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CHEMISTRY AND TECHNOLOGY OF RARE, TRACE, AND RADIOACTIVE ELEMENTS

Extraction of Gd, Tb, and Dy from Nitrate Media with a Mixture of Technical Di-2-Ethylhexyl Phosphoric Acid and Tributylphosphate

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Abstract—The extraction of medium–heavy rare-earth elements, such as gadolinium (Gd), terbium (Tb), and dysprosium (Dy), with extractant mixtures that comprise technical di-2-ethylhexyl phosphoric acid (D2EHPA) and tri-*n*-butyl phosphate (TBP) has been investigated individually and in their simultaneous presence. Synergistic coefficients and separation factors of the Tb/Gd, Dy/Gd, and Dy/Tb pairs of elements have been calculated. The mathematical simulation of the extraction isotherm has been performed based on the example of Gd and some assumptions about the chemical composition of the extracted complexes have been made.

Keywords: extraction, separation, rare-earth elements, di-2-ethylhexyl phosphoric acid, tri-*n*-butyl phosphate

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INTRODUCTION

The synergistic effect, which consists of an increase in the extractability of an element when extracted with a mixture of extractants compared with the sum of extraction values obtained in individual extractants, has been known for a long time and studied rather thoroughly. It was determined that the synergistic effect is not characteristic for all extracted elements and manifested under certain conditions; the nature and the ratio of extractants in the mixture, the acidity of the aqueous phase, the nature of a diluent, the concentration of an extracted element, and the concentration of extractants in the mixture play a significant role. A slight change in the conditions may give rise to the complete disappearance of synergism or even to the appearance of an antagonistic effect.

The magnitude of the synergistic effect depends on the nature of an extracted element. For example, it can be very large upon the extraction of U(VI) with a mixture of organophosphorus acids (OPAs) and neutral organophosphorus compounds (NOPCs) [1], but much less in the case of rare-earth elements (REEs) [2].

When REEs are extracted with a mixture of extractants, the separation factor of lanthanides can be increased in a number of cases [3]; therefore, studies on the extraction of REEs with extractant mixtures are continued. For REEs, the synergistic effect was observed upon the extraction with mixtures of β-diketones with carboxylic acids [4] and with NOPCs [5, 6], mixtures of oxides and alkylamines [7], mixtures of OPAs with NOPCs [8], and with quaternary ammonium salts (QASes) [9], mixtures of QASes and NOPCs [9, 10], mixtures of calix [4]arene carboxylic acids with primary alkylamines [11], etc.

In this work, the extraction of medium-heavy REEs (Gd, Tb, and Dy) with the extractant mixtures that comprise tri-*n*-butyl phosphate (TBP) and di-2-ethylhexyl phosphoric acid (D2EHPA) was studied individually and in their simultaneous presence. The practical emphasis, i.e., the use of the available technical D2EHPA and the choice of the concentration ratio of REEs in their simultaneous presence, which is typical of industrial solutions, is characteristic of this study.

EXPERIMENTAL

Pure grade $Gd(NO_3)_3 \cdot 6H_2O$, $2TbO_2 \cdot Tb_2O_3$, and Dy_2O_3 served as the starting REE compounds. For conversion into nitrates, Tb and Dy oxides were dissolved by prolonged boiling in heated concentrated nitric acid. The initial concentration of HNO_3 in the aqueous phase was 0.1 mol/L. Technical di-2-ethylhexyl phosphoric acid and tri-*n*-butyl phosphate of chemically pure grade were used as extractants; tolu-

Table 1. Distribution coefficients and separation factors of Gd, Tb, and Dy upon their extraction into solutions with starting D2EHPA with a purity grade of 98% and with a purity grade of 83.5% at $[Ln^{3+}] = 0.25$ mol/L, $[HNO_3] = 0.1$ mol/L, [D2EHPA] = 1.0 mol/L, and an organic phase : aqueous phase ratio of 1 : 1

Starting D2EHPA	D_{Gd}	D_{Tb}	D_{Dy}	$\beta_{Tb/Gd}$	$\beta_{Dy/Gd}$	$\beta_{Dy/Tb}$
D2EHPA 98%	0.41	0.76	1.00	1.85	2.43	1.32
D2EHPA 83%	0.20	0.21	0.32	1.05	1.6	1.52

ene ($C_6H_5CH_3$) of analytically pure grade was used as a diluent.

