

## EXTRACTION OF EUROPIUM FROM ACIDIC AQUEOUS SOLUTIONS INTO NITROBENZENE BY DICARBOLIDE IN THE PRESENCE OF POLYETHYLENE GLYCOL

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Extraction of microamounts of  $^{152,154}\text{Eu}$  from the aqueous solutions of perchloric acid ( $c(\text{HClO}_4) = 0.1-0.5 \text{ mol l}^{-1}$ ) was studied in the presence of  $3 \cdot 10^{-4}-0.3 \text{ mol l}^{-1}$  of polyethylene glycol PEG 400 (L) by the nitrobenzene solutions of Co(III)-dicarbolidate (3,3'-commo-bis(undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate) (-1),  $\{(\pi-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11})_2\text{Co}\}^-$ , henceforth only  $\text{B}^-$ ) of the concentration  $c(\text{dicarbolidate}) = 10^{-3}-10^{-1} \text{ mol l}^{-1}$ . Maxima of the Eu distribution ratio dependence on the concentration of polyethylene glycol are explained by the competition reactions between the positively charged europium complexes ( $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuLH}}_1^{2+}$ , and  $\overline{\text{EuL}}_2^{3+}$ ,  $\overline{\text{EuL}_2\text{H}}_2^{2+}$ , or  $\overline{\text{EuL}}_3^{3+}$ ) and protonized polyethylene glycol ( $\overline{\text{HL}}^+$ ) in the organic phase. The respective equilibrium extraction constants were determined.

The extraction of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  by the the nitrobenzene solutions of dicarbolidate in the presence of polyethylene glycols PEG 400, PEG 300, and PEG 200 has been followed in our previous studies<sup>1,2</sup>.

Because also trivalent lanthanides, *e.g.*,  $\text{Eu}^{3+}$ , are extracted in this system and the dependence of their distribution ratios on the concentration of polyethylene glycol has also characteristic maxima (about one order of magnitude<sup>3</sup>), it seems interesting both from the theoretical and practical points of view<sup>4</sup> to deal with this problem in more detail.

Similarly as in the case of bivalent cations these maxima appear for all concentrations of the dicarbolidate and for all molecular weights of polyethylene glycols in the range from 200 to 20 000 and their position is shifted with the increasing concentration of dicarbolidate towards higher concentrations of polyethylene glycol. It can be therefore assumed that also the extraction of trivalent elements by dicarbolidate in the presence of polyethylene glycol is governed by a mechanism analogous to the extraction of bivalent ions of alkaline earths. The initial increase of the distribution ratio is probably caused by the formation of complexes of the type  $\overline{\text{EuLH}}_x^{(3+x)+}$  (where L means the molecule of polyethylene glycol), that is more hydrophobic than the original  $\text{Eu}^{3+}$  ion and is therefore more easily extracted into the organic phase.

Further increase of the polyethylene glycol concentration is accompanied by a higher extraction of the protonized molecule of PEG,  $\overline{HL}^+$ , so that the concentration of the extractant (or, better, the concentration of  $\overline{H}^+$ ) in the organic phase decreases and hence the distribution ratio decreases, too.

The aim of the present study is — similarly as in the previous papers<sup>1,2</sup> — to verify this hypothesis by a quantitative (or, at least, semiquantitative) description of the extraction equilibria in the system  $\text{Eu}^{3+}$ -PEG 400-nitrobenzene-dicarbolide- $\text{HClO}_4$  and to calculate the values of the equilibrium constants corresponding to the individual equilibrium reactions.

## EXPERIMENTAL

All reagents used were of the analytical grade; 0.1M solution of dicarbolide in the form of an acid  $\text{H}^+(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}^-$  was prepared by the following procedure: the nitrobenzene solution of the cesium salt was transformed, after the addition of 20% (v/v) n-propanol, into the acid form by threefold shaking with equal volumes of 1M- $\text{HNO}_3$ . n-Propanol was removed from the organic phase by twelvefold washing with 1M- $\text{HNO}_3$  and twofold shaking with distilled water removed the excess nitric acid. The solutions with lower concentrations of dicarbolide were prepared by dilution of the 0.1M solution with nitrobenzene. PEG 400 for synthesis (E. Merck, Darmstadt), the average molecular weight of which is — according to the producer — in the range 380 to 420, with the average number of oxyethylene groups  $\bar{n} = 7-9$  ( $\text{HOCH}_2(\text{CH}_2\text{O}-\text{CH}_2)_n-\text{CH}_2\text{OH}$ ), was used without further purification.

The specific activity of  $^{152,154}\text{Eu}$  (in the nitrate form) was about  $6.3 \cdot 10^{10}$  Bq/g of Eu and its radiochemical purity was checked by gamma spectrometry.

The extraction experiments were carried out in 10 ml glass probes with glass stoppers. 1 ml of each phase was shaken for 1 hour at the temperature of  $25 \pm 0.2^\circ\text{C}$  in a water thermostat.

The distribution ratios of europium were determined radiometrically by the measurement of gamma activity using the well-type NaI(Tl) scintillator.

## RESULTS AND DISCUSSION

The dependence of the europium distribution ratio ( $D_{\text{Eu}}$ ) on PEG concentration ( $c_L$ ) was measured at five concentrations of dicarbolide,  $c_B = 10^{-3}$ ,  $2.5 \cdot 10^{-3}$ ,  $5 \cdot 10^{-3}$ ,  $5 \cdot 10^{-2}$ , and  $10^{-1} \text{ mol l}^{-1}$  and at three values of acidity,  $c_{\text{HClO}_4} = 10^{-1}$ ,  $2.5 \cdot 10^{-1}$ , and  $5 \cdot 10^{-1} \text{ mol l}^{-1}$ . The concentrations of PEG ranged from  $3 \cdot 10^{-4}$  to  $0.3 \text{ mol l}^{-1}$ .

