, but changes in Np(VI) spectrum are not so marked. The Np(VI) complex with LR exhibits a wide region of monotonously growing absorption below 500 nm.

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

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

Am(V), contrary to Np(V), is fairly stable in phase of LR. It reduces slowly to Am(III) at the rate of about 1 % per hour. Am(VI) disappears on contact with phase of LR 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 phase of LR. Therefore, the LR 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 V, +1.37 V and +1.60 V respectively. The results of actinides' extraction in various oxidation states are shown in Table 4.

Table 4. Extraction of Np, Pu and Am in various oxidation states with LR from 4 M HNO₃
Initial amount of DPDBCMPO in the runs with Pu and Am is 30 mg per 1.5 ml and 1.2 ml of the stock solutions, respectively; this one in the runs with Np(IV), Np(VI) and Np(V) is 16.3 mg, 16.3 mg, and 13.4 mg, respectively. The volume of Np stock solutions was 1.2 ml. The volume of LR for Pu and Am is 0.033 ml, for Np(IV) and Np(VI) is 0.018 ml, and for Np(V) is 0.015 ml.

Actinide (An)	[An], M			D[a]	E[a], %
	in initial solution	in LR phase	in aqueous phase		
Np(IV)	1.52×10⁻³	0.100	6.20×10⁻⁶	1.6×10⁴	99.6
Np(V)	1.47×10⁻³	0.050	8.44×10⁻⁴	60	43.0
Np(VI)	1.72×10⁻³	0.113	2.10×10⁻⁵	5.4×10³	98.8
Pu(III)	3.01×10⁻³	0.132	4.44×10⁻⁵	3.0×10³	98.5
Pu(IV)	3.30×10⁻³	0.147	8.80×10⁻⁶	1.7×10⁴	99.7
Pu(VI)	3.59×10⁻³	0.151	9.90×10⁻⁵	1.5×10³	97.1
Am(III)	0.81×10⁻³	0.029	1.50×10⁻⁵	1.9×10³	98.2
Am(V)	1.55×10⁻³	0.030	0.72×10⁻³	42	54.0

[a] - Distribution coefficients, D, and extraction efficiencies, E, were calculated by equations (1) and (2):

$$D = [An]_{LR}/[An]_{aq}$$ (1);

$$E = (D/D+V_{aq}/V_{LR})\times100$$ (2),

where $[An]_{LR}$ and $[An]_{aq}$ denote the equilibrium concentrations of actinides in the LR and aqueous phases, respectively; V_{LR} and V_{aq} denote the volumes of those.

The presented data show a typical tendency of extraction parameters from oxidation state of recovered elements. The distribution coefficients and extraction efficiency are decreasing depending on valent state in the following order: (IV) > (VI) ·≥ (III) >> (V). The concentration factor varies from 60 to 80.

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

The use LR 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.

0.01M solution of Pr in 3 M HNO_3 was used in the experiment. The sample of molten aluminum phosphate glass was powdered. Immobilization of the reagent on a glass powder was done as follows. 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 by stirring and the product was dried at ambient temperature. Matrix of aluminum phosphate glass (2.5 g) contained 0.3 g DPDBCMPO. The prepared powder-like mass (1.73 g), containing $5.0 \cdot 10^{-4}$ moles of the reagent, was placed into a chromatographic column (5 mm i.d. and 40 mm h). At the first stage 1 ml of 3M HNO_3 was passed through the column to transform DPDBCMPO into LR. After that 5 ml of nitric acid solution, containing $5 \cdot 10^{-5}$ moles of praseodymium passed through the column, followed washing by 2 ml of 1 M HNO_3 at the rate of about 0.18 ml/min. The concentration of Pr(III) was measured spectrophotometrically.

Residual concentration of Pr(III) in the collected volume of solution after sorption and washing was $3 \cdot 10^{-4}$ M. Thus, as much as 99 % of 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 hours. 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 the ground matrix in nitric acid.

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 physical state of the product of their interaction and an extraction capacity of the compound formed. The use of the compound of reagent with nitric acid (LR) permits extraction of the metals in question more effectively in comparison with extraction by the DPDBCMPO solutions in organic solvents. It is promising for the processing acidic highly radioactive wastes because the use of toxic and environmentally hazardous organic solvents can be avoided.

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