The concentrations of individual REEs in the initial and equilibrium aqueous phases, as well as in the reextract, were determined by complexometric titration with a solution of Trilon B in the presence of the xylenol orange indicator by the procedures described in [12]. The REE content in the organic phase was calculated from the difference between the concentrations in the initial and equilibrium aqueous phases in the case when the concentration in the latter did not exceed 0.3 mol/L. The error in determining the distribution coefficient increases at a higher concentration and, in this case, REEs were extracted from the organic phase by double washing with HNO_3 (2 mol/L, organic phase : aqueous phase = 1 : 1); the REE concentration in the organic phase was calculated based on the REE content in the reextracts.

The concentrations of REEs in the initial and equilibrium aqueous phases in their simultaneous presence, as well as in the reextracts, were determined by the method of mass spectrometry with inductively coupled plasma (ICP-MS) on an Elan-6100 instrument.

The D2EHPA concentration was determined by potentiometric titration with a solution of an NaOH aliquot in a 50% aqueous solution of isopropanol. Changes in the electromotive force during the titration were monitored with an Elite 3320 pH meter. The potentiometric titration showed that the content of the base substance (D2EHPA) in the initial technical acid sample was 58.0% (1.8 mol/L), and the content of mono-2-ethylhexyl phosphoric acid (M2EHPA) in the mixture was 27.3% (1.2 mol/L). The rest pertained to inert impurities (14.7%).

Technical D2EHPA was purified from M2EHPA by the procedure described in [13], which consists in the treatment with 10% ammonia solution containing 20 g/L of NH_4NO_3 and in the subsequent contact of the organic phase with nitric acid (120 g/L) and washing it with water. The potentiometric titration of the sample showed the absence of M2EHPA. The content of D2EHPA after its purification from M2EHPA increased to 83% (2.5 mol/L). An attempt was made to purify the resulting D2EHPA from neutral impurities by the methods (also described in [13]) via the formation of a copper salt or by the treatment of a toluene solution with a mixture that consists of ethyl alcohol saturated with KOH and water, then with H_2SO_4 and water. In the first case, it was possible to increase the concentration of D2EHPA to about 90%, but with a low yield (12%); in the second case, the yield of 90% D2EHPA was higher (43%), but the transition of a part of the diluent into a separate phase was observed. Therefore, technical D2EHPA in the further study of the extraction of REEs was only purified from M2EHPA.

Considering that neutral impurities in D2EHPA (tri-esters and alcohols [13]) should affect its extracting ability and selectivity with respect to REEs, the extraction capacities of technical D2EHPA and higher-grade D2EHPA (98.5%, the concentration is 3.0 mol/L) commercially available from Sigma-Aldrich (United States) were compared.

RESULTS AND DISCUSSIONS

For this experiment, solutions of technical 83% D2EHPA (preliminarily purified from M2EHPA) and 98.5% D2EHPA in toluene with an identical concentration of 1.0 mol/L were prepared, and individual Gd, Tb, and Dy were extracted under identical conditions. The distribution coefficients were determined, and the separation factors of the above-mentioned rare-earth elements were calculated. The results are given in Table 1.

The distribution coefficients and separation factors of the metals (besides $\beta_{Dy/Tb}$) are significantly higher in the case of extraction with pure D2EHPA. Apparently, neutral impurities contained in technical D2EHPA suppress the extraction process as a consequence of the interaction of the protons of D2EHPA with oxygen atoms of neutral impurities. However, the addition of TBP can improve the extraction parameters of the process when using technical D2EHPA in the case when a synergistic effect is present.

