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Extraction of Rare-Earth Elements(III) from Nitric Acid Solutions with Bis(diarylphosphorylmethyl)benzenes

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Abstract—Extraction of micro quantities of rare-earth elements(III) from HNO_3 solutions as complexes with *bis*(diarylphosphorylmethyl)benzenes depending on the nature of organic diluent and HNO_3 concentration in equilibrium aqueous phase was studied, the stoichiometry of extracted complexes was determined. The effect of structure of a bridge between two phosphine oxide fragments in an extractant molecule on the efficiency and selectivity of rare-earth elements(III) extraction was considered.

Bidentate neutral organophosphorus compounds (BNOPCs), in particular substituted alkylenediphosphine dioxides, are known to show high extraction ability toward actinides and rare-earth elements (REEs) in nitric acid solutions [1, 2]. Extraction properties of methylenediphosphine dioxides were studied in the most detail [3–5]. It was found [5] that the extraction ability of these compounds toward actinides and rare-earth elements increases considerably when alkyl groups at one or two phosphorus atoms are replaced by aryl fragments. The reasons of this phenomenon named in the literature as an "effect of anomalous aryl strengthening" (EAAS) of extracted complexes [5] was discussed many times in the literature [3–8]. Elongation of the alkylene bridge in molecules of tetraphenylalkylenediphosphine dioxides is accompanied by decrease in their extraction ability toward Am(III) and light REE(III) [5] and change in the extraction order in REE(III) series, which results in change in the within-group selectivity of these extractants [9]. In certain cases, the replacement of the alkylene bridge in tetraphenylalkylenediphosphine dioxides by ethylene glycol fragments leads to the growth of extraction ability of the corresponding phosphoryl-containing podands toward REE(III)

[10]. *o*-Oxyphenylenemethylenediphosphine dioxides with aryl substituents at the phosphorus atoms exhibit especially high extraction ability toward REE(III) and Am(III) [11]. A considerable EAAS is observed on extraction of REE(III) and Am(III) with these compounds from nitric acid solutions. This effect is exhibited in a lesser extent on extraction of REE(III) and Am(III) with solutions of *meta* isomers of *bis*(diarylphosphorylmethyl)benzenes in chloroform [12, 13].

There are no systematic data in the literature on the extraction of REE(III) with (diarylphosphorylmethyl)benzenes, therefore the aim of this work is to study the effect of structure of bridge between the phosphoryl groups of extractant molecule on extraction efficiency and within-group selectivity for REE(III). For this purpose, we considered certain features of interfacial distribution of REE(III) nitrates between aqueous HNO_3 solutions and solutions of *bis*(diarylphosphorylmethyl)benzenes **I** and **II** in organic diluents. Data on the extraction of REE(III) with dioxides **III–V**, phosphoryl-containing podands **VI**, **VII**, and monophosphoryl compound **VIII** were presented for comparison.