The obtained dependence of  $\log D_{\text{Eu}}$  on  $\log c_L$  is given in Table I and Fig. 1.

The value of the extraction constant for the  $\text{Eu}^{3+}$  extraction by the nitrobenzene solution of dicarbolide was determined by separate extraction experiments (Table II) and it was found that  $K_{e,x}(\text{Eu}^{3+}) = 27$  (the standard deviation of the average value as determined from five measurements is 3).

In spite of the fact that polyethylene glycol used in these experiments cannot be taken for a chemical individuum, as it contains oligomers with the molecular weight

TABLE I

Dependence of the distribution ratio of europium on the concentration of polyethylene glycol PEG 400 for the extraction of europium by the nitrobenzene solution of dicarbolid (c(dicarbolid) = 0.001–0.1 mol l<sup>-1</sup>) from the aqueous solutions of HClO<sub>4</sub> (c(HClO<sub>4</sub>) = 0.2–1.0 mol l<sup>-1</sup>)

$$c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.1 \text{ mol l}^{-1}$$

– 2.365, 2.384<sup>a</sup>, – 2.240, 2.501; – 2.063, 2.626; – 1.939, 2.742; – 1.842, 2.758; – 1.638, 2.735;  
– 1.541, 2.891; – 1.365, 2.967; – 1.240, 2.911; – 1.064, 2.653; – 0.939, 2.446; – 0.842, 2.270;  
– 0.638, 2.071; – 0.541, 1.958;

$$c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.05 \text{ mol l}^{-1}$$

– 3.541, 0.970; – 3.240, 1.174; – 3.063, 1.320; – 2.939, 1.447; – 2.842, 1.507; – 2.638, 1.682;  
– 2.541, 1.747; – 2.365, 1.939; – 2.240, 2.043; – 2.063, 2.153; – 1.939, 2.225; – 1.842, 2.266;  
– 1.638, 2.288; – 1.541, 2.232; – 1.365, 2.057; – 1.240, 1.887; – 1.064, 1.614; – 0.939, 1.517;  
– 0.842, 1.407; – 0.638, 1.243; – 0.541, 1.146;

$$c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.005 \text{ mol l}^{-1}$$

– 3.541, – 0.804; – 3.240, – 0.493; – 3.063, – 0.378; – 2.939, – 0.260; – 2.842, – 0.217; – 2.638,  
– 0.081; – 2.541, – 0.071; – 2.365, – 0.040; – 2.240, – 0.074; – 2.063, – 0.188; – 1.939, – 0.268;  
– 1.842, – 0.326; – 1.638, – 0.529; – 1.541, – 0.636;

$$c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.0025 \text{ mol l}^{-1}$$

– 3.541, – 1.316; – 3.240, – 1.043; – 3.063, – 0.913; – 2.939, – 0.868; – 2.842, – 0.790; – 2.638,  
– 0.737; – 2.541, – 0.730; – 2.462, – 0.699; – 2.365, – 0.720; – 2.240, – 0.738; – 2.063, – 0.877;  
– 1.939, – 0.948; – 1.842, – 1.001; – 1.638, – 1.249; – 1.541, – 1.372;

$$c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.001 \text{ mol l}^{-1}$$

– 3.541, – 1.954; – 3.240, – 1.745; – 3.063, – 1.685; – 2.939, – 1.556; – 2.842, – 1.550; – 2.638;  
– 1.523; – 2.541, – 1.522; – 2.462, – 1.503; – 2.365, – 1.526; – 2.240, – 1.595; – 2.063, – 1.827;  
– 1.939, – 1.945; – 1.842, – 2.082; – 1.638, – 2.379; – 1.541, – 2.565;

$$c(\text{HClO}_4) = 0.2513 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.1 \text{ mol l}^{-1}$$

– 3.541, 0.406; – 3.240, 0.524; – 3.063, 0.604; – 2.939, 0.682; – 2.842, 0.740; – 2.638, 0.904;  
– 2.541, 0.961; – 2.365, 1.121; – 2.240, 1.239; – 2.063, 1.356; – 1.939, 1.491; – 1.842, 1.527;  
– 1.638, 1.652; – 1.541, 1.641; – 1.365, 1.634; – 1.240, 1.572; – 1.064, 1.291; – 0.939, 1.135;  
– 0.842, 0.970; – 0.638, 0.768; – 0.541, 0.678;

$$c(\text{HClO}_4) = 0.5039 \text{ mol l}^{-1}, c(\text{dicarbolid}) = 0.1 \text{ mol l}^{-1}$$

– 1.939, 0.443; – 1.842, 0.539; – 1.638, 0.634; – 1.541, 0.762; – 1.365, 0.634; – 1.240, 0.603;  
– 1.064, 0.345; – 0.939, 0.137;

<sup>a</sup> Data given in the sequence: log c<sub>L</sub>, log D.

higher and lower than 400 (ref.<sup>5</sup>), the results of our previous studies<sup>1,2</sup> indicate that its behaviour in the extraction system is not substantially different from the behaviour of a polymer with the molecular weight equal to the average molecular weight.

