



EXTRACTION PROPERTIES OF BIS[N-ALKYL-N-(2-DIPHENYLPHOSPHORYLETHYL)]DIGLYCOLAMIDES IN PERCHLORATE MEDIA

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A. N. Turanov,^a V. K. Karandashev,^b V. A. Khvostikov,^b K. V. Tcarkova,^c
O. I. Artyushin,^d and N. A. Bondarenko^{c*}

^a Osipyan Institute of Solid State Physics, Russian Academy of Sciences,
ul. Akad. Osip'yana 2, Chernogolovka, Moscow Oblast, 142432 Russia

^b Institute of Microelectronics Technology and High Purity Materials, Russian
Academy of Sciences, ul. Akad. Osip'yana 6, Chernogolovka,
Moscow Oblast, 142432 Russia

^c National Research Center "Kurchatov Institute", pl. Akad. Kurchatova 1,
Moscow, 123182 Russia

^d Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, str. 1, Moscow, 119334 Russia

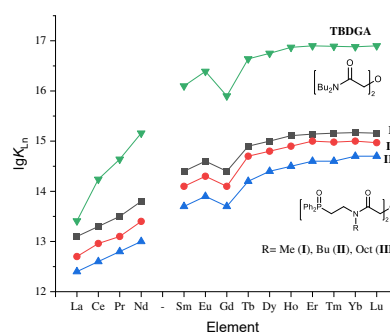
Abstract

The extraction properties of bis[N-alkyl-N-(2-diphenylphosphorylethyl)]diglycolamides [Ph₂P(O)CH₂CH₂N(R)C(O)CH₂]₂O (R = Me, Bu, Oct) towards rare-earth element(III) ions are studied in perchlorate media. It is established that the modification of diglycolamides with additional P(O)Ph₂ coordinating groups in the amide units of the molecule leads to an increase in the efficiency of extraction of rare-earth element(III) ions from perchloric acid solutions.

Key words: extraction, rare-earth element(III) ions, diglycolamides, perchloric acid.

Introduction

Individual rare-earth elements (REEs) and their compounds are extensively used in many high-tech fields of science and engineering, for example, in the production of modern high-coercive magnetic materials, luminophores, working elements for laser technology, and radiopharmaceuticals. Extraction methods have gained widespread popularity in extraction, concentration, and separation for REE(III) ions. The high extraction ability is characteristic of neutral mono- and multidentate organophosphorus compounds [1–8] as well as diglycolic acid diamides (DGA). Among the latter, tetraoctyl diglycolamide (TODGA) has been studied in the most detail since it exhibits valuable extraction properties such as compatibility with any saturated hydrocarbons, high hydrolytic and radiolytic stability [9–13]. It was established that upon complexation with REE(III) ions, TOGDA acts as a tridentate ligand [14]. The effect of the DGA structure on the extraction ability and selectivity was thoroughly explored [9–13]. In particular, the elongation of alkyl substituents was found to lead to a significant increase in the solubility of an extracting agent in organic solvents; however, it is accompanied by a decrease in the extraction efficiency of Am(III) and Eu(III) ions [9]. The replacement of the central ether oxygen atom in the TOGDA molecule for the C(O) group results in reduced extraction ability towards U(VI), Th(IV), and Nd(III) ions [15]. Based on the concept of preorganization of the ligands that take part in complex formation with metal ions, a series of multifunctional



compounds containing two, three, or four diglycolamide moieties were obtained [16–18]. Some of these compounds exhibited a higher extraction ability and selectivity compared to the starting diglycolamides.

Previously, we proposed an alternative approach to the modification of DGA that consists in the introduction of additional coordinating P=O groups into the amide unit of the molecule. We developed an original method for the synthesis of diglycolic acid bis[N-alkyl-N-(2-diphenylphosphorylethyl)]amides [Ph₂P(O)CH₂CH₂N(R)C(O)CH₂]₂O (I–III) (R = Me, Bu, Oct) and studied their spectral characteristics [19]. It was shown that the introduction of two P=O groups capable of coordinating with metal ions into the amide moieties of the DGA molecule leads to an increase in the efficiency of U(VI) extraction and a decrease in that of Th(IV) and REE(III) ions from nitric acid solutions when using dichloroethane solutions of modified DGAs I–III [20].