I

IIa, b
IIa, R = Ph; **IIb**, R = *p*-Tol

III−V III, *n* = 1; **IV**, *n* = 4; **V**, *n* = 5

VI

VII

VIII
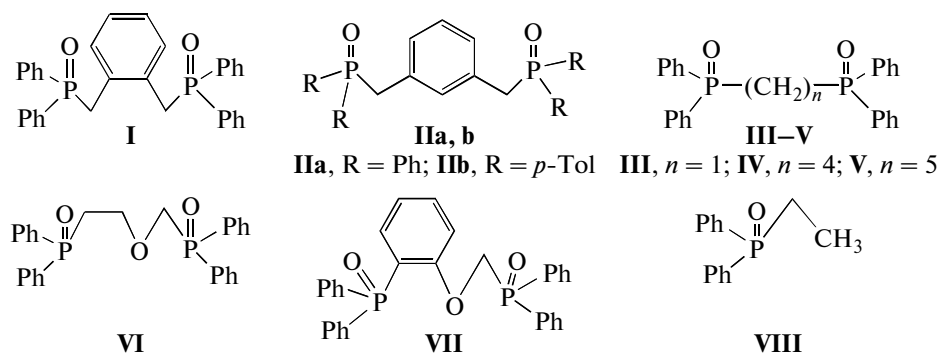
EXPERIMENTAL

1,2-Phenylene-*bis*(methylene)*bis*(diphenylphosphine oxide) (I). A mixture of 2.50 g (0.013 mol) of diphenylphosphinous acid, 1.22 g (0.007 mol) of *o*-xylylene dichloride, and 15 mL of hexamethyldisilazane was stirred for 6 h at 110°C in a dry argon flow and evaporated in a vacuum. The residue was dissolved in 15 mL of CHCl$_3$, the solution was washed with 15% solution of Na$_2$CO$_3$ (2 × 15 mL), water (2 × 15 mL), and diluted (1 : 1) HCl (2 × 15 mL) and evaporated in a vacuum. The residue was chromatographed on a column with silica gel L (eluent used was CHCl$_3$ and CHCl$_3$: *i*-PrOH (100 : 1)). Yield 3.15 g (89%), mp 282−284°C (ethanol) (283−284°C [14]).

1,3-Phenylene-*bis*(methylene)*bis*(diphenylphosphine oxide) (IIa). Diphenylphosphinous acid−acetone complex (3.05 g, 0.012 mol) was kept for 3 h at 1 mmHg and 150−160°C (in a bath), 10 mL of hexamethyldisilazane was added, and the mixture was kept for 3 h at 110°C in a dry argon flow, next 0.87 g (0.005 mol) of *m*-xylylene dichloride was added, the mixture was stirred at 110°C for 8 h and concentrated in a vacuum. The residue was dissolved in 15 mL of CHCl$_3$, the solution was washed with 15% solution of Na$_2$CO$_3$ (2 × 15 mL), water (2 × 15 mL), and diluted (1 : 1) HCl (2 × 15 mL) and evaporated in a vacuum. The residue was chromatographed on a column with silica gel L (eluent used was CHCl$_3$ and CHCl$_3$: *i*-PrOH (100 : 1)). Yield 1.90 g (75.0%), mp 89−92°C (benzene−hexane) (91−93°C [15]).

^{1}H NMR (CDCl$_3$, δ, ppm): 3.53 (d, 4H, $^2J_{H-P}$ = 13.80 Hz, P(O)C$\underline{H}_2$-Ar), 6.88 (m, 4H, Ar−H), 7.41−7.68 (m, 10H, Ar−H).

^{31}P NMR (CDCl$_3$, δ, ppm): 39.02.

1,3-Phenylene-*bis*(methylene)*bis*(di(*p*-tolyl)phosphine oxide) (IIb). A mixture of 3.66 g (0.016 mmol) of di(*p*-tolyl)phosphinous acid and 16 mL of hexamethyldisilazane was stirred for 3 h at 110°C, next 1.23 g (0.007 mol) of *m*-xylylene dichloride was added, the mixture was stirred at 110°C for additional 15 h and evaporated in a vacuum. The residue was dissolved in 15 mL of CHCl$_3$, the solution was washed with 15% solution of Na$_2$CO$_3$ (2 × 15 mL), water (2 × 15 mL),

and diluted (1 : 1) HCl and evaporated in a vacuum. The residue was chromatographed on a column with silica gel L (eluent used was CHCl$_3$ and CHCl$_3$: *i*-PrOH (100 : 1)). Yield 2.60 g (67%), mp 148−150°C (benzene−hexane).

For C$_{36}$H$_{36}$O$_2$P$_2$ anal. calcd. (%): C, 76.85; H, 6.46; P, 11.01.

Found (%): C, 76.76, 76.80; H, 6.34, 6.43; P, 11.00, 10.97.

^{1}H NMR (CDCl$_3$, δ, ppm): 2.99 (s, 6H, 2Ar-C$\underline{H}_3$), 3.50 (d, 4H, $^2J_{H-P}$ = 13.80 Hz, P(O)C$\underline{H}_2$-Ar), 6.93 (m, 4H, Ar−H), 7.02−7.56 (m, 8H, Ar−H).

^{31}P NMR (CDCl$_3$, δ, ppm): 39.18.

We described the synthesis of tetraphenylmethylenediphosphine dioxide **III** earlier [16].

