

The use of 100% diphenyl(dibutylcarbamoylmethyl)phosphine oxide in the extraction of metals from nitric acid solutions

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A change in the physical state of diphenyl(dibutylcarbamoylmethyl)phosphine oxide (D ϕ DBCMPPO) upon contact with an acidic solution is described and the composition of the complex formed by the reagent and the acid is established. The quantitative characteristics of the extraction capacity of this complex are found using praseodymium as an example, and the advantages of using 100% D ϕ DBCMPPO are shown.

Reagents of the kind bidentate neutral organophosphorus compounds (BNOC), in particular, diaryl(dialkylcarbamoylmethyl)phosphine oxides (CMPO), are known to be promising reagents for the extraction of radionuclides (lanthanides and actinides) from the acidic waste solutions of radiochemical usage.^{1–4} Therefore, studies dealing with the behaviour of BNOC in the extraction of radionuclides are of primary scientific and practical importance.

The reagents of this class are solid powders. On contact with an acidic solution, the physical state of the carbamoyls [D ϕ DBCMPPO, diphenyl(dioctylcarbamoylmethyl)phosphine oxide, octylphenyl(diisobutylcarbamoylmethyl)phosphine oxide], dioxides (DPDO) as well as monoxides (trioctylphosphine oxide, triphenylphosphine oxide) changes; they transform with time into liquid oils, not miscible with the aqueous phase. This phenomenon was found for the first time for D ϕ DBCMPPO and was described previously.⁵ In this paper, we present the results of a study on the behaviour of D ϕ DBCMPPO used as an extractant (100%) for the extraction of praseodymium from nitric acid solutions.

The experimental procedures are briefly described. The concentration of praseodymium in solutions was determined on a 'Shimadzu' recording spectrophotometer connected to a PC. The PC provided control of the spectrophotometer and processing of the optical absorption spectra recorded. It was shown preliminarily that the optical density of 0.02–0.0004 M solutions of praseodymium in 1 M HNO₃ obeys the Lambert–Beer law at the absorption maximum (444 nm). The calculated molar absorptivity, equal to $9.4 \pm 0.8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, is in good agreement with the published data.⁶ It has been shown that the molar absorptivity of praseodymium decreases linearly following an increase in the concentration of nitric acid; it is equal to $8.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in 1 M HNO₃ and $4.7 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in 10 M HNO₃.

Thus, the above data indicate that spectrophotometry can be used for the quantitative determination of metals extracted from nitric acid solutions.

Extraction of praseodymium from nitric acid solutions with 100% D ϕ DBCMPPO. Extraction of praseodymium from nitric acid solutions with 100% D ϕ DBCMPPO was carried out by the following procedure. An exactly weighed aliquot of Pr(NO₃)₃·6H₂O was dissolved in 1 M HNO₃. The resulting solution was used for the preparation of working solutions of praseodymium with the required concentrations of the metal and required acidities. A weighed aliquot of the carbamoyl was introduced as powder into a working solution of praseodymium of a particular volume. The resulting mixture was shaken for 3 min and centrifuged; the concentration of praseodymium in the aqueous phase was determined by spectrophotometry. These operations were repeated as new aliquots of the reagent were introduced into the tested solution.

It was found that in 0.12 M HNO₃, the reagent remains in solution over the period of extraction and centrifugation as a loose powder. In 1 M HNO₃ over the same period, the reagent forms a lump of irregular shape which looks as if it is covered by an oily film. When the acidity is increased further, the

Table 1 Extraction of praseodymium with 100% D ϕ DBCMPPO from nitric acid solutions. The volume of nitric acid solution was 2 ml; the initial concentration of Pr^{III} in the nitric acid solution was 4×10^{-3} M.

[HNO ₃]/M	Concentration ^a of D ϕ DBCMPPO/ 10^{-3} M	Molar absorptivity, <i>D</i>	Extraction efficiency, <i>E</i> (%)
0.12	8	0.028	2.75
	20	0.098	8.5
	40	0.205	17.0
	60	0.278	21.75
	80	0.290	22.5
	120	0.311	23.75
1.0	300	0.311	23.75
	10	0.143	12.5
	20	0.572	33.5
	30	4.69	64.1
	50	7.91	88.8
	60	–	100
2.5	10	0.414	29.3
	20	2.78	73.6
	30	12.56	92.6
	40	–	100
4.0	10	0.587	37.0
	20	5.479	84.6
	30	–	100
6.0	10	0.625	38.7
	20	2.852	74.0
	30	–	100
8.0	5	0.233	18.9
	10	0.606	37.2
	15	1.804	64.3
	20	11.93	92.3
	25	–	100
10.0	5	0.455	31.3
	10	1.365	57.7
	15	2.569	72.0
	20	–	100

^aThe concentration of D ϕ DBCMPPO is conventional: calculated for a diluting agent with volume of aqueous phase 2 ml.

reagent transforms into the liquid state more easily, and the excess of D ϕ DBCMPPO needed to attain 100% extraction of the metal becomes smaller (Table 1).