TABLE II

Extraction of europium by the nitrobenzene solution of dicarbolide from the aqueous solution of perchloric acid

$c(\text{HClO}_4)$ $\text{mol l}^{-1}$	$c_{\text{B}}$ $\text{mol l}^{-1}$	$\log D_{\text{Eu}}$
0.1005	0.1	1.568
0.1005	0.05	0.528
0.1005	0.005	-2.623
0.2513	0.1	0.260
0.5039	0.1	-0.751

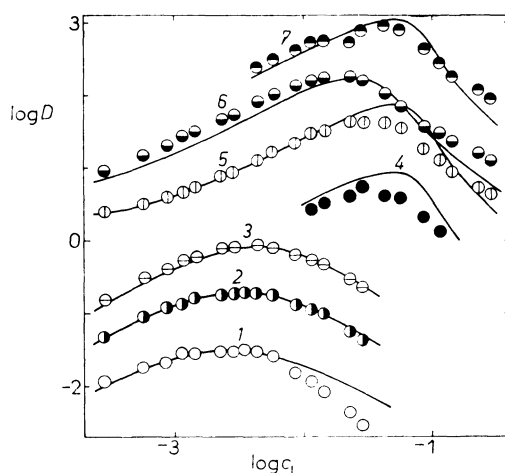
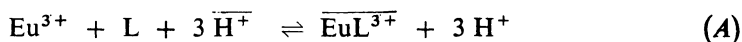


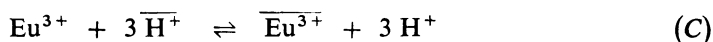
FIG. 1

Logarithm of  $\text{Eu}^{3+}$  distribution ratio as a function of the total analytical concentration of PEG in the system  $\text{Eu}^{3+}$ -water- $\text{HClO}_4$ -PEG 400-dicarbolide-nitrobenzene. 1  $c(\text{HClO}_4) = 0.1005 \text{ mol} \cdot \text{l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.001 \text{ mol l}^{-1}$ ; 2  $c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.0025 \text{ mol l}^{-1}$ ; 3  $c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.005 \text{ mol l}^{-1}$ ; 4  $c(\text{HClO}_4) = 0.504 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.1 \text{ mol l}^{-1}$ ; 5  $c(\text{HClO}_4) = 0.251 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.1 \text{ mol} \cdot \text{l}^{-1}$ ; 6  $c(\text{HClO}_4) = 0.1005 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.05 \text{ mol l}^{-1}$ ; 7  $c(\text{HClO}_4) = 0.1005 \text{ mol} \cdot \text{l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.1 \text{ mol l}^{-1}$ . Solid curves are calculated for  $\log K_{\text{ex}}(\text{HL}^+) = 2.67$ ,  $\log K_{\text{ex}}(\text{EuL}^{3+}) = 6.20$ ,  $\log K_{\text{ex}}(\text{EuLH}_2^{2+}) = 4.74$ , and  $\log K_{\text{ex}}(\text{EuL}_2^{3+}) = 8.82$

The dependence of the logarithm of the distribution ratio maxima ( $\log D_{\text{Eu}}$ ) on the logarithm of the dicarbolide concentration is approximately linear with the slope 2.3 while the dependence of  $\log D_{\text{Eu}}$  on the aqueous phase acidity is also linear with the slope  $-3.3$ . From these results it is evident that the experimental data cannot be explained by the mechanism that would be a complete analogy of the strontium extraction, as proposed in our previous paper, *i.e.*, by the reactions

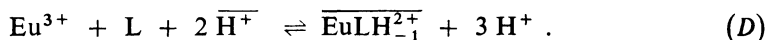


together with the extraction of  $\text{Eu}^{3+}$  ion itself, without polyethylene glycol



(species in the organic phase are denoted by a bar).

The most probable explanation of the differences between the dependences of  $\log D_{\text{Eu}}$  on  $\log c_{\text{B}}$  can be based on the assumption that the hydrogen ion is split off during the extraction of  $\text{Eu}^{3+}$  ion with polyethylene glycol and the species  $\overline{\text{EuLH}_2^+}$  is formed so that the overall reaction will be given by



From the equilibrium data it is impossible to decide whether the hydrogen atom would be split off from the polyethylene glycol molecule or from a water molecule of the hydration shell of the extracted complex.

Assuming that the activity coefficients are constant, the overall equilibrium in the system under study can be described by the europium extraction equations (reactions (A), (C), (D)),

$$K_{\text{ex}}(\text{Eu}^{3+}) = \frac{[\overline{\text{Eu}^{3+}}][\text{H}^+]^3}{[\text{Eu}^{3+}][\overline{\text{H}^+}]^3} \quad (1)$$

$$K_{\text{ex}}(\text{EuL}^{3+}) = \frac{[\overline{\text{EuL}^{3+}}][\text{H}^+]^3}{[\text{Eu}^{3+}][\overline{\text{H}^+}]^3[\text{L}]} \quad (2)$$

$$K_{\text{ex}}(\text{EuLH}_2^+) = \frac{[\overline{\text{EuLH}_2^+}][\text{H}^3]}{[\text{Eu}^{3+}][\overline{\text{H}^+}]^2[\text{L}]} \quad (3)$$

together with the equilibrium reactions of polyethylene glycol with the hydrogen ion in the organic phase (reaction (B))

$$K_{\text{ex}}(\text{HL}^+) = \frac{[\overline{\text{HL}^+}]}{[\text{L}][\overline{\text{H}^+}]} \quad (4)$$

and in the aqueous phase (reaction (E))



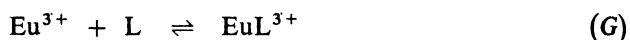
$$K_{H1} = [HL^+]/[L][H^+]. \quad (5)$$

Similarly as in our previous papers also the distribution of the non-protonized polyethylene glycol between the aqueous and organic phases (reaction (F)) is taken into consideration



$$K_D = [\bar{L}]/[L]. \quad (6)$$

The value of  $K_D = 1.1 \cdot 10^{-3}$  was taken from paper<sup>6</sup>. The formation of the europium complex with polyethylene glycol is also considered,



$$K_1(EuL^{3+}) = [EuL^{3+}]/[Eu^{3+}][L]. \quad (7)$$

Because only trace amounts of europium were used, the effect of its concentration on the extraction equilibria of the polyethylene glycol complexes in the aqueous and organic phases can be neglected in the overall balance.