1,4-*bis*(Diphenylphosphoryl)-2-oxabutane (VI). Potassium hydroxide (0.1 g, 1.8 mmol) and 2.3 g (10.0 mmol) of diphenylvinylphosphine oxide were added to a solution of 2.3 g (10.0 mmol) of 2-diphenylphosphorylmethanol in 25 mL of dry dioxane. The mixture was heated to 80°C, cooled to 20°C and kept for 48 h, then the solvent was removed in a vacuum. Twenty five milliliters of water was added to the residue and the mixture was extracted with CHCl$_3$ (3 × 20 mL). The extract was washed with diluted (1 : 1) HCl (25 mL), water (3 × 20 mL) and the solvent was removed in a vacuum. The residue was chromatographed on a column with silica gel (eluent used was CHCl$_3$). Yield 2.5 g (52%), mp 179−180°C (benzene−hexane).
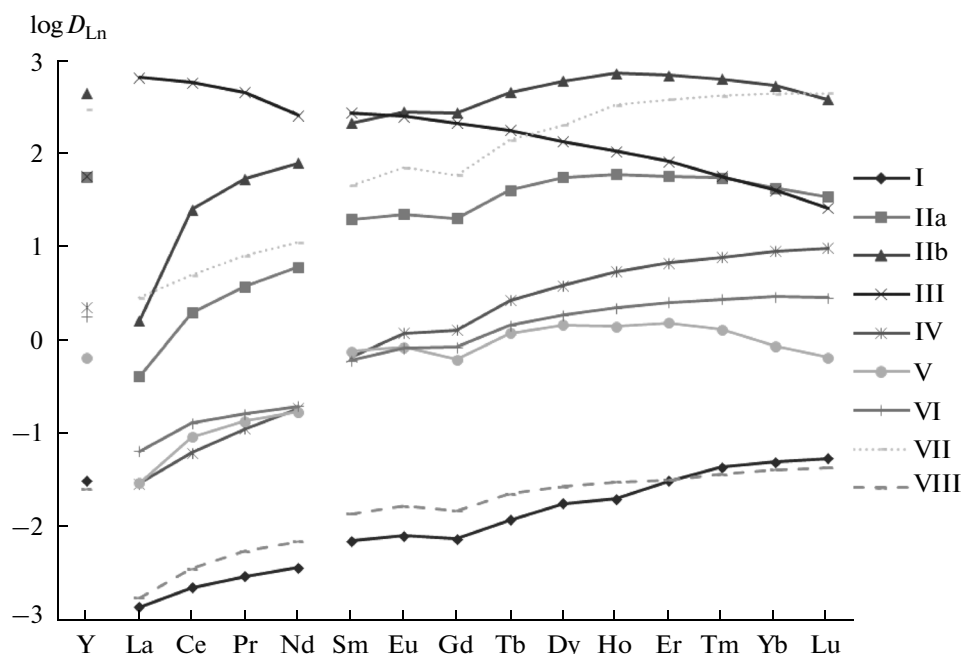
For C$_{27}$H$_{26}$O$_3$P$_2$ anal. calcd. (%): C, 70.70; H, 5.67; P, 13.47.

Found (%): C, 76.70, 70.56; H, 5.45, 5.43; P, 13.20, 13.35.

^{1}H NMR (CDCl$_3$, δ, ppm): 2.64 (m, 2H, OCH$_2$C$\underline{H}_2$P(O)Ph$_2$), 3.88 (m, 2H, C$\underline{H}_2$CH$_2$P(O)Ph$_2$), 4.20 (2H, $^2J_{H-P}$ = 8.0 Hz, C$\underline{H}_2$P(O)Ph$_2$) 7.44 (m, 12H, Ar−H), 7.72 (m, 8H, Ar−H).

^{31}P NMR (CDCl$_3$, δ, ppm): 27.55, 29.39.

Compounds **IV**, **V**, **VII**, and **VIII** were obtained as described in [17−19].

Fig. 1. Extraction of REE(III) from 4 M solution of NH_4NO_3 with 0.01 M solutions of compounds **I**, **IIa**, **IIb**, **III−VII** [9] and 0.02 M solution of compound **VIII** [9] in dichloroethane.

Solvents used in extraction experiments were nitrobenzene, 1,2-dichloroethane, chloroform, and toluene of reagent grade without additional purification. Extractant solutions were prepared from precisely weighed amounts.