It is known that the extraction of actinides and REE(III) ions with solutions of bidentate organophosphorus compounds [21, 22] as well as substituted diglycolamides [23, 24] and dipicolinamides [25] increases significantly when passing from nitric acid to perchloric acid media. The possible reasons for such a "perchlorate effect" were discussed in a number of reports [22–26]. This effect was used to increase the efficiency of concentration of U(VI), Am(III), and REE(III) ions from nitric and phosphoric acid solutions by adding small amounts of HClO₄ or alkali metal perchlorates to the aqueous phase [21].

In this work, we continued the investigations on the extraction properties of modified DGAs **I–III** and studied the extraction of REE(III) ions in perchlorate media compared to the well-known extracting agent tetrabutyl diglycolamide (TBDGA), which behavior under similar conditions was studied by our research group earlier [27]. It should be noted that there are no related data for tetraoctyl diglycolamide in a perchlorate medium. Dichloroethane was used as a solvent due to the limited solubility of diamides **I–III** in chloroform.

Results and discussion

The influence of substituents at the nitrogen atom in diamides **I–III** on the efficiency of extraction of REE(III) ions from NaClO₄ solutions was examined. As can be seen from Fig. 1, the values of D_{Ln} increase in the series **III** < **II** < **I** as the length of the alkyl substituent at the nitrogen atom decreases. This is likely to be associated with the effect of the steric factor during complexation with Ln³⁺ ions. The efficiency of extraction of REE(III) ions from perchlorate solutions increases with increasing atomic number (Z). This is connected with an increase in the stability of REE(III) complexes with hard (according to the hard and soft acids and bases theory) ligands as the charge density of Ln³⁺ ions increases due to a decrease in their ionic radii with increasing Z [28]. A similar D_{Ln} – Z dependence was observed upon the extraction of REE(III) ions with DGA solutions from nitrate [20] and perchlorate [27] media. Of note is a minimum on the $\lg D_{Ln}$ – Z dependence in the case of Gd(III) (Fig. 1), which was also observed in other extraction systems [20, 27]. However, in the literature this fact is only stated.

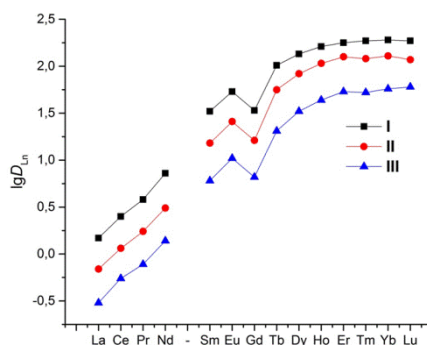


Figure 1. REE(III) distribution coefficients upon extraction with 0.005 M dichloroethane solutions of compounds **I–III** from 0.01 M NaClO₄ solutions.

The stoichiometry of the extracted complexes was determined by the equilibrium shift method. At the constant concentration of extracting agents in the organic phase, an increase in the concentration of NaClO₄ in the aqueous phase is accompanied by an increase in D_{Ln} , and the slopes of the $\lg D_{Ln}$ – $\lg[\text{ClO}_4^-]$ dependences are close to 3 (Fig. 2). This indicates the participation of three ClO₄[–] anions in the formation of the extracted complexes.

Figure 3 shows the results of determining the stoichiometric metal–ligand **II** ratio in the extracted complexes. At a constant concentration of NaClO₄ in the aqueous phase, the slopes of the $\lg D_{Ln}$ – $\lg[L]$ dependences are close to 3. This implies the extraction of REE(III) ions with diamide **II** in the form of trisol-

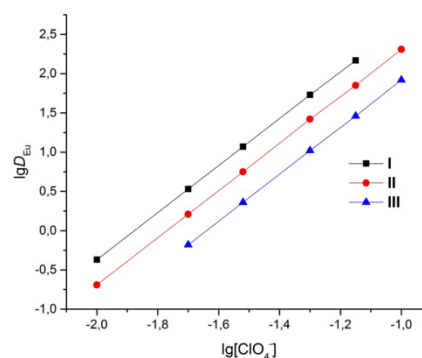


Figure 2. Dependence of the Eu(III) distribution coefficients on the concentration of NaClO₄ in the aqueous phase upon extraction with 0.001 M dichloroethane solutions of compounds **I–III**.

