

EUROPIUM AND CERIUM EXTRACTION BY THE NITROBENZENE SOLUTION OF DICARBOLIDE IN THE PRESENCE OF POLYETHYLENE GLYCOLS

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Extraction of Eu^{3+} and Ce^{3+} microamounts from 0.1–0.4M perchloric acid by the nitrobenzene solution of dicarbolyde $\text{H}^+[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ in the presence of polyethylene glycols ($\bar{M}_r = 200, 300, 400$) has been studied. The equilibrium data and the typical maxima on the dependences of the metal distribution ratio on the total analytical concentration of polyethylene glycol in the system can be explained assuming that the species $\text{ML}_{\text{org}}^{3+}$, $\text{ML}_{2\text{org}}^{3+}$, $\text{ML}_{3\text{org}}^{3+}$, $\text{MLH}_{-1\text{org}}^{2+}$, and HL_{org}^+ (where $\text{M}^{3+} = \text{Eu}^{3+}, \text{Ce}^{3+}$; L = polyethylene glycol) are extracted into the organic phase. The values of extraction and equilibrium constants in the organic phase were determined and the effect of the polyethylene glycol molecular weight on the equilibrium constants and on the abundances of individual species in the organic phase is discussed. It has been found that the addition of polyethylene glycol to the acid – nitrobenzene – dicarbolyde system increases the values of the separation factors $\alpha_{\text{Ce}/\text{Eu}}$.

In our previous papers^{1–4} we have studied the extraction of Sr and Ba by the nitrobenzene solutions of bis-1,2-dicarbollyl-cobalt(III)-acid (henceforth denoted dicarbolyde, H^+B^-) in the presence of either polyethylene glycols (denoted PEG, in equations and formulas by the symbol L) with the average molecular weight of 200–400 (PEG 200–PEG 400) or linear polyethers containing 2–6 oxygen atoms, and also the extraction of europium in the presence of PEG 400. We have shown that the extraction equilibria as well as the typical maxima on the dependences of the extracted metal distribution ratios on the total (analytical) concentration of the polyoxy compound in the system under study (the concentrations are always taken relatively to the volume of one phase) can be explained by the competition of the extracted metal charged complexes with the protonized ligand HL_{org}^+ in the compensation of the dicarbolyde anion negative charge in the organic phase. The composition of the extracted metal complexes depends on the nature of the metal ion and also on the character of the ligand. In the europium extraction in the presence of PEG 400 a series of complexes ($\text{EuL}_{\text{org}}^{3+}$, $\text{EuL}_{2\text{org}}^{3+}$, $\text{EuL}_{3\text{org}}^{3+}$, and $\text{EuLH}_{-1\text{org}}^{2+}$) were found in the organic phase and, moreover, the formation of europium complexes with PEG in the aqueous phase ($\text{EuL}_{\text{aq}}^{3+}$ and/or $\text{EuLH}_{-1\text{aq}}^{2+}$) cannot be excluded.

In the papers mentioned above also the theoretical expressions for the dependences of the maximum position on the curves of the extracted metal distribution ratios

(D_M) vs the total (analytical) concentration of the ligand in the system (c_L) were derived for certain special conditions and it has been demonstrated that they are in good agreement with the experimental data.

The aim of the present study was to find out whether the europium extraction mechanism mentioned above could be used also for the description of the extraction in the presence of lower polyethylene glycols (PEG 200 and 300) and for cerium extraction in the presence of PEG 200, 300, and 400, for the determination of the composition of complexes present in the organic phase, of the extraction constants and stability constants in the organic phase, as well as for the determination of the dependences of these constants on the molecular weight of PEG. Another aim was to investigate whether and how the separation factors $\alpha_{Ce/Eu}$ ($= D_{Ce}/D_{Eu}$) were affected by the addition of polyethylene glycol to the extraction system, and, eventually, to find the dependence of $\alpha_{Ce/Eu}$ on the molecular weight of the respective polyethylene glycol.

In spite of the fact that the europium extraction in the presence of PEG 400 was already described in our previous study, these measurements in the system water-HClO₄-PEG 400-nitrobenzene-dicarbollide were repeated in order to be able to compare the europium and cerium extraction under as similar conditions as possible.

Because the model described above cannot explain the extraction of Eu³⁺ and Ce³⁺ in the presence of PEG 600 and 1 000 (similarly as it is the case with Sr²⁺ and Ba²⁺) the results obtained with these polyethylene glycols will be published in one of our next communications.