The distribution of micro amounts of REE(III) on their combined presence was studied on model solutions 4 mol/L NH_4NO_3 or 0.1−7 mol/L HNO_3. Initial concentration of each REE(III) nitrate was 1×10^{-5} mol/L. Extraction experiments were conducted in test tubes with ground stoppers at ambient temperature and volume ratio of organic and aqueous phase of 1 : 1. The phases were contacted in an apparatus for stirring at the rate of 60 rpm for 1 h, which is sufficient to reach constant values of REE distribution ratios (D_{Ln}).

The concentration of REE(III) in initial and equilibrium aqueous solutions was determined by inductively coupled plasma mass spectrometry using Thermo Elemental X-7 mass spectrometer (USA) by previously described procedure [20]. Content of elements in organic phase was determined after back extraction with 0.1 M solution of hydroxyethylidenediphosphonic acid, distribution ratios were calculated as the ratios of their concentrations in equilibrium phases. Error of determination of distribution ratios was not larger 5%. Concentration of HNO_3 in equilibrium aqueous phases was determined by potentiometric titration with KOH solution.

RESULTS AND DISCUSSION

Effect of structure of bridge between phosphoryl groups in molecules of dioxides **I−VII** on the efficiency of REE(III) extraction and within-group selectivity of the extractants was assessed by comparison of D_{Ln} values determined under the same experimental conditions (Fig. 1). A decrease of D_{Ln} with increase in atomic number (Z) of REE is observed for tetraphenylmethylenediphosphine dioxide **III**. The same character of dependence of $\log D_{Ln}$ vs Z was observed for extraction of REE(III) with other BNOPCs with methylene bridge between phosphoryl groups [21, 22], which was explained by increase in the hydration energy of REE(III) ions due to decrease of their ionic radii as Z rises [23]. It was shown [9] that the elongation of the alkylene bridge in molecules of dioxides $Ph_2P(O)(CH_2)_nP(O)Ph_2$ leads to inversion of dependence of $\log D_{Ln}$ vs Z. This results in the consecutive decrease of separation factor for La and Lu ($\beta_{La/Lu} = D_{La}/D_{Lu}$) in the series of dioxides from 25 ($n = 1$, compound **III**) to 0.003 ($n = 4$, compound **IV**).

Figure 1 shows that D_{Ln} increases with Z in the extraction of REE(III) with compounds **I**, **IIa**, **IIb**, and **IV−VII**. The nature of fragment connecting phosphoryl groups in these molecules substantially affects both REE(III) extraction efficiency and the magnitude of separation factor for Lu and La ($\beta_{La/Lu} = D_{La}/D_{Lu}$). The replacement of one methylene group in the alkylene bridge of dioxide **IV** by oxygen atom leads to negligible growth of D_{Ln} for light REE(III) and drop of D_{Ln} on extraction of heavy REE(III) with podand **VI**. The replacement of dimethylene bridge in podand

log D_{Ln}
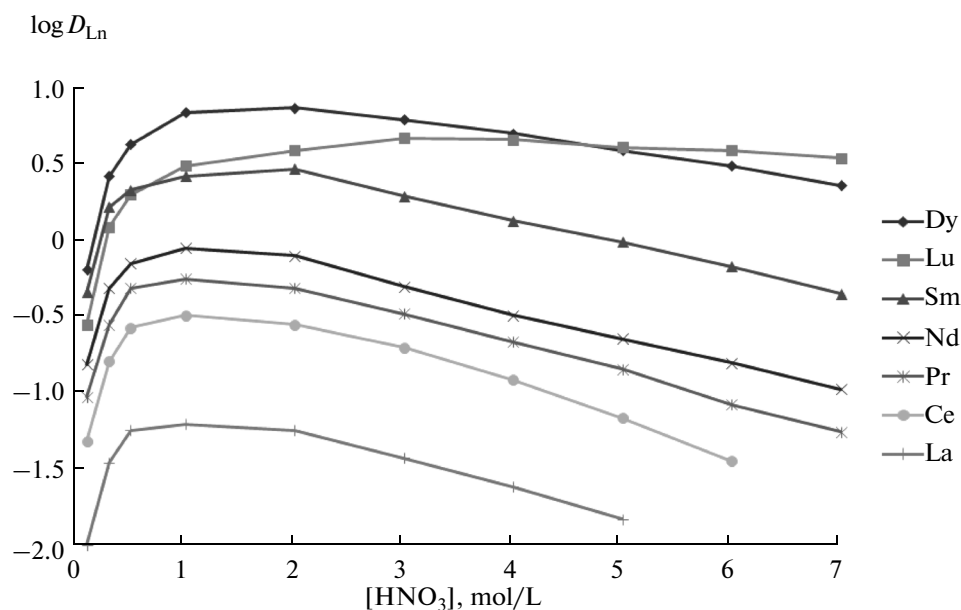
Fig. 2. Dependence of REE(III) distribution ratios on HNO$_3$ concentration in equilibrium aqueous phase on extraction with 0.01 M solution of compound **IIb** in dichloroethane.