The equilibrium concentrations  $[L]$ ,  $[H^+]$ , and  $[\bar{H}^+]$  can be obtained by a numeric solution of the following set of equations

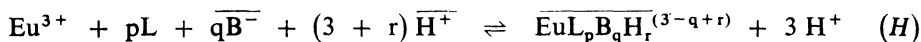
$$[\bar{H}^+] = c_B/(1 + K_{ex}(HL^+)[L]) \quad (8)$$

$$[H^+] = c_H/(1 + K_{H1}[L]) \quad (9)$$

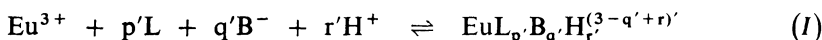
$$c_L = (1 + K_D + K_{ex}(HL^+)[H^+] + K_{H1}[H^+])[L]. \quad (10)$$

(The relations derived in our previous paper<sup>1</sup> would neglect the decrease of  $H^+$  ion concentration due to the formation of  $HL^+$  complex. This is not fully justified in the concentration range of  $c_B$  and  $c_L$  used in this study). At the given acidities of both phases it also follows that  $[\bar{B}^-] \approx c_B, cf.^{1,2}$ .

Reactions of europium in the system can be most generally described by the reactions of the type



(europium is transferred into the organic phase), and



(for europium complexes in the aqueous phase).

The distribution ratio of europium is then given by

$$D_{\text{Eu}} = \frac{\sum K_{\text{ex}}(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}) [\text{L}]^p [\overline{\text{B}^-}]^q [\overline{\text{H}^+}]^{3+r} [\text{H}^+]^{-3}}{\{1 + \sum K(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}) [\text{L}]^{p'} [\text{B}^-]^{q'} [\text{H}^+]^{r'}\}}, \quad (11)$$

where  $K_{\text{ex}}(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+})$  and  $K(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+})$  are the equilibrium constants of the reactions (H) and (I), respectively, that are defined as follows

$$K_{\text{ex}}(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}) = \frac{[\overline{\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}}] [\text{H}^+]^3}{[\text{Eu}^{3+}] [\text{L}]^p [\overline{\text{B}^-}]^q [\overline{\text{H}^+}]^r} \quad (12)$$

$$K(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}) = \frac{[\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+}]}{[\text{Eu}^{3+}] [\text{L}]^{p'} [\text{B}^-]^{q'} [\text{H}^+]^{r'}}. \quad (13)$$

Assuming that in the regions of maxima of the functions  $D_{\text{Eu}} = f(\log c_{\text{L}})$  the extraction of  $\text{Eu}^{3+}$  ions by dicarbolidate is negligible (which, due to the large increase of  $D_{\text{Eu}}$ , cannot cause any large error) and assuming that the existence of Eu-PEG and  $\text{H}^+$ -PEG complexes in the aqueous phase is also negligible (which is proved below) it is possible to derive for the position of maxima the following equation (14) (by a procedure analogous to that used in our previous study<sup>1</sup>),

$$c_{\text{L}}^{\text{max}} = (c_{\text{B}}/(3+r)) + \beta/(3+r-1), \quad (14)$$

where  $\beta = 1/K_{\text{ex}}(\text{HL}^+)$  and  $c_{\text{L}}^{\text{max}}$  is the concentration of PEG that corresponds to the maximum on the curve of  $\log D_{\text{Eu}}$  vs  $\log c_{\text{L}}$ .

An adequate model of europium extraction was found by the comparison of a series of chemically acceptable systems, for which the most probable values of the constants  $K_{\text{ex}}(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)'+})$  (henceforth for brevity written in the form  $K_{\text{ex}}(p, q, r)$ ) were found by the minimization of the sum of squares of the differences between the experimental and calculated values of  $\log D_{\text{Eu}}$  using the computer program LETAGROP (ref.<sup>7,8</sup>), i.e., by the minimization of the expression

$$U = \sum (\log D_{\text{Eu}}^{\text{exp}} - \log D_{\text{Eu}}^{\text{calc}})^2. \quad (15)$$

The results are summarized in Table III.

From this table it is evident that the assumption of the extraction of  $\overline{\text{EuL}}^{3+}$  complex (together with the extraction of  $\text{Eu}^{3+}$  ion itself) does not conform to the experimental data ( $U = 37$ ). Neither the assumption of the existence of  $\text{HL}^+$  and  $\text{EuL}^{3+}$  complexes in the aqueous phase ( $c_f^2$ ) could improve the disagreement as the minimum value of  $U$  was found for zero values of the constants of these species. On the other hand, considering the existence of another complex,  $\overline{\text{EuLH}}_{-1}^{2+}$ , the agreement between the theoretical and experimental values becomes substantially better ( $U = 3.943$ ).

It can be therefore assumed that in course of the reaction of europium with polyethylene glycol the hydrogen ion is split off, either partially or completely, in dependence on the concentration of the reaction components. The hydrogen ion can be split off either from the hydroxyl group of polyethylene glycol or from a water molecule of the hydration shell of  $\text{Eu}^{3+}$  ion, which cannot be decided from the thermodynamic measurements.