EXPERIMENTAL

The reagents and experimental procedures used were the same as in our previous studies. Polyethylene glycols PEG 200, PEG 300, and PEG 400 (Koch-Light) with the average molecular weight 200, 300, and 400, respectively, were used without any further purification. The nitrobenzene solution of dicarbollide (0.1M) in the form of the acid H⁺[(C₂B₉H₁₁)₂Co]⁻ was prepared and analysed using the procedure described in the paper³. The radionuclides ^{152,154}Eu and ¹⁴⁴Ce were of the standard radiochemical purity.

Extraction experiments were carried out in 10 ml glass probes with polyethylene stoppers, 2 ml of each phase were shaken for one hour at the temperature of 25 ± 1°C. The Eu and Ce distribution ratios were determined radiometrically (in the case of Ce after the establishment of the radioactive equilibrium between ¹⁴⁴Ce and ¹⁴⁴Pr) using a well-type scintillation detector and the gamma analyzer NK 350 (Gamma, Budapest).

RESULTS AND DISCUSSION

In the systems under study the dependences of log D_{Eu} and log D_{Ce} , respectively, on the logarithm of the total (analytical) concentration of PEG in the system (log c_L) were experimentally measured for various concentrations of perchloric acid in the

aqueous phase ($c(\text{HClO}_4) = 0.1-0.4 \text{ mol} \cdot \text{l}^{-1}$) and for various concentrations of dicarbollide in the organic phase ($c(\text{H}^+\text{B}^-) = 0.01-0.05 \text{ mol} \cdot \text{l}^{-1}$). The individual combinations of perchloric acid and extractant concentrations were chosen so that $-1 < \log D < 2.5$. The results are summarized in Tables I–VI and in the case of Ce extraction in the presence of PEG 200 they are also illustrated in Fig. 1. All the concentrations of perchloric acid, dicarbollide, and polyethylene glycol are taken relatively to the volume of one phase ($V_{\text{aq}} = V_{\text{org}}$). The value of the Eu extraction constant in the system perchloric acid–nitrobenzene–dicarbollide ($K_{\text{ex}}(\text{Eu}^{3+}) = 27$) was taken from our previous study. The extraction constant $K_{\text{ex}}(\text{Ce}^{3+}) = 33$ was calculated from the extraction data of Benešová⁵. The distribution constants $K_{\text{D}} = 1.6 \cdot 10^{-3}$ (PEG 200), $1.5 \cdot 10^{-3}$ (PEG 300), and $1.3 \cdot 10^{-3}$ (PEG 400) are those used in our previous study².

TABLE I

The distribution ratio of europium in dependence on the concentration of polyethylene glycol PEG 200 for the europium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.01-0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1-0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_{\text{L}}$ and $\log D_{\text{Eu}}$ are given for each point

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 0.570; -3.000, 0.692; -2.745, 0.848; -2.495, 1.015; -2.252, 1.119;
 -2.000, 1.397; -1.745, 1.583; -1.495, 1.721; -1.252, 1.793; -1.000, 1.766;
 -0.745, 1.608; -0.495, 1.403; -0.252, 1.255;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.316; -3.000, -0.148; -2.745, 0.033; -2.495, 0.219; -2.252, 0.415;
 -2.000, 0.605; -1.745, 0.759; -1.495, 0.857; -1.252, 0.890; -1.000, 0.790;
 -0.745, 0.587; -0.495, 0.413; -0.252, 0.247;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -1.226; -3.000, -1.081; -2.745, -0.903; -2.495, -0.752; -2.252, -0.590;
 -2.000, -0.458; -1.745, -0.346; -1.495, -0.288; -1.252, -0.289; -1.000, -0.415;
 -0.745, -0.675; -0.495, -0.811; -0.252, -0.961;

$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.390; -3.000, -0.289; -2.745, -0.130; -2.495, 0.031; -2.252, 0.216;
 -2.000, 0.417; -1.745, 0.608; -1.495, 0.760; -1.252, 0.854; -1.000, 0.828;
 -0.745, 0.710; -0.495, 0.492; -0.252, 0.318;

$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -1.359; -3.000, -1.245; -2.745, -1.100; -2.495, -0.916; -2.252, -0.731;
 -2.000, -0.561; -1.745, -0.372; -1.495, -0.211; -1.252, -0.124; -1.000, -0.141;
 -0.745, -0.247; -0.495, -0.425; -0.252, -0.580

TABLE II

The distribution ratio of cerium in dependence on the concentration of polyethylene glycol PEG 200 for the cerium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.01-0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1-0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_L$ and $\log D_{\text{Ce}}$ are given for each point

$$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1} \quad c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$$