Extraction of Individual Gd, Tb, and Dy Using Solutions of D2EHPA and TBP

To calculate the synergistic effect (in the case of its detection), the extraction of individual lanthanides

Table 2. Dependence of the distribution coefficients of Gd, Tb, and Dy on the concentration of D2EHPA at $[Ln]_{init}$ = 0.25 mol/L and $[HNO_3]_{init}$ = 0.1 mol/L

C_{D2EHPA}, mol/L	D_{Gd}	D_{Tb}	D_{Dy}
0	0	0	0
0.1	0.02	0.04	0.02
0.2	0.04	0.06	0.06
0.3	0.06	0.07	0.10
0.4	0.06	0.11	0.15
0.5	0.08	0.12	0.17
0.7	0.13	0.15	0.21
0.8	0.15	0.20	0.30
0.9	0.20	0.20	0.30
1.0	0.20	0.21	0.32

Table 3. Dependence of the distribution coefficients of Tb and Dy on concentration of TBP at $[Ln]_{init}$ = 0.25 mol/L and $[HNO_3]_{init}$ = 0.1 mol/L

C_{TBP}, mol/L	D_{Tb}	D_{Dy}
1.0	0.04	0.02
0.9	0.03	~0.01
0.8	0.02	~0.01
0.7	0.02	~0.01

(0.25 mol/L) with solutions of D2EHPA and TBP depending on the extractant concentration was preliminary studied. The data on the extraction of Gd, Tb, and Dy with solutions of D2EHPA (Table 2) confirm the well-known fact that the extractability of REEs in solutions of D2EHPA increases upon an increase in the atomic number [14]. The absence of a monotonic increase in the extractability with an increase in the D2EHPA concentration, which is observed for each of the elements, cans probably be attributed to the fact that, when Ln is extracted into the organic phase from a weakly acidic solution, the acidity of the latter increases significantly due to the displacement of protons into the aqueous phase, which unfavorably affects the extraction and reduces the positive effect of increasing the extractant concentration.

The study of the dependence of the extraction of Gd, Tb, and Dy (0.25 mol/L) from 0.1 mol/L HNO_3 with solutions of TBP on the extractant concentration (up to 1 mol/L TBP) showed that the distribution coefficient does not exceed the determination error (0.01) in the entire range of TBP concentrations, the extraction of Tb only starts at a TBP concentration of 0.7 mol/L, and the extraction of Dy can only be detected at a TBP concentration of 1.0 mol/L (Table 3).

The small distribution coefficients of the studied lanthanides upon their extraction with TBP are explained by the low concentration of NO_3^- ions in the aqueous phase. It was interesting to see whether the additions of TBP to D2EHPA would affect the extractability of lanthanides.

Extraction of Individual Gd, Tb, and Dy with the D2EHPA + TBP Extractant Mixture

A series of experiments on the extraction of individual Gd, Tb, and Dy from nitrate solutions with a concentration of 0.25 mol/L REE with a mixture of extractants that is present in a total concentration of 1.0 mol/L was carried out using the method of isomolar series. The obtained distribution coefficients for the studied lanthanides are given in Table 4.

Table 4. Dependence of the distribution coefficients and separation factors of Gd, Tb, and Dy at the extraction of individual lanthanides on total concentration of D2EHPA and TBP extractants at $[Ln^{3+}]$ = 0.25 mol/L, $[HNO_3]$ = 0.1 mol/L, [D2EHPA+TBP] = 1.0 mol/L, and an organic phase : aqueous phase ratio of 1 : 1

[D2EHPA], mol/L	[TBP], mol/L	D_{Gd}	D_{Tb}	D_{Dy}	$\beta_{Tb/Gd}$	$\beta_{Dy/Gd}$	$\beta_{Dy/Tb}$
0.0	1.0	0.00	0.04	0.02	0.00	0.00	0.50
0.1	0.9	0.02	0.06	0.05	3.00	2.50	0.83
0.2	0.8	0.04	0.07	0.11	1.75	2.75	1.57
0.3	0.7	0.06	0.08	0.16	1.33	2.67	2.00
0.4	0.6	0.06	0.18	0.19	3.00	3.17	1.06
0.5	0.5	0.07	0.21	0.22	3.00	3.14	1.05
0.6	0.4	0.09	0.27	0.25	3.00	2.78	0.93
0.7	0.3	0.21	0.28	0.28	1.33	1.33	1.00
0.8	0.2	0.23	0.32	0.35	1.39	1.52	1.09
0.9	0.1	0.28	0.33	0.43	1.18	1.54	1.30
1.0	0.0	0.20	0.21	0.32	1.05	1.60	1.52