Further decrease of the sum of squares of deviations can be achieved under the assumption that the complexes  $\overline{\text{EuL}}^{3+}$  or  $\overline{\text{EuLH}}_{-1}^{2+}$ , respectively, can react with another molecule of PEG and give the species  $\overline{\text{EuL}}_2^{3+}$ ,  $\overline{\text{EuL}}_2\text{H}_{-1}^{2+}$ , or eventually  $\overline{\text{EuL}}_3^{3+}$ . It is known from the literature that trivalent lanthanides are in the nitrobenzene solution solvated by a higher number of water molecules than the bivalent ions of alkaline earths<sup>9</sup> so that a higher number of OEU (oxyethylene units) is required for their complete replacement, *i.e.* higher than 8–9 (corresponding to the PEG 400 molecule) that was found for  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  (ref.<sup>2</sup>). Also the dependence of  $\log D_{\text{max}}$  on the relative molecular weight of PEG has a maximum for PEG 1000 (ref.<sup>3</sup>) in contrast to  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  where the maximum was found for PEG 400. The experimental data can be best fitted by a model assuming the extraction of the species  $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ ,  $\overline{\text{EuL}}_2^{3+}$ , and  $\overline{\text{EuL}}_3^{3+}$  ( $U = 1.1034$ ).

From Table III it is evident that the extraction constant of the  $\text{EuL}_2^{3+}$  complex is determined with a low precision ( $s(K) > K$ , where  $s(K)$  is the standard deviation of the constant  $K_{\text{ex}}(\text{EuL}_2^{3+})$ ). Computations revealed that in the given set this complex is present only in a very narrow range of concentrations  $c_L$  and its participation on the total concentration of extracted europium never exceeds 11%.

The model assuming the extraction of the species  $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ , and  $\overline{\text{EuL}}_3^{3+}$  fits the experimental data practically identically ( $U = 1.114$ ). However, models that assume the extraction of  $\overline{\text{EuL}}_3^{3+}$  species into the organic phase lead to such a shape of the dependence of  $\log D$  vs  $\log c_L$  that is in disagreement with the experimentally observed shape.

The agreement between the theoretical and experimental values of  $\log D$  can be made still better if we assume also the formation of  $\text{EuL}^{3+}$  complexes in the aqueous phase. However, the decrease of  $U$  is not significant ( $U = 0.9757$ ) (for the complex  $\text{EuLH}_{-1}^{2+}$  in the aqueous phase the decrease of  $U$  is still lower,  $U = 1.092$ ).



It can be proved that the model considering the extraction of the species  $\overline{\text{EuL}^{3+}}$ ,  $\{\overline{\text{EuLH}}_{-1}^{2+}, \text{B}^{-}\}$ , and  $\overline{\text{HL}^{+}}$  (along with other Eu complexes in the organic phase) is – under the assumption that  $K_{\text{ex}}(\text{EuL}^{3+}) \geq K_{\text{ex}}(\text{EuL}_2^{3+})/K_{\text{ex}}(\text{HL}^{+})$  – mathematically equivalent to the model assuming that the species extracted into the organic phase are  $\overline{\text{EuL}^{3+}}$ ,  $\overline{\text{EuL}_2^{3+}}$ , and  $\overline{\text{HL}^{+}}$ .

Similarly also the combination of the species  $\overline{\text{EuL}_2^{3+}}$ ,  $\overline{\text{EuL}_3^{3+}}$ , and  $\overline{\text{HL}^{+}}$  is under certain conditions mathematically equivalent to the extraction of the species  $\overline{\text{HL}^{+}}$ ,  $\overline{\text{EuL}_2^{3+}}$ , and  $\{\overline{\text{EuL}_2\text{H}}_{-1}, \text{B}^{-}\}$ , and in the limit case (when  $K_{\text{ex}}(\text{EuL}_2^{3+}) = K_{\text{ex}}(\text{EuL}_3^{3+})/K_{\text{ex}}(\text{HL}^{+})$ ) it is equivalent also to the extraction of only  $\overline{\text{HL}^{+}}$  and  $\{\overline{\text{EuL}_2\text{H}}_{-1}^{2+}, \text{B}^{-}\}$ . From the extraction data alone it is therefore impossible to decide which species actually exists in the organic phase. However, no association was observed in the extraction systems with nitrobenzene solutions of dicarbollide while the solvation by several molecules of ligands is quite common. It is therefore reasonable from the chemical point of view to prefer models that do not assume the association of the extracted complex with the molecule of dicarbollide.

In the case of simpler models (extraction of  $\overline{\text{Eu}^{3+}}$ ,  $\overline{\text{EuL}^{3+}}$ ,  $\overline{\text{EuL}_2^{3+}}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ ) the agreement of the theoretical and experimental values of  $\log D$  can be improved also by the introduction of the assumption of protonization of the polyethylene glycol molecule in the aqueous phase (reaction (E)). However, the theoretical dependence of  $\log D$  vs  $\log c_L$  exhibits an increase of  $\log D$  for  $\log c_L > 0.13$  (due to the decrease of  $\text{H}^{+}$  concentration in the aqueous phase as a consequence of the formation of  $\text{HL}^{+}$  species) that does not correspond to the experiment.

Because at sufficiently high concentrations of the dicarbollide in the  $\text{Eu}^{3+}$ – $\text{HClO}_4$ –PEG system (*cf.* Figs 3 and 4) the contribution of  $\overline{\text{Eu}^{3+}}$  ions to the total concentration of extracted europium is not always negligible (in contrast to the extraction of  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$  (*cf.*<sup>2</sup>)), it is possible to calculate from the experimental data given in Table I also the value of the extraction constant of the  $\text{Eu}^{3+}$  ion. Two alternate models were treated in this way, *i.e.*, the model assuming the extraction of the species  $\overline{\text{EuL}^{3+}}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ , and  $\overline{\text{EuL}_2^{3+}}$ , and the more complex model assuming the extraction of the species  $\overline{\text{EuL}^{3+}}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ ,  $\overline{\text{EuL}_2^{3+}}$ , and  $\overline{\text{EuL}_3^{3+}}$ . In both cases the obtained values of  $\log K_{\text{ex}}(\text{Eu}^{3+})$  (1.63 and 1.52, respectively) are close to the value measured in the system in the absence of polyethylene glycol (1.43).