-3.000, 1.015; -2.745, 1.184; -2.495, 1.343; -2.252, 1.489; -2.000, 1.643;
-1.745, 1.804; -1.495, 1.959; -1.252, 2.062; -1.000, 2.040; -0.745, 1.905;
-0.495, 1.707; -0.252, 1.483;

$$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1} \quad c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$$

-3.000, 0.302; -2.745, 0.507; -2.495, 0.673; -2.252, 0.831; -2.000, 0.979;
-1.745, 1.121; -1.495, 1.189; -1.252, 1.204; -1.000, 1.070; -0.745, 0.897;
-0.495, 0.681; -0.252, 0.574;

$$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1} \quad c(\text{H}^+, \text{B}^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$$

-3.000, -0.571; -2.745, -0.385; -2.495, -0.233; -2.252, -0.059; -2.000, 0.057;
-1.745, 0.110; -1.495, 0.154; -1.252, 0.112; -1.000, -0.014; -0.745, -0.230;
-0.495, -0.350; -0.252, -0.526;

$$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1} \quad c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$$

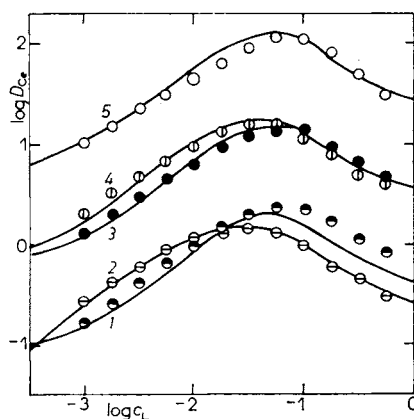
-3.000, 0.108; -2.745, 0.293; -2.495, 0.471; -2.252, 0.640; -2.000, 0.801;
-1.745, 0.966; -1.495, 1.063; -1.252, 1.128; -1.000, 1.135; -0.745, 0.974;
-0.495, 0.828; -0.252, 0.672;

$$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1} \quad c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$$

-3.000, -0.775; -2.745, -0.594; -2.495, -0.374; -2.252, -0.183; -2.000, -0.021;
-1.745, 0.175; -1.495, 0.306; -1.252, 0.371; -1.000, 0.359; -0.745, 0.228;
-0.495, 0.058; -0.252, -0.081

FIG. 1.

Logarithm of the Ce^{3+} distribution ratio as a function of the total (analytical) concentration of polyethylene glycol PEG 200. $c(\text{HClO}_4)/\text{mol} \cdot \text{l}^{-1}$, $c(\text{H}^+, \text{B}^-)/\text{mol} \cdot \text{l}^{-1}$: Curve 1 0.4, 0.05; 2 0.1, 0.01; 3 0.2, 0.05; 4 0.1, 0.025; 5 0.1, 0.05. Solid curves were calculated for the constants given in Table VII (model $\text{Ce}_{\text{org}}^{3+}$, $\text{CeL}_{\text{org}}^{3+}$, $\text{CeLH}_{-1\text{org}}^{2+}$, $\text{CeL}_{2\text{org}}^{3+}$, $\text{CeL}_{3\text{org}}^{3+}$, and HL_{org}^+)



In the interpretation of experimental data we have used the mechanism proposed in our previous paper⁴ dealing with Eu^{3+} extraction in the presence of PEG 400, *i.e.*, assuming that in the system $\text{M}^{3+}\text{-HClO}_4\text{-water-PEG-dicarbolide-nitrobenzene}$ (where $\text{M}^{3+} = \text{Eu}^{3+}$ or Ce^{3+}) the following reactions take place: distribution of PEG between the aqueous and nitrobenzene phases,



extraction of protonized PEG into the organic phase,

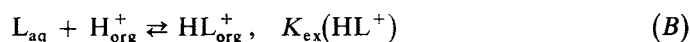


TABLE III

The distribution ratio of europium in dependence on the concentration of polyethylene glycol PEG 300 for the europium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.01\text{--}0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1\text{--}0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_L$ and $\log D_{\text{Eu}}$ are given for each point

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 0.819; -3.000, 1.007; -2.745, 1.222; -2.495, 1.428; -2.252, 1.616;
 -2.000, 1.823; -1.745, 1.940; -1.495, 1.973; -1.252, 1.787; -1.000, 1.502;
 -0.745, 1.223; -0.495, 1.023;