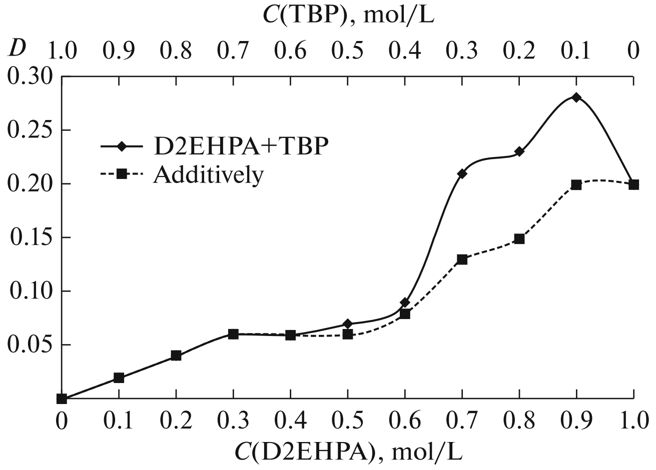

Fig. 1. Dependences of $D_{\mathrm{Gd}^{3+}}$ on concentrations of D2EHPA and TBP during extraction with their isomolar mixtures.

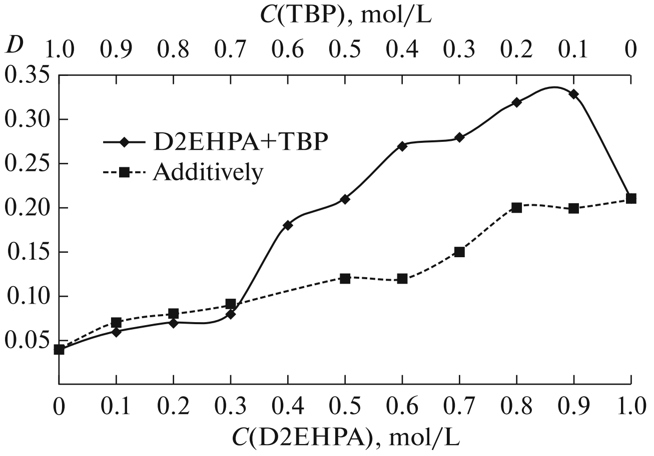

Fig. 2. Dependences of $D_{\mathrm{Tb}^{3+}}$ on concentrations of D2EHPA and TBP during extraction with their isomolar mixtures.

The data of Table 4 show that the distribution coefficients of lanthanides are the highest upon the extraction with the mixture comprised of 0.9 mol/L of D2EHPA and 0.1 mol/L of TBP.

Using the formula, $\beta = D_1/D_2$, where D_1 and D_2 are the distribution coefficients that are better and worse, respectively, than the distribution coefficient of the extracted metal, the separation factors of REEs were calculated. The results are also given in Table 4.

The Tb/Gd and Dy/Gd separation factors calculated as the ratio of the distribution coefficients for the extraction of individual elements at a D2EHPA : TBP concentration ratio of 0.6 mol/L : 0.4 mol/L are higher than at the maximum point, i.e., at D2EHPA : TBP = 0.9 mol/L : 0.1 mol/L; on the contrary, the Dy/Tb separation is better with a D2EHPA : TBP concentration ratio of 0.9 mol/L : 0.1 mol/L.

Evaluation of Synergistic Effect upon the Extraction of Individual Gd, Tb, and Dy with the Extractant Mixture Comprising D2EHPA and TBP

The presence of a synergistic (or antagonistic) effect upon the extraction with a mixture of extractants by the method of isomolar series is clearly evident when the graphical dependences of the metal distribution coefficients obtained experimentally and calculated as the sum of the distribution coefficients in the case of the extraction with individual extractants are compared.