Also the calculated values of the extraction constant of the species  $\overline{\text{HL}^{+}}$ ,  $\log K_{\text{ex}}(\text{HL}^{+}) = 2.67 - 2.91$  (Table III) are nearly identical with the values obtained in our previous paper<sup>2</sup> for the strontium extraction ( $\log K_{\text{ex}}(\text{HL}^{+}) = 2.91$ ) and barium extraction ( $\log K_{\text{ex}}(\text{HL}^{+}) = 2.83$ ) in an analogous system. Because these values were obtained by independent measurements (extraction of  $\text{Eu}^{3+}$  in the systems with and without PEG, or the extraction of  $\text{Eu}^{3+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ) the observed agreement can be taken for a proof of the correctness of the proposed mechanism.

TABLE III

Comparison of various models of europium extraction from the aqueous solutions of perchloric acid by the nitrobenzene solution of dicarbolide in the presence of polyethylene glycol PEG 400. The species  $\text{EuL}_p\text{B}_q\text{H}_r(3-q+r)^+$  are written in an abbreviated form as  $(p, q, r)$  ( $c(\text{HClO}_4) = 0.1-0.5 \text{ mol l}^{-1}$ ,  $c(\text{dicarbolide}) = 0.001-0.1 \text{ mol l}^{-1}$ ;  $c_L = 3 \cdot 10^{-4}-0.3 \text{ mol l}^{-1}$ )

Model <sup>a</sup>	$\log K_{ex}(\text{HL}^+)$	$\log K_{ex}(p, q, r)$	$U^b$	$s^c$
(1, 0, 0)	2.11 ± 0.21	6.49(6.72)	36.99	0.5794
(1, 0, -1)	2.59 ± 0.24	4.94(5.17)	7.712	0.2768
(1, 0, 0), (1, 0, -1)	2.41 ± 0.21	6.01 ± 0.20, 4.55 ± 0.20	3.943	0.1938
(1, 0, -1), (1, 1, -1)	2.68 ± 0.11	4.76 ± 0.14, 6.20 ± 0.17	2.357	0.1498
(1, 0, 0), (1, 0, -1), (2, 0, 0)	2.67 ± 0.14	6.20 ± 0.17, 4.74 ± 0.18, 8.82(9.11)	2.351	0.1502
(1, 0, 0), (1, 0, -1), (1, 1, -1)	2.67 ± 0.14	5.25(6.04), 4.74 ± 0.17, 6.15(6.39)	2.345	0.1502
(1, 0, 0), (1, 0, -1), (2, 0, -1)	2.91 ± 0.20	6.52 ± 0.22, 4.97 ± 0.22, 6.67(7.01)	1.781	0.1309
(1, 0, 0), (1, 0, -1), (2, 0, 0), (2, 0, -1)	2.90 ± 0.18	6.47 ± 0.20, 4.96 ± 0.21, 8.96(9.32) 6.55(6.88)	1.564	0.1232
(1, 0, 0), (1, 0, -1), (2, 0, 0), (3, 0, 0)	2.81 ± 0.10	6.39 ± 0.12, 4.91 ± 0.13, 8.17(8.77), 10.46(10.73)	1.103	0.1035
(1, 0, 0), (1, 0, -1), (2, 0, 0), (2, 1, -1)	2.81 ± 0.07	6.39 ± 0.12, 4.91 ± 0.08, 7.99(8.76), 7.66 ± 0.24	1.103	0.1035
(1, 0, 0), (1, 0, -1), (3, 0, 0)	2.81 ± 0.10	6.40 ± 0.12, 4.91 ± 0.13, 10.48(10.75)	1.114	0.1035
(1, 0, 0), (1, 0, -1), (2, 0, 0)	2.81 ± 0.19	6.36(6.56), 4.90 ± 0.18, 8.91 ± 0.22	1.482	0.1205
(2, 0, -1), (3, 0, -1)		5.57(6.63), 7.09(7.42),		
(1, 0, 0), (1, 0, -1), (3, 0, 0) eq. (G)	2.79 ± 0.12	6.37 ± 0.13, 4.90 ± 0.15, 10.75(11.03) 0.88(1.20) <sup>d</sup>	0.976	0.0973

TABLE III  
(Continued)

Model <sup>a</sup>	$\log K_{ex}(HL^+)$	$\log K_{ex}(p, q, r)$	$U^b$	$s^c$
(1, 0, 0), eq(E)	(1, 0, -1), (2, 0, 0)	6.56 ± 0.20, 5.09 ± 0.21, 9.13(9.45) 0.72(0.93) <sup>e</sup>	1.499	0.1206
(0, 0, 0) <sup>f</sup> , (2, 0, 0)	(1, 0, -1)	1.63(1.88), 6.15 ± 0.20, 4.75 ± 0.16, 8.84(9.13)	2.298	0.1494
(0, 0, 0), (2, 0, 0)	(1, 0, 0), (1, 0, -1), (3, 0, 0)	1.52(1.74), 6.37 ± 0.13, 4.92 ± 0.13 8.24(8.80), 10.46(10.73)	1.094	0.1036