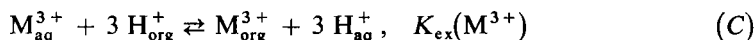
$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 0.209; -3.000, 0.424; -2.745, 0.650; -2.495, 0.841; -2.252, 1.042;
 -2.000, 1.164; -1.745, 1.156; -1.495, 1.008; -1.252, 0.774; -1.000, 0.518;
 -0.745, 0.287; -0.495, 0.053;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.601; -3.000, -0.387; -2.745, -0.208; -2.495, -0.038; -2.252, 0.063;
 -2.000, 0.076; -1.745, -0.060; -1.495, -0.242; -1.252, -0.416; -1.000, -0.634;
 -0.745, -0.851; -0.495, -1.138;

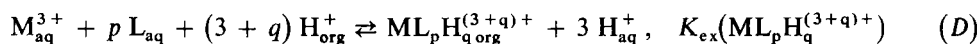
$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.137; -3.000, 0.038; -2.745, 0.221; -2.495, 0.446; -2.252, 0.636;
 -2.000, 0.822; -1.745, 0.943; -1.495, 0.957; -1.252, 0.796; -1.000, 0.517;
 -0.745, 0.276; -0.495, 0.088

$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -1.099; -3.000, -0.930; -2.745, -0.729; -2.495, -0.499; -2.252, -0.316;
 -2.000, -0.155; -1.745, -0.014; -1.495, -0.001; -1.252, -0.146; -1.000, -0.403;
 -0.745, -0.625; -0.495, -0.818

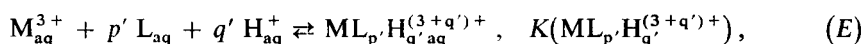
exchange of Eu^{3+} or Ce^{3+} , respectively, between the aqueous and organic phases,



extraction of the species $\text{ML}_p\text{H}_q^{(3+q)+}$ into the organic phase,



and, eventually, the formation of the complexes of the type $\text{ML}_p \cdot \text{H}_q^{(3+q')+}$ in the aqueous phase,



where

$$K_D = [\text{L}]_{\text{org}}/[\text{L}]_{\text{aq}} \quad (\text{I})$$

TABLE IV

The distribution ratio of cerium in dependence on the concentration of polyethylene glycol PEG 300 for the cerium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.01\text{--}0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1$ to $0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_L$ and $\log D_{\text{Ce}}$ are given for each point

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 1.204; -3.000, 1.385; -2.745, 1.569; -2.495, 1.770; -2.252, 1.960;
 -2.000, 2.131; -1.745, 2.259; -1.495, 2.240; -1.252, 2.051; -1.000, 1.726;
 -0.745, 1.472; -0.495, 1.255;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 0.573; -3.000, 0.781; -2.745, 0.970; -2.495, 1.157; -2.252, 1.311;
 -2.000, 1.410; -1.745, 1.414; -1.495, 1.233; -1.252, 0.987; -1.000, 0.751;
 -0.745, 0.509; -0.495, 0.318;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.182; -3.000, -0.015; -2.745, 0.170; -2.495, 0.299; -2.252, 0.369;
 -2.000, 0.391; -1.745, 0.231; -1.495, 0.050; -1.252, -0.128; -1.000, -0.357;
 -0.745, -0.511; -0.495, -0.779;

$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, 0.295; -3.000, 0.485; -2.745, 0.673; -2.495, 0.847; -2.252, 1.015;
 -2.000, 1.168; -1.745, 1.281; -1.495, 1.277; -1.252, 1.096; -1.000, 0.810;
 -0.745, 0.591; -0.495, 0.330;

$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.252, -0.538; -3.000, -0.353; -2.745, -0.148; -2.495, 0.014; -2.252, 0.189;
 -2.000, 0.381; -1.745, 0.468; -1.495, 0.468; -1.252, 0.298; -1.000, 0.023;
 -0.745, -0.209; -0.495, -0.402

$$K_{\text{ex}}(\text{HL}^+) = [\text{HL}^+]_{\text{org}}/[\text{H}^+]_{\text{org}} [\text{L}]_{\text{aq}} \quad (2)$$

$$K_{\text{ex}}(\text{M}^{3+}) = [\text{M}^{3+}]_{\text{org}} [\text{H}^+]_{\text{aq}}^3/[\text{M}^{3+}]_{\text{aq}} [\text{H}^+]_{\text{org}}^3 \quad (3)$$

$$K_{\text{ex}}(\text{ML}_p\text{H}_q^{(3+q)+}) = [\text{ML}_p\text{H}_q^{(3+q)+}]_{\text{org}} [\text{H}^+]_{\text{aq}}^3/[\text{M}^{3+}]_{\text{aq}} [\text{L}]_{\text{aq}}^p [\text{H}^+]_{\text{org}}^{(3+q)} \quad (4)$$

$$K(\text{ML}_p\text{H}_q^{(3+q'+)+}) = [\text{ML}_p\text{H}_q^{(3+q'+)+}]_{\text{aq}}/[\text{M}^{3+}]_{\text{aq}} [\text{L}]_{\text{aq}}^{p'} [\text{H}^+]_{\text{aq}}^{q'} \quad (5)$$