The dependences of the distribution coefficients (for individual Gd, Tb, and Dy, respectively) on the concentrations of D2EHPA and TBP when extracted with extractant mixtures at a total concentration of 1.0 mol/L (data from Table 4) and the additive distribution coefficients (D_{D2EHPA} + D_{TBP}) calculated using the data from Tables 2 and 3 are given in Figs. 1–3.

When REEs are extracted with a mixture of the D2EHPA and TBP extractants, the curves contain obvious maxima that are absent in the curves obtained additively for these two extractants, which indicates the presence of a synergistic effect. The value of the synergistic effect S was evaluated by comparing the distribution coefficients of the studied elements upon their extraction

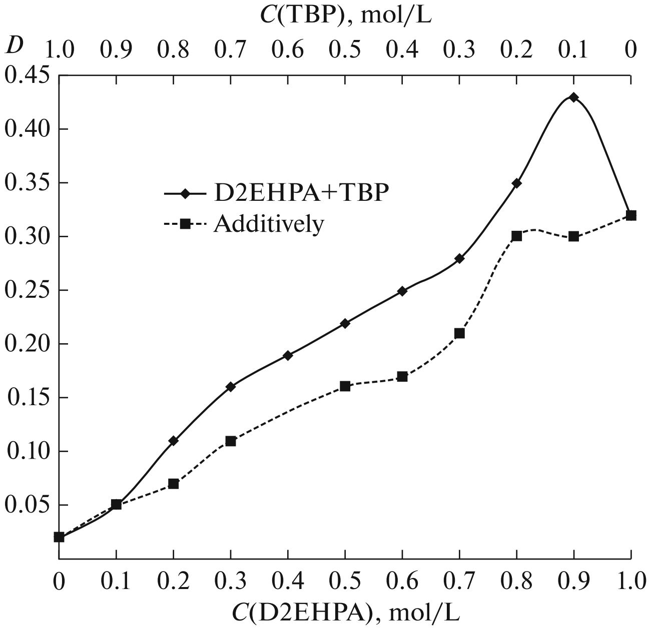

Fig. 3. Dependences of $D_{\mathrm{Dy}^{3+}}$ on the concentrations of D2EHPA and TBP during extraction with their isomolar mixtures.

Table 5. Synergistic effect upon extraction of Ln^{3+} with a mixture of D2EHPA and TBP extractants at $[Ln^{3+}] = 0.25$ mol/L, $[HNO_3] = 0.1$ mol/L, [D2EHPA+TBP] = 1.0 mol/L, and an organic phase : aqueous phase ratio of 1: 1

No.	[D2EHPA], mol/L	[TBP], mol/L	S_{Gd}	S_{Tb}	S_{Dy}
1	0.9	0.1	1.57	1.65	1.51
2	0.8	0.2	1.53	1.58	1.32
3	0.7	0.3	1.74	1.40	1.15

with individual extractants (additively) and upon their extraction with a mixture of extractants using the following formula: $S = D_{D2EHPA+TBP}/(D_{D2EHPA} + D_{TBP})$. The synergistic effect values for the points that correspond to the maxima in the curves shown in Figs. 1–3 are given in Table 5. The obtained results show that, in the case of the extraction of individual Gd, Tb, and Dy with a mixture of D2EHPA and TBP, the synergistic effect is of a small magnitude.

Extraction of Gd, Tb, and Dy in their Simultaneous Presence with the D2EHPA + TBP Extractant Mixture

The mass contents of elements in the initial aqueous phase were 66.0% Gd, 5.7% Tb, and 28.3% Dy (Gd : Tb : Dy = 13 : 1 : 6) when their total concentration was 1.0 mol/L. This ratio of Gd, Tb, and Dy corresponded to the mass concentration ratio of these elements in a solution of REEs obtained from phosphogypsum.