VI molecule by *o*-phenylene fragment is accompanied by considerable enhancement of D_{Ln} on extraction with podand **VII** (Fig. 1), the difference in the extraction ability of these compounds $D_{Ln}(VII)/D_{Ln}(VI)$ rises in the series of REE(III) from 43.5 (La) to 148 (Ho) and then remains constant. At the same time, the total effect of introduction of ethereal oxygen atom and *o*-phenylene fragment into molecule of dioxide **IV** leads to decrease of $D_{Ln}(VII)/D_{Ln}(IV)$ in the series of REE(III) from 98 (La) to 46 (Lu) that causes drop of $\beta_{Lu/La}$ in passing from compound **IV** (330) to **VII** (155).

The replacement of tetramethylene bridge in the molecule of dioxide **IV** by *o*-phenylene fragment leads to the sharp drop of D_{Ln} and $\beta_{Lu/La}$ on extraction with compound **I**. The extraction ability of compound **I** is not larger than that of monodentate compound **VIII** (Fig. 1) which may be caused by steric hindrances for the bidentate coordination of ligand **I** on complexation with Ln^{3+} ions. On the other hand, its *meta* isomer, compound **IIa**, shows much larger extraction ability and Lu/La selectivity than dioxide **V** with pentamethylene fragment between PO groups. The extraction ability of dioxide **IIa** toward Tm(III), Yb(III), and Y(III) equals to that of dioxide **III**. The data of Fig. 1 shows that dioxide **IIa** has lower extraction ability and Lu/La selectivity than podand **VII**, however, the selectivity of extraction of light REE(III) in the system with compound **IIa** is markedly higher ($\beta_{Sm/La}$ = 48 and 16 for **IIa** and **VII**, respectively). The replacement of phenyl groups in compound **IIa** by *p*-tolyl fragments leads to considerable increase in the

extraction ability of compound **IIb** and its selectivity ($\beta_{Lu/La}$ = 234, $\beta_{Sm/La}$ = 132).

Compound **IIa** extracts REE(III) from acidic solutions considerably less efficiently than from neutral solutions. Thus, the values of D_{Eu} for extraction with 0.01 M solution of compound **IIb** in dichloroethane from 4 M solutions of HNO$_3$ and NH$_4$NO$_3$ are 1.8 and 282, respectively, which is caused by considerable co-extraction of HNO$_3$ [13]. We studied the effect of HNO$_3$ concentration in aqueous phase on the extraction of REE(III) with solutions of compound **IIb** in dichloroethane (Fig. 2) and obtained a dependence of log D_{Ln} versus [HNO$_3$] with maximum, which corresponds to the extraction of coordinatively–solvated REE(III) nitrates. This character of dependence of log D_{Ln} on [HNO$_3$] is associated with salting-out effect of NO$_3^-$ ions and binding of the extractant by nitric acid, as well as change in the values of activity coefficients of REE(III) nitrates depending on [HNO$_3$]. The position of maximum on the lg D_{Ln} vs [HNO$_3$] curve is shifted to the region of larger acidity of aqueous phase as Z value increases. In the region of low and moderate HNO$_3$ concentration in equilibrium aqueous phase, D_{Ln} value rises with Z.