<sup>a</sup> For each model the first value in the column of logarithms of constants gives  $\log K_{ex}(HL^+)$  - reaction (B), Eq. (4), and the following value gives  $\log K_{ex}(EuL_p B_q H_r)$  - reaction (H), Eq. (11), in the sequence corresponding to the sequence of complexes in the preceding column. The following values were used for computations:  $K_D = 1.1 \cdot 10^{-3}$  and  $K_{ex}(Eu^{3+}) = 27$  (if not stated otherwise, cf. note f). The reliability interval of constants is, in agreement with ref. 7, given as  $\pm 3s(K)$ , where  $s(K)$  is the standard deviation of the constant  $K$ . These values are expressed in the logarithmic scale using the approximate relation  $\log K = \log \{K + 1.5s(K)\} - \log \{K - 1.5s(K)\} > 0.2K$  this relation is not valid and then only the upper limit is given in the parentheses, in the form  $\log K = \log K(\log \{K + 3s(K)\})$ ; <sup>b</sup> for 108 experimental points, <sup>c</sup>  $s$  is the standard deviation ( $s = [U/(n - N)]^{1/2}$ ), where  $n$  is the number of experimental points and  $N$  is the number of unknown equilibrium constants; <sup>d</sup>  $\log K_1(EuL^{3+})$  - reaction (G), Eq. (7); <sup>e</sup>  $\log K_{111}$  - reaction (E), Eq. (5); <sup>f</sup>  $\log K_{ex}(Eu^{3+})$  was calculated from the extraction data in the system Eu-HClO<sub>4</sub>-PEG-dicarbolide-nitrobenzene. Its error was calculated similarly as for other constants (cf. note a), so that it differs from the data given in the text for the constant determined from separate measurements in absence of PEG.

The dependences of the participation of individual species on the total analytical concentration of europium present in the organic phase or on the total analytical concentration of the extracted polyethylene glycol were calculated for all systems under study. These dependences for the lowest ( $0.001 \text{ mol l}^{-1}$ , Fig. 2) and highest ( $0.1 \text{ mol l}^{-1}$ , Fig. 3) concentrations of dicarbolide in the organic phase are given for the model assuming the extraction of the species  $\overline{\text{Eu}}^{3+}$ ,  $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ ,  $\overline{\text{EuL}}_3^{3+}$ , and  $\overline{\text{HL}}^+$ . For comparison, Fig. 4 presents the same dependences calculated for the species  $\overline{\text{Eu}}^{3+}$ ,  $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuLH}}_{-1}^{2+}$ ,  $\overline{\text{EuL}}_2^{3+}$ , and  $\overline{\text{HL}}^+$  and for the dicarbolide concentration  $c_B = 0.1 \text{ mol l}^{-1}$  (the dependence for  $c_B = 0.001 \text{ mol l}^{-1}$  is in this concentration region similar to the dependence given in Fig. 2 –  $\overline{\text{EuLH}}_{-1}^{2+}$  is the predominant species).

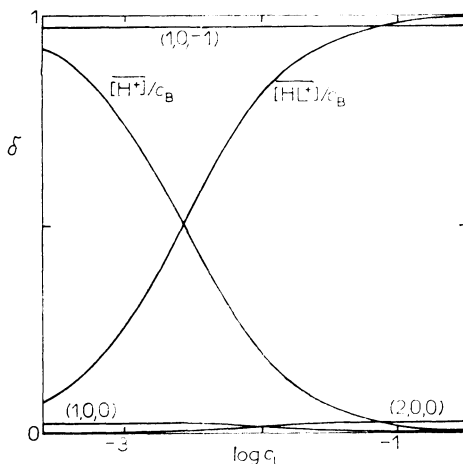


FIG. 2

Composition of complexes in the organic phase for the model (1, 0, 0), (1, 0, -1), and (2, 0, 0). The following data are given: the portion of extracted  $\text{Eu}^{3+}$  and that of individual complexes  $\overline{\text{EuL}}_p\overline{\text{B}}_q\overline{\text{H}}_r^{3-q+r}$  in the organic phase from the total analytical concentration of europium in the organic phase  $\delta$ , and the portions of the species  $\overline{\text{H}}^+$  and  $\overline{\text{HL}}^+$  from the total concentration of dicarbolide in the system (practically all dicarbolide is present in the organic phase<sup>1</sup>)  $\delta'$ ,  $\delta''$  on the logarithm of the total analytical concentration of PEG 400 in the system. Extraction of europium by the 0.001M nitrobenzene solution of dicarbolide from 0.1005M-HClO<sub>4</sub> in water. The complexes  $\overline{\text{EuL}}_p\overline{\text{B}}_q\overline{\text{H}}_r^{3-q+r}$  are written in the abbreviated form (p, q, r), the value  $\delta = \frac{[p, q, r]}{\sum [p, q, r]}$ ,  $\delta' = \frac{[\overline{\text{H}}^+]}{c_B}$  and  $\delta'' = \frac{[\overline{\text{HL}}^+]}{c_B}$  were calculated using the extraction constants from Table III for the set (1, 0, 0), (1, 0, -1), and (2, 0, 0) and the constant  $K_{ex}(\text{Eu}^{3+}) = 27$

It is evident that at  $c_B = 0.001 \text{ mol l}^{-1}$  practically all europium ( $\sim 97\%$ ) is extracted in the form of  $\overline{\text{EuLH}}_{-1}^{2+}$  species. The contribution of the extracted species  $\overline{\text{Eu}}^{3+}$ ,  $\overline{\text{EuL}}^{3+}$ ,  $\overline{\text{EuL}}_2^{3+}$ , and  $\overline{\text{EuL}}_3^{3+}$ , respectively, increases with the increasing concentration of dicarbolide in the organic phase (Figs 3 and 4) (their extraction degree increases with the third power of  $c_B$ , the extraction of the  $\overline{\text{EuLH}}_{-1}^{2+}$  complex only with the square of  $c_B$ ).