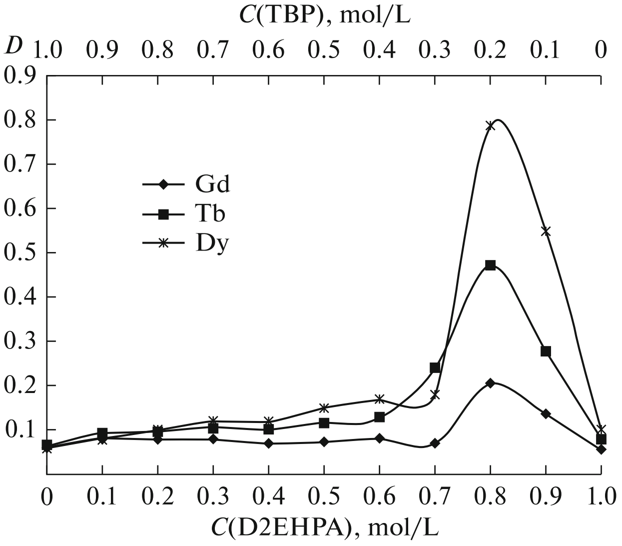

Fig. 4. Dependence of $D_{(Gd,Tb,Dy)^{3+}}$ on concentrations of D2EHPA and TBP during extraction with a mixture of extractants in the simultaneous presence of REEs at $C_{\Sigma(Gd,Tb,Dy)init} = 1$ mol/L and $C_{\Sigma(D2EHPA,TBP)} = 1$ mol/L.

Using the method of isomolar series, the experiments on the extraction of Gd, Tb, and Dy with a mixture of the D2EHPA and TBP extractants at a total concentration of 1 mol/L were carried out. The results are given in Fig. 4.

As can be seen from the data given in Fig. 4, an apparent maximum is observed upon extraction with a mixture of 0.8 mol/L D2EHPA and 0.2 mol/L TBP, which is comparable with the data obtained for individual REEs upon the extraction with a mixture of extractants, when the synergistic effect was observed at a close ratio of extractant concentrations (see Figs. 1–3).

The formation of an extractable compound that contains a salt in its composition that is formed by the metal ion and organic acid and is solvated additionally by a neutral extractant is considered to be the main reason for the synergistic effect upon the extraction of metals with a mixture of acidic and neutral extractants [15]. These compounds are more thermodynamically stable and more lipophilic than metal compounds with individual extractants, which leads to an increase in the degree of extraction of the extractable compound into the organic phase compared to the degree of extraction with solutions of individual extractants. To determine the chemical composition of extractable lanthanide compounds upon extraction from nitrate media with a mixture of the D2EHPA and TBP extractants, the method of mathematical simulation of the extraction isotherms was used.

Mathematical Simulation of the Extraction Isotherm on the Example of the Extraction of Gd from Nitrate Media with a Mixture of the D2EHPA and TBP Extractants

The extraction isotherm of Gd was obtained under the following experimental conditions: the concentrations of Gd in solutions prior to the extraction were varied in the range of 2–350 g/L; $[HNO_3] = 0.1$ mol/L, [D2EHPA] = 0.9 mol/L, and [TBP] = 0.1 mol/L (Table 6).

In the EXTREQ-2 program developed by Stepanov and Slavinskii [16], an algorithm for compiling a set of equations that take into account the formation of one or more synergistic complexes was developed. The mathematical simulation of the extraction isotherm of gadolinium was performed based on the mechanism of the formation of a compound comprising two extractants (synergistic complex) and the formation of individual complexes with each of the extractants (with D2EGFK and with TBP) in the organic phase.

The following possible ratios were considered in the formation of extractable complexes:

Ln : D2EHPA : TBP = 1 : 1 : 1; 1 : 2 : 1, 1 : 2 : 3, 1 : 3 : 1, and 1 : 1 : 3;

Ln : D2EHPA = 1 : 1, 1 : 2, and 1 : 3;

Ln : TBP = 1 : 1, 1 : 2, and 1 : 3.

Table 6. Equilibrium concentrations of Gd^{3+} in the aqueous and organic phases after the extraction at $[HNO_3]$ = 0.1 mol/L, [D2EHPA] = 0.9 mol/L, and [TBP] = 0.1 mol/L

No.	C_{aq}, g/L	C_{org}, g/L
1	0.29	1.66
2	0.98	2.16
3	1.96	2.75
4	5.89	3.92
5	10.20	4.71
6	14.91	4.71
7	24.33	5.49
8	39.25	4.71
9	60.44	10.20
10	89.49	11.78
11	105.97	15.07
12	125.60	15.70
13	154.64	15.70
14	174.27	18.84
15	196.25	21.98
16	262.25	27.47
17	286.52	31.40
18	318.71	31.40

The minimum relative error upon the simulation of the isotherm (6.97%) was obtained assuming that the following complexes are involved in the extraction: Ln : D2EHPA : TBP = 1 : 3 : 1 (complex 1), Ln : D2EHPA = 1 : 2 (complex 2), and Ln : TBP = 1 : 1 (complex 3). The contents of Gd complexes in the organic phase are given in Fig. 5.