Quantitative extraction of the element can also be accomplished from weakly acidic solutions if the reagent is converted into the liquid state beforehand by shaking it with nitric acid (2–3 M). Thus, praseodymium present at a concentration of 4×10^{-3} M is completely extracted from 0.12 M HNO₃ by shaking for 3 min with the reagent transformed preliminarily into its compound with nitric acid. When D ϕ DBCMPPO is used as a powder (see Table 1, acidity 0.12 M), the degree of extraction of the metal does not exceed 24%, despite the fact that an almost 75-fold excess of the reagent (0.3 M) with respect to the metal is used. When the concentration of Pr(NO₃)₃ is high (3 M) but the acidity is low (0.12 M), D ϕ DBCMPPO is not converted into the liquid state.

Thus, the acidity of the solution and the interaction of nitric acid with the reagent are crucial factors determining the

Table 2 Correlation between the weight of the dry reagent and the reagent transformed into the liquid state. In entries 1, 3 and 6, the concentration of the acid was 4.7 M, and the volumes were 8, 4 and 2 ml, respectively. In entries 2, 4 and 5, the concentration of the acid was 4.18 M, and the volume was 2 ml.

Entry	Weight of the dry carbamoyl/g	Weight of the liquid carbamoyl/g
1	0.9396	1.2056
2	0.6936	0.8796
3	0.5839	0.7398
4	0.4159	0.5340
5	0.2254	0.3263
6	0.1050	0.1290

physical state of the reagent and its extraction capacity.

Interaction of D ϕ DBCMPO with nitric acid. Previously, the interaction of triethylphosphine oxide, dibutyl(diethylcarbamoylmethyl)phosphine oxide, phenylethyl(diethylcarbamoylmethyl)phosphine oxide, D ϕ DBCMPO, dibutyl-*N,N*-diethylcarbamoylmethylphosphonate and tributylphosphate with nitric acid had been studied in dichloroethane and tetrachloromethane by thermometric titration and by IR spectroscopy.⁷ It was shown that at a [D ϕ DBCMPO]:[HNO₃] ratio ranging from 1:1 to 1:4, complexes of the composition 1:1 and 1:2 are formed. The first molecule of nitric acid adds to the phosphoryl group (P=O) and the second molecule adds to the carbamoyl group (C=O). No complexes of other compositions were detected even at a considerable excess of the acid.

It was of interest to consider the interaction of D ϕ DBCMPO with nitric acid in the absence of an organic solvent and to elucidate the relationship between the weight of the dry reagent taken and the volume of the liquid phase resulting from the interaction of the reagent with the acid. In particular, this is necessary for the calculation of the distribution factors for extraction of elements. In the majority of cases, the [HNO₃]:[D ϕ DBCMPO] ratios were chosen to be greater than 10, because these ratios provide the most efficient extraction of transplutonium and rare earth elements with solutions of this reagent in organic solvents.¹⁻⁴

For this purpose, the following procedure was used. A sample of D ϕ DBCMPO powder was placed into a previously weighed volumetric test tube, and its weight was determined. The required volume of HNO₃ of a known concentration was then added, and its weight was also determined. The test tube containing the acid and the D ϕ DBCMPO powder was shaken for 3 min, and the mixture was centrifuged for 10 min to separate the phases. It was found that this duration of contact was sufficient for the reagent to transform into a liquid oily phase, which could be easily separated from the aqueous phase. The test tube with the contents was weighed once again to make a correction for the slight concentration of the solution during centrifugation. After that, the aqueous solution was completely removed from the tube (the remaining aqueous phase was removed from the surface of the oily liquid and from the walls of the tube by purging with argon). The tube was weighed once again, and the weight of the liquid reagent was determined as the difference. The results of these experiments are listed in Table 2.

The density of the liquid carbamoyl determined by pycnometry was equal to $1.163 \pm 0.012 \text{ g cm}^{-3}$. Thus, the volume of the liquid reagent can be easily found from its weight and density, the weight being calculated from the weighed aliquot of dry D ϕ DBCMPO.

The increase in the weight of the reagent upon contact with a solution of nitric acid indicates that a compound of the reagent with nitric acid is formed. The solubility of this compound (the viscous oily liquid) in an aqueous nitric acid solution (1.34 mg mL^{-1} , according to a previous study⁵) plays no significant role in the weight balance.