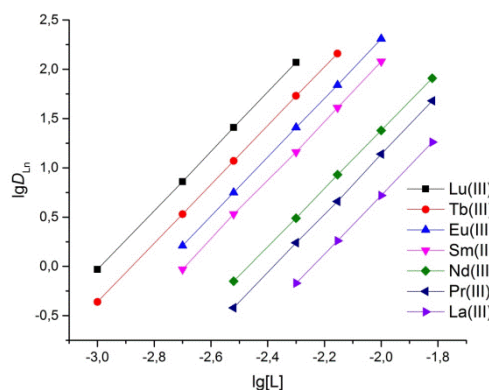
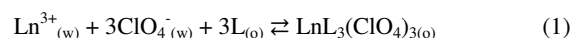


Figure 3. Dependence of the REE(III) distribution coefficients on the concentration of compound **II** in dichloroethane upon extraction from 0.01 M NaClO₄ solution.

vates. The same REE(III)/ligand ratio was achieved in the case of compounds **I** and **III**. Complexes of a similar composition were detected earlier upon extraction of REE(III) ions with dichloroethane solutions of TBDGA [27].

Taking into account the data on the stoichiometry of the extracted complexes, the process of extraction of REE(III) ions from perchlorate solutions with compounds **I–III** (L) can be described by the following equation



where symbols (o) and (w) denote the components of the organic and aqueous phases, respectively. The REE(III) extraction constants (K_{Ln}) are expressed as follows

$$K_{Ln} = \frac{[\text{LnL}_3(\text{ClO}_4)_3]_{(o)}[\text{Ln}^{3+}]_{(w)}^{-1}[\text{ClO}_4^-]_{(w)}^{-3}[\text{L}]_{(o)}^{-3}}{D_{Ln}[\text{ClO}_4^-]_{(w)}^{-3}[\text{L}]_{(o)}^{-3}} \quad (2)$$

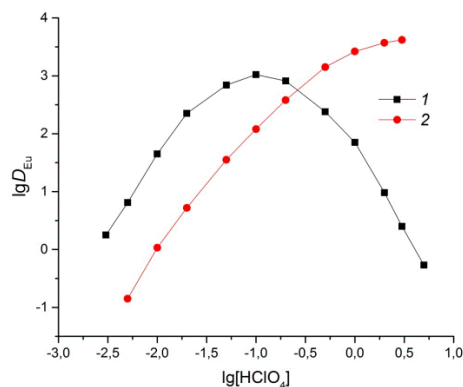
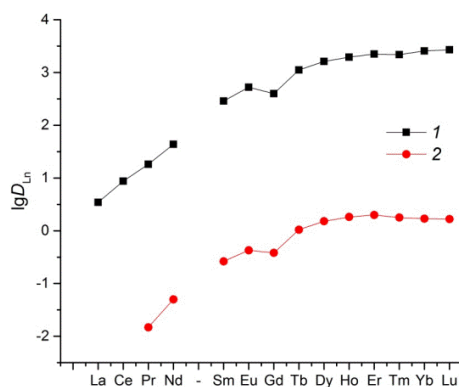
The values of the REE(III) extraction constants for compounds **I–III**, calculated by the least squares method, are listed in Table 1. For comparison, the values of K_{Ln} for TBDGA are also presented [27]. It can be seen that the extraction ability of compounds **I–III** towards REE(III) ions is almost two orders of magnitude lower than that of TBDGA. Apparently, the phosphoryl groups in compounds **I–III** do not take part in the complexation with REE(III) ions. Moreover, the donor ability of C=O groups in compounds **I–III**, which are involved in the complexation with REE(III) ions, is significantly reduced due to the negative induction effect of the phosphoryl groups in the amide units of these compounds.