The process of the formation of these complexes can be expressed by the following reaction equations:

(1) the formation of a mixed complex (see complex 1 in Fig. 5)

$$\mathrm{Gd(NO_3)_{3aq} + 3H(C_8H_{17})_2PO_{4org} + (C_4H_9)_3PO_{4org}}$$
$$\mathrm{= Gd[(C_8H_{17})_2PO_4]_3(C_4H_9)_3PO_{4org} + 3HNO_{3aq};}$$

(2) the formation of a complex by the cation exchange mechanism (see complex 2 in Fig. 5)

$$\mathrm{Gd(NO_3)_{3aq} + 2H(C_8H_{17})_2PO_{4org}}$$
$$\mathrm{= Gd[(C_8H_{17})_2PO_4]_2(NO_3)_{org} + 2HNO_{3aq};}$$

(3) the formation of a complex by the solvate mechanism (see complex 3 in Fig. 5)

$$\mathrm{Gd(NO_3)_{3aq} + (C_4H_9)_3PO_{4org}}$$
$$\mathrm{= Gd(NO_3)_3 \cdot (C_4H_9)_3PO_{4org}.}$$

The dependences of the equilibrium concentration of a free extractant for D2EHPA and TBP on the concentration of gadolinium nitrate in the organic phase for the proposed model are shown in Fig. 6.

It can be seen that no free tri-*n*-butyl phosphate remains after reaching a gadolinium concentration of 0.15 mol/L in the organic phase, and further extraction only proceeds with the formation of complex 2, i.e., $Gd[(C_8H_{17})_2PO_4]_2(NO_3)$, when Gd is extracted with a mixture of 0.9 mol/L D2EHPA and 0.1 mol/L TBP.

Separation of Gd, Tb, and Dy upon their Extraction with the D2EHPA + TBP Extractant Mixture When They Are Simultaneously Present in a Solution

Based on the experimental results given in Fig. 4, the separation factors for the Tb/Gd, Dy/Gd, and

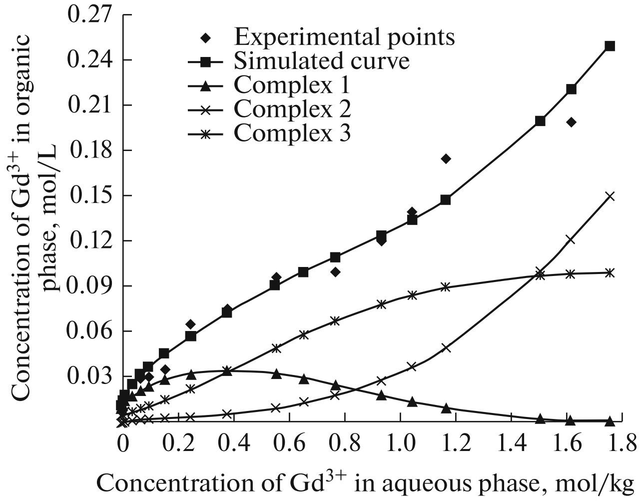

Fig. 5. Concentration of Gd^{3+} in organic phase as a function of concentration in aqueous phase for model with complexes 1, 2, and 3.