The nature of organic solvent exhibits a considerable effect on the extraction efficiency of REE(III) with compound **IIb** from nitric acid solutions. The values of D_{Ln} increase in the series: toluene < chloroform < nitrobenzene < dichloroethane (Fig. 3). The position of nitrobenzene in this series differs from similar dependences for REE(III) and Am(III) extraction
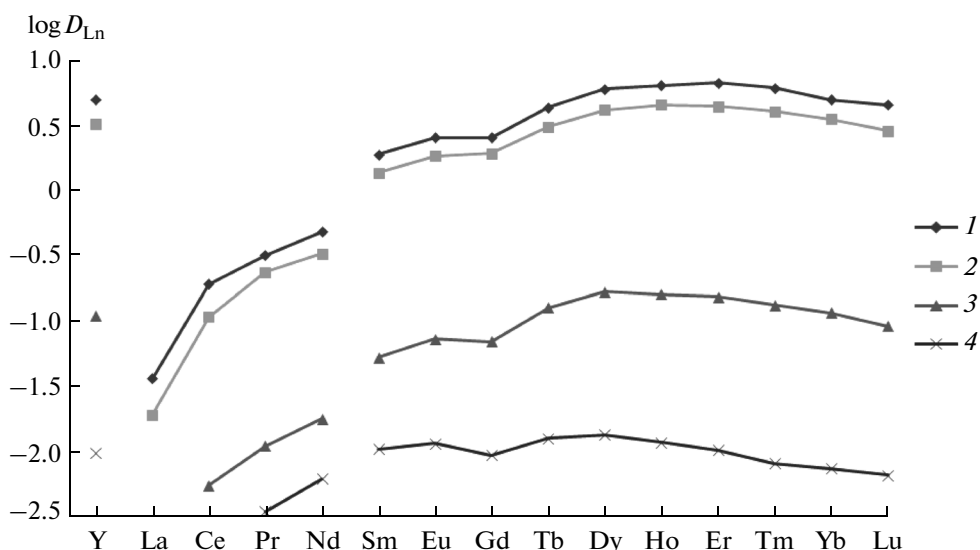
Fig. 3. Extraction of REE(III) from 3 M HNO_3 solution with 0.01 M solutions of compound **IIb** in dichloroethane (*1*), nitroben-zene (*2*), chloroform (*3*), and toluene (*4*).
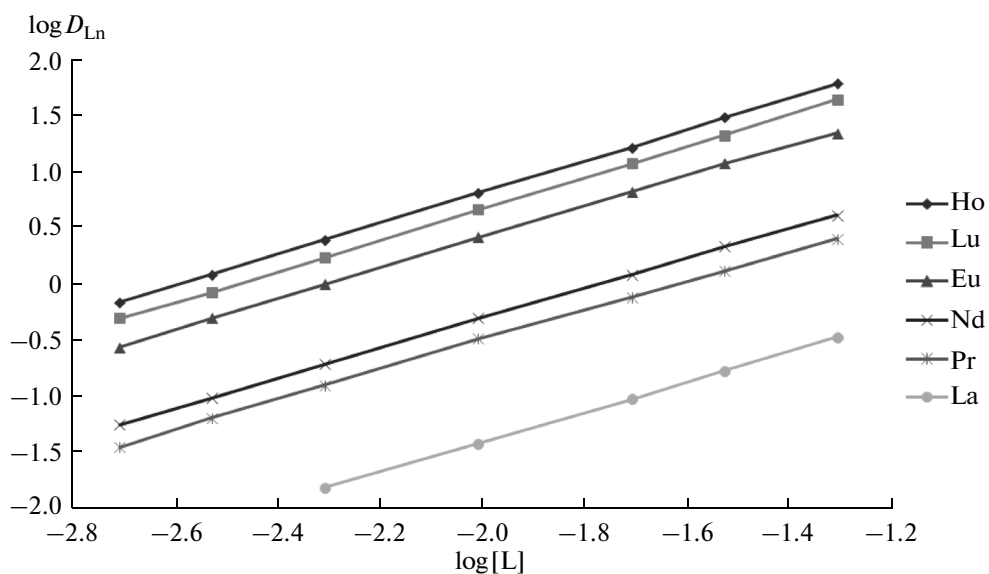

Fig. 4. Dependence of REE(III) distribution ratios on concentration of compound **IIb** in dichloroethane on extraction from 3 M HNO_3 solution.

from nitric acid solutions with other BNOPC [24, 25] when the use of nitrobenzene as a diluent leads to considerable growth of extraction efficiency as compared with solutions in dichloroethane. This feature seems to be associated with a considerable solvation of compound **IIb** by nitrobenzene.