To calculate the quantity of acid bound to the carbamoyl group, the volumes and concentrations of the acid in the initial solution and in the solution obtained after extraction were used.

Table 3 Praseodymium extraction under various conditions.

Extraction method	Pr ^{III} distribution factor	Pr ^{III} extraction efficiency (%)
IR	1.34	52
LE with DCE	0.095	8.7
LE with DCE ^a	0.097	8.8
IR	1.61	62
LE with fluoropol	0.48	32.5
LE with fluoropol ^a	0.45	30.8

In each case, the acidity was determined by pycnometry and by titration. The average values were used in the calculations. Weighed portions of dry D ϕ DBCMPO of 0.498, 0.506 and 0.505 g (or 1.34, 1.36 and 1.36 mmol) were found to absorb 0.089, 0.085 and 0.085 g (1.41, 1.35 and 1.35 mmol) of nitric acid, respectively. This corresponds to a reagent:nitric acid molar ratio close to 1. The total gain in weight upon formation of the liquid phase of the complex amounted to 0.141, 0.161 and 0.145 g, respectively. The fact that the total excess weights are greater than the weights of the absorbed acid (by 0.052, 0.076 and 0.06 g, respectively) can be explained by assuming that water is incorporated in the complex. The quantities of water correspond to a reagent:water ratio ranging from 2 to 3. Thus, in this case (unlike the previous study⁷) a complex of composition D ϕ DBCMPO·HNO₃·*n*H₂O (*n* = 2–3) is formed.

The optical absorption spectrum of this compound is a curve, which increases monotonically following a decrease in the wavelength starting from 500 nm. The spectrum of the Pr complex with the reagent in the form of D ϕ DBCMPO·HNO₃·*n*H₂O is virtually identical to that of an aqueous solution of praseodymium in nitric acid. The only difference between them is that the absorption bands are slightly (by 2–3 nm) displaced to longer wavelengths. The molar absorptivity is 8.9, *i.e.* it is equal to that of the aqueous solution of praseodymium.

Thus, upon contact of D ϕ DBCMPO with a nitric acid solution, the reagent changes its physical state and passes into a viscous liquid as the complex D ϕ DBCMPO·HNO₃·*n*H₂O, where *n* = 2–3. It was of interest to compare the characteristics of extraction of metals by the reagent as the compound with nitric acid (below referred to as RE) and by the reagent in its usual form dissolved in the organic phase (below referred to as LE). This was done using praseodymium as the standard metal.

Extraction of praseodymium by the compound of the reagent with nitric acid (IR) and by the reagent dissolved in an organic solvent (LE). Dichloroethane and fluoropol – in which D ϕ DBCMPO exhibits the maximum extraction capacity⁵ – were used as solvents for the reagent. The experiment was carried out as follows. Two aliquots of a solution with equal volumes (2 ml), acidities (5.8 M) and praseodymium concentrations (0.008 M) were prepared. A weighed sample (18.56 mg) of the dry reagent was added to the first aliquot, so that its concentration (0.025 M) exceeded the praseodymium concentration by a factor of three (the condition for extraction by 50%). An equal volume (2 ml) of an organic solution containing the same quantity of the reagent in an appropriate solvent was introduced into the second aliquot. The mixtures were then shaken for 3 min and centrifuged, and the aqueous phases were analysed for the remaining metal. After that, an equivalent volume of solvent was added to the first heterogeneous solution. The extraction followed by centrifugation and by the analysis of the aqueous phase for Pr was repeated (marked ^a in Table 3). The results obtained are presented in Table 3.

It can be seen that the efficiency of praseodymium extraction by a compound of the reagent with nitric acid (D ϕ DBCMPO·HNO₃·*n*H₂O) is about twice that of the standard liquid extraction by the same reagent in fluoropol and is six times greater than that of liquid extraction by the reagent in dichloroethane. When the reagent with the metal is dissolved in a solvent and brought into contact with the same aqueous phase, re-extraction of the metal into water occurs, according to its distribution factor corresponding to liquid extraction.

Thus, this study has shown that upon contact with a solution of nitric acid, the D ϕ DBCMPO powder changes its physical state and is converted with time into a viscous oily liquid, not miscible with the aqueous phase. The acidity of the solution and the interaction of nitric acid with the reagent are crucial factors determining both the physical state of the product of their interaction and the extraction capacity of this compound with respect to metals. The use of the complex formed by the reagent with nitric acid (D ϕ DBCMPO \cdot HNO $_3$ \cdot n H $_2$ O, where $n = 2-3$) permits more efficient extraction of metals than liquid extraction by D ϕ DBCMPO dissolved in organic solvents. This method is promising for the processing of highly radioactive acidic wastes, because in this case, the use and subsequent utilisation of toxic organic solvents is avoided.

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