Table 1. Extraction constants of REE(III) ions K_{Ln} from perchlorate solutions with dichloroethane solutions of compounds I–III and TBDGA

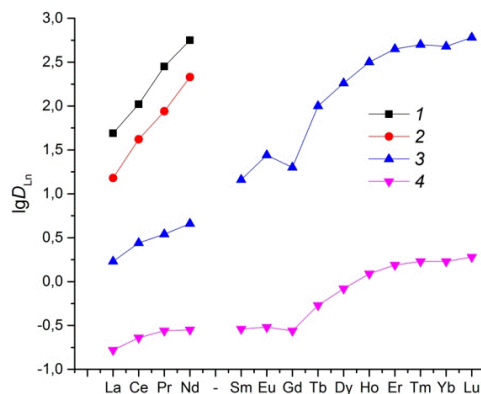
REE(III)	$\lg K_{Ln}$ (I)	$\lg K_{Ln}$ (II)	$\lg K_{Ln}$ (III)	$\lg K_{Ln}$ (TBDGA) [27]
La	13.07 ± 0.05	12.74 ± 0.05	12.38 ± 0.05	13.41
Ce	13.30 ± 0.05	12.96 ± 0.05	12.64 ± 0.05	14.24
Pr	13.48 ± 0.05	13.14 ± 0.05	12.79 ± 0.05	14.64
Nd	13.76 ± 0.05	13.39 ± 0.05	13.04 ± 0.05	15.16
Sm	14.42 ± 0.06	14.08 ± 0.06	13.68 ± 0.06	16.10
Eu	14.63 ± 0.05	14.31 ± 0.05	13.92 ± 0.05	16.39
Gd	14.43 ± 0.06	14.10 ± 0.06	13.72 ± 0.06	15.90
Tb	14.91 ± 0.05	14.65 ± 0.05	14.21 ± 0.05	16.64
Dy	15.03 ± 0.06	14.82 ± 0.06	14.42 ± 0.06	16.75
Ho	15.11 ± 0.05	14.93 ± 0.05	14.54 ± 0.05	16.87
Er	15.14 ± 0.06	15.01 ± 0.06	14.63 ± 0.06	16.90
Tm	15.16 ± 0.05	14.98 ± 0.05	14.62 ± 0.05	16.89
Yb	15.17 ± 0.06	15.01 ± 0.06	14.66 ± 0.05	16.88
Lu	15.16 ± 0.05	14.97 ± 0.05	14.68 ± 0.05	16.90

We compared the effect of the concentration of HClO_4 in the equilibrium aqueous phase on the value of the REE(III) distribution coefficients upon extraction with dichloroethane solutions of diamide II and TBDGA [27] (Fig. 4). In the system with TBDGA, the dependence of D_{Ln} on $[\text{HClO}_4]$ has a maximum, the presence of which can be explained by the salting out effect of ClO_4^- ions and binding of the extracting agent with perchloric acid, which is typical for the extraction of REE(III) ions by the solvate mechanism [7]. In the case of extraction with a solution of diamide II, the values of D_{Ln} increase with an increase in the concentration of HClO_4 in a much larger range of $[\text{HClO}_4]$ than in the case of the extraction with TBDGA solution (Fig. 4). In the region of low HClO_4 concentrations, TBDGA extracts REE(III) ions much more efficiently than diamide II; however, at $[\text{HClO}_4] > 0.4 \text{ M}$ $D_{Ln}(\text{II}) > D_{Ln}(\text{TBDGA})$. With an increase in $[\text{HClO}_4]$, this difference increases and at $[\text{HClO}_4] = 3 \text{ M}$ the values of D_{Ln} upon extraction with diamide II are three orders of magnitude higher than in the system with TBDGA (Fig. 5). We believe that this is due to the fact that in the HClO_4 -TBDGA system, the C=O groups of the extracting agent involved in the complexation with REE(III) ions are blocked, while in the system with diamide II, HClO_4 interacts mainly with the phosphoryl groups of the extracting agent, leaving the C=O groups free for the interaction with REE(III) ions. In other words, the modification of the DGA molecule by introducing two P=O groups into its amide units "protects" the C=O groups of the extracting agent from binding to HClO_4 and thereby leads to a significant increase in the efficiency of REE(III) extraction with compounds I–III from perchloric acid solutions.