Protonization of polyethylene glycols PEG 200–400 (the formation of HL^+ species) in the aqueous phase was never proved in our previous studies and therefore we did not take it into consideration even in this study.

TABLE V

The distribution ratio of europium in dependence on the concentration of polyethylene glycol PEG 400 for the europium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.01-0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1$ to $0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_L$ and $\log D_{\text{Eu}}$ are given for each point

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, 0.879; -3.252, 1.072; -3.000, 1.283; -2.745, 1.499; -2.495, 1.760;
 -2.252, 1.924; -2.000, 2.102; -1.745, 2.196; -1.495, 1.979; -1.252, 1.685;
 -1.000, 1.359; -0.745, 1.099;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, 0.368; -3.252, 0.586; -3.000, 0.796; -2.745, 1.050; -2.495, 1.251;
 -2.252, 1.406; -2.000, 1.481; -1.745, 1.318; -1.495, 0.991; -1.252, 0.703;
 -1.000, 0.443; -0.745, 0.186;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, -0.401; -3.252, -0.177; -3.000, 0.019; -2.745, 0.204; -2.495, 0.360;
 -2.252, 0.367; -2.000, 0.235; -1.745, -0.011; -1.495, -0.208; -1.252, -0.454;
 -1.000, -0.671; -0.745, -0.982;

$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, -0.097; -3.252, 0.076; -3.000, 0.290; -2.745, 0.507; -2.495, 0.738;
 -2.252, 0.931; -2.000, 1.086; -1.745, 1.177; -1.495, 1.045; -1.252, 0.666;
 -1.000, 0.372; -0.745, 0.164;

$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1}$ $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, -1.067; -3.252, -0.881; -3.000, -0.676; -2.745, -0.420; -2.495, -0.229;
 -2.252, -0.038; -2.000, 0.111; -1.745, 0.252; -1.495, 0.088; -1.252, -0.251;
 -1.000, -0.532; -0.745, -0.753

The value of the extracted metal distribution ratio is then given by Eq. 4

$$D_M = \frac{\sum_0^N K_{ex} (ML_p H_q^{(3+q)^+}) [L]_{aq}^p [H^+]_{org}^{(3+q)} [H^+]_{aq}^{-3}}{\{1 + \sum_1^{N'} K (ML_p H_q^{(3+q)^+}) [L]_{aq}^{p'} [H^+]_{aq}^{q'}\}} \quad (6)$$

where N and N' mean the number of complexes present in the organic and aqueous phases, respectively.

The unknown values of free concentrations $[H^+]_{org}$ and $[L]_{org}$ were calculated on the basis of the previously derived relations¹ (that are valid under the assumption

TABLE VI

The distribution ratio of cerium in dependence on the concentration of polyethylene glycol PEG 400 for the cerium extraction by the nitrobenzene solution of dicarbollide ($c(H^+, B^-) = 0.01-0.05 \text{ mol} \cdot \text{l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.1$ to $0.4 \text{ mol} \cdot \text{l}^{-1}$). The values of $\log c_L$ and $\log D_{Ce}$ are given for each point

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(H^+, B^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, 1.157; -3.252, 1.346; -3.000, 1.563; -2.745, 1.802; -2.495, 2.005;
 -2.252, 2.201; -2.000, 2.361; -1.745, 2.471; -1.495, 2.275; -1.252, 1.856;
 -1.000, 1.529; -0.745, 1.268;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(H^+, B^-) = 0.025 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, 0.638; -3.252, 0.823; -3.000, 1.061; -2.745, 1.240; -2.495, 1.444;
 -2.252, 1.611; -2.000, 1.648; -1.745, 1.494; -1.495, 1.145; -1.252, 0.864;
 -1.000, 0.610; -0.745, 0.387;

$c(\text{HClO}_4) = 0.10 \text{ mol} \cdot \text{l}