From the comparison of Figs 3 and 4 it is evident that for lower concentrations of PEG ( $c_L \leq 3 \cdot 10^{-2} \text{ mol l}^{-1}$ ) the contributions of the species  $\overline{\text{EuL}}^{3+}$  and  $\overline{\text{EuLH}}_{-1}^{2+}$  are practically identical for both models. This is true also for other sets tested in this study and therefore the existence of the  $\overline{\text{EuL}}^{3+}$  and  $\overline{\text{EuLH}}_{-1}^{2+}$  complexes can be taken for proved. Also their stability constants are relatively reliable (Table III). With the increasing concentration of PEG also higher complexes are formed but the relative participation of individual species on the total concentration of extracted europium remains uncertain similarly as the eventual existence of the  $\overline{\text{EuL}}^{3+}$  complex in the aqueous phase. As to these species, they can play a role only at relatively high concentrations of PEG in the aqueous phase when the constant values of the activity

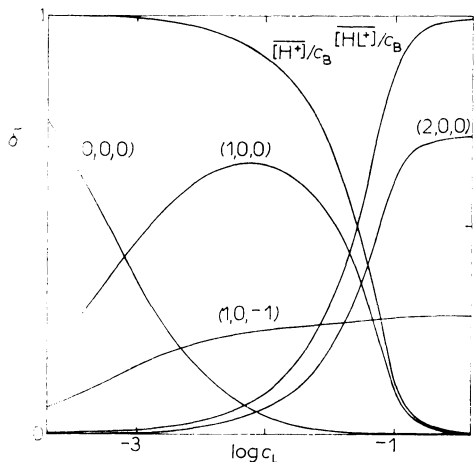


FIG. 3

Composition of complexes in the organic phase for the extraction by the 0.1M solution of dicarbolide. For all other conditions — *cf.* captions to Fig. 2

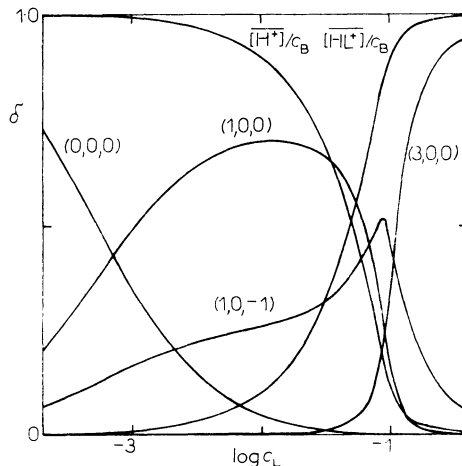


FIG. 4

Composition of complexes in the organic phase, calculated for the model (1,0,0), (1,0,-1), and (3,0,0) for the extraction of europium by the 0.1M solution of dicarbolide. For all other conditions — *cf.* captions to Fig. 2

coefficients cannot be guaranteed. Then it cannot be unambiguously decided whether the differences between the values of  $U$  for various models are due to the presence of a certain complex or whether they can be ascribed to the non-ideality of the system.

The explanation of the maxima on the curves of  $\text{Eu}^{3+}$  extraction by dicarbolide in the presence of PEG is therefore analogous to the case of bivalent ions  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . In both cases there is a competition between the extractable complex of the metal and the protonized PEG with respect to the anionic extractant in the organic phase. However, the composition of the extracted complex cannot be determined in this case as unambiguously as it was possible in the case of the bivalent ions  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . It seems probable that a higher number of complexes is extracted into the organic phase. The species  $\overline{\text{EuL}}^{3+}$  and  $\overline{\text{EuLH}}_{-1}^{2+}$  are predominant at lower concentrations of PEG (in dependence on the concentration of the extractant). Their existence was convincingly proved in this study. It is also evident that with the increase of the ligand concentration these species react with 1–2 other molecules of PEG forming thus higher complexes, most probably  $\overline{\text{EuL}}_2^{3+}$ ,  $\overline{\text{EuL}}_2\overline{\text{H}}_{-1}^{2+}$ , and  $\overline{\text{EuL}}_3^{3+}$ ; however, their participation on the total extraction of europium cannot be unambiguously determined from our data.

#### LIST OF SYMBOLS

$B^-$	dicarbollylcobaltate anion $\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$
$c_B$	total analytical concentration of dicarbollylcobaltate (initial concentration of the dicarbolide in the organic phase)
$c_L$	total analytical concentration of polyethylene glycol
$c_L^{\text{max}}$	the value of $c_L$ corresponding to the maximum on the dependence of $\log D_{\text{Eu}}$ vs $\log c_L$
$D_{\text{Eu}}$	europium distribution ratio in the system under study
$L$	polyethylene glycol PEG 400 (in equations and formulas)
PEG	polyethylene glycol PEG 400 (in the text)
$K_D$	distribution constant of polyethylene glycol in the water–nitrobenzene system; Eq. (6)
$K_{\text{ex}}(\text{HL}^+)$	extraction constant of polyethylene glycol by the nitrobenzene solution of dicarbolide; Eq. (4)
$K_{\text{ex}}(\text{EuL}^{3+})$	extraction constant of the species $\text{EuL}^{3+}$ ; Eq. (2)
$K_{\text{ex}}(\text{EuLH}_{-1}^{2+})$	extraction constant of the species $\text{EuLH}_{-1}^{2+}$ ; Eq. (3)
$K_{\text{ex}}(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)+})$	extraction constant of the species with the general formula $\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)+}$ ; Eq. (11)
$K_{\text{H1}}$	protonization constant of polyethylene glycol in water; Eq. (5)
$K_1(\text{EuL}^{3+})$	stability constant of the europium complex with polyethylene glycol in water; Eq. (7)
$U$	sum of squares of differences between the experimental and calculated values of $\log D_{\text{Eu}}$ ; Eq. (14)
$K(\text{EuL}_p\text{B}_q\text{H}_r^{(3-q+r)+})$	stability constant of the species $\text{EuL}_p\text{B}_q\text{H}_r$ in water; Eq. (12)

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