The effect of adding NaClO_4 to an aqueous phase containing HNO_3 , HCl , or H_2SO_4 on the extraction of REE(III) with dichloroethane solutions of diamide II was further explored. As can be seen from Fig. 6, such an addition to the HNO_3 solution leads to a significant increase in D_{Ln} . The value of the "perchlorate effect", expressed here as $D_{Ln}(\text{HNO}_3 + \text{ClO}_4^-)/D_{Ln}(\text{HNO}_3)$, increases in the REE(III) series from 10 for La(III) to 316 for Lu(III) as the hydration energy of Ln^{3+} ions increases with increasing value of Z. In the presence of ClO_4^- ions in the aqueous phase, the selectivity of REE(III) extraction

**Figure 4.** Dependence of the Eu(III) distribution coefficients on the concentration of HClO_4 in the equilibrium aqueous phase upon extraction with 0.001 M dichloroethane solutions of TBDGA (I) and diamide II (2).**Figure 5.** REE(III) distribution coefficients upon extraction with 0.0005 M dichloroethane solutions of diamide II (I) and TBDGA (2) from 3 M HClO_4 solutions.

enhances significantly: the value of the Lu(III) and La(III) separation factor ($\beta_{Lu/La} = D_{Lu}/D_{La}$) increases from 11.5 in the system with HNO_3 to 355 in the presence of ClO_4^- ions. In systems with HCl and H_2SO_4 , the magnitude of the "perchlorate effect" is even higher since, in the absence of ClO_4^- ions, diamide II practically does not extract REE(III) ions from solutions of these acids ($D_{Ln} < 10^{-2}$).

**Figure 6.** REE(III) distribution coefficients upon extraction with 0.01 M diamide II solutions in dichloroethane from 3 M HCl (I), H_2SO_4 (2), HNO_3 (3) solutions containing 0.3 M NaClO_4 (1–3), and 3 M HNO_3 (4).

Experimental

Diamides **I–III** were synthesized according to the published procedure [19]. 1,2-Dichloroethane (reagent grade, Vekton) was purchased from a commercial source and used without further purification. The solutions of the extracting agents were prepared using precisely weighed samples. The ratio of the volumes of the aqueous and organic phases was 1/1.

The initial aqueous solutions were prepared by dissolving the corresponding REE(III) perchlorates in water followed by the addition of NaClO₄ or HClO₄ until the required concentration. All REE(III) ions (except for Pm) were present in the solution; the initial concentration of each of them was 2 μM. The phases were contacted upon stirring with the rate of 60 rpm at room temperature for 1 h, which is sufficient for establishing the constant values of distribution coefficients (D_{Ln}).

The concentrations of REE(III) ions in the initial and equilibrium aqueous solutions were determined using inductively coupled plasma mass spectrometry on an XSeries II mass spectrometer (Thermo Scientific, USA). The content of metal ions in the organic phase was defined as the difference between their concentrations before and after extraction. The values of D_{Ln} were calculated as the ratios of their concentrations in the equilibrium organic and aqueous phases. The error in determining the distribution coefficients did not exceed 10%. The concentration of HClO₄ in the equilibrium aqueous phase was defined by potentiometric titration with a standard NaOH solution.

Conclusions

To summarize the results presented, it was shown that the introduction of two P=O groups into the amide units of the DGA molecule leads to an increase in the efficiency of REE(III) extraction from perchloric acid solutions when using dichloroethane solutions of modified diglycolamides **I–III**. The possibility of improving the efficiency of REE(III) extraction from solutions of nitric, hydrochloric, and sulfuric acids by adding small amounts of alkali metal perchlorates to the aqueous phase was also demonstrated.

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Corresponding author

* E-mail: bond039@mail.ru. (N. A. Bondarenko)

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