Stoichiometric ratio REE(III) : extractant in the extracted complexes was determined by dilution method. Obtained data (Fig. 4) show that compound **IIb** extracts REE(III) as mono- and disolvates. Under

similar conditions, dioxide **III** and its tetratolyl-sub-stituted analog extracts REE(III) as di- and trisolvates [26, 27]. The decrease of solvation numbers in the extracted complexes of REE(III) with ligand **IIb** may be caused by the growth of steric hindrances in **IIb** molecule as compared with methylenediphosphine dioxides.

The comparison of extraction efficiency of REE(III) from HNO_3 solutions of moderate concentration showed that the extraction efficiency of *meta*
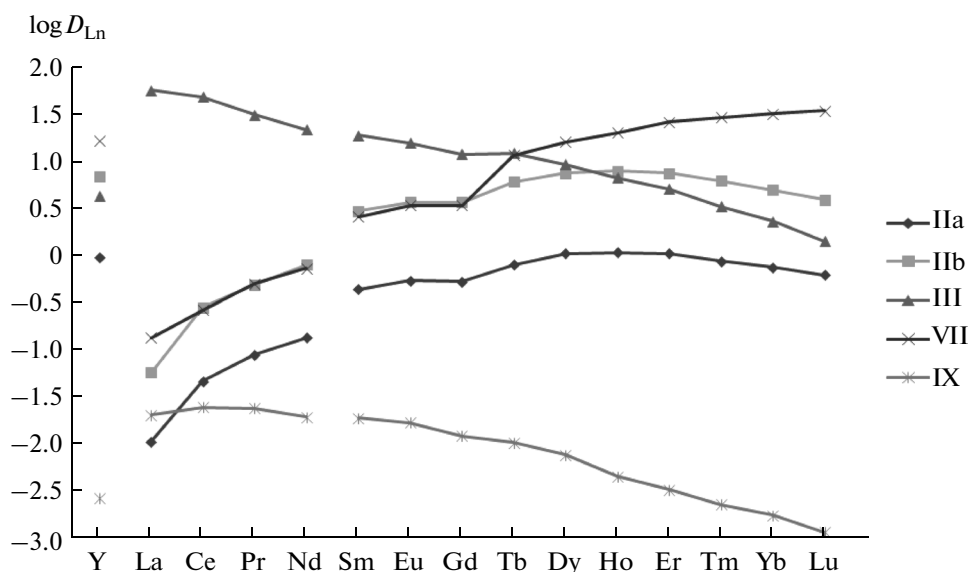
Fig. 5. Extraction of REE(III) from 2 M HNO_3 solution with 0.01 M solutions of compounds **IIa**, **IIb**, **III**, **VII**, and (dibutylcarbamoylmethyl)diphenylphosphine oxide (**IX**) [28] in dichloroethane.

isomers of *bis*(diarylphosphorylmethyl)benzenes **IIa** and **IIb** is lower than that of tetraphenylmethylenediphosphine dioxide **III** but considerably larger than the extraction efficiency of (dibutylcarbamoylmethyl)diphenylphosphine oxide (**IX**) (Fig. 5), whereas compound **I** does not extract REE(III) under these conditions ($D_{Ln} < 2 \times 10^{-3}$). Supplementary study is required to reveal the cause of higher extraction ability and Lu/La selectivity of podand **VII** as compared with dioxides **IIa** and **IIb**.

The presented data showed that the structure of bridge between the phosphoryl groups in BNOPC molecule has a considerable effect on both extraction ability and extraction order in the REE(III) series. 1,3-*bis*(Diarylphosphorylmethyl)benzenes exhibit high extraction ability toward heavy REE(III) and can be used for the selective recovery and preconcentration of these elements from nitric acid solutions.

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