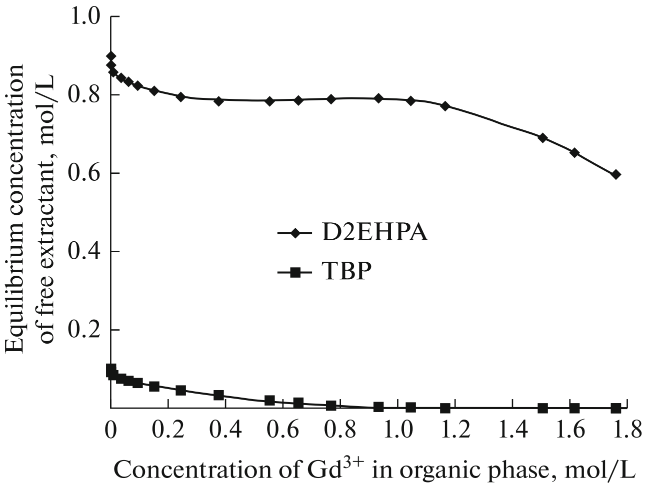

Fig. 6. Dependence of equilibrium concentration of free extractant on concentration of Gd^{3+} in organic phase.

Table 7. Separation factors of REEs in their simultaneous presence at $[\mathrm{Ln}^{3+}_{\mathrm{tot}}]$ = 1.0 mol/L, $[\mathrm{HNO_3}]$ = 0.1 mol/L, [D2EHPA+TBP] = 1.0 mol/L, and an organic phase : aqueous phase ratio of 1 : 1

Trial no.	C_{D2EHPA}, mol/L	C_{TBP}, mol/L	$\beta_{\mathrm{Tb/Gd}}$	$\beta_{\mathrm{Dy/Gd}}$	$\beta_{\mathrm{Dy/Tb}}$
1	0.0	1.0	1.0	0.9	0.9
2	0.1	0.9	1.1	1.0	0.9
3	0.2	0.8	1.2	1.3	1.1
4	0.3	0.7	1.3	1.5	1.1
5	0.4	0.6	1.5	1.8	1.2
6	0.5	0.5	1.6	2.1	1.3
7	0.6	0.4	1.6	2.1	1.3
8	0.7	0.3	3.5	2.6	0.7
9	0.8	0.2	2.3	3.9	1.7
10	0.9	0.1	2.0	4.0	2.0
11	1.0	0.0	1.4	1.7	1.2

Dy/Tb pairs were calculated (Table 7). The data calculated from the curves given in Fig. 4 show that the separation factors at the points of maxima are as follows: 3.9 for the Dy/Gd pair, 2.0 for the Dy/Tb pair, and 2.0 for Tb/Gd pair. However, the separation factor for the Tb/Gd pair increases to 3.5 following an increase in the content of TBP in the mixture to 0.3 mol/L.

CONCLUSIONS

It has been shown that small additions of TBP (0.1–0.3 mol/L at a total extractant concentration of 1 mol/L) give rise to an increase in the distribution coefficients of Gd, Tb, and Dy compared with the additive values obtained upon both the extraction of individual REEs from solutions and upon the extraction in their simultaneous presence, when technical D2EHPA that contain no M2EHPA (with a basic substance content of 83%) is used as an extractant.

The maximum value of the synergistic effect is 1.74 for Gd, 1.65 for Tb, and 1.51 for Dy. The extractability series is as follows: Dy > Tb > Gd.

The mathematical simulation of the extraction isotherm of gadolinium with a mixture of 0.9 mol/L D2EHPA and 0.1 mol/L TBP by using the EXTREQ-2 program show that the minimum relative error of the isotherm simulation (about 7%) is obtained assuming that the following complexes are involved in the extraction: $\mathrm{Gd[(C_8H_{17})_2PO_4]_3 \cdot (C_4H_9)_3PO_4}$, $\mathrm{Gd[(C_8H_{17})_2PO_4]_2(NO_3)}$, and $\mathrm{Gd(NO_3)_3 \cdot (C_4H_9)_3PO_4}$.

Variations in the composition of 1 mol of D2EHPA + TBP extractant mixture upon the extraction of Gd, Tb, and Dy in their simultaneous presence allows one to select favorable conditions for separation along the Dy/Tb line (β = 2.0) with the isolation of Dy (at a TBP concentration of 0.1 mol/L in the mixture of extractants) and subsequent separation (at a TBP concentration of 0.3 mol/L in the mixture of extractants) along the Tb/Gd line (β = 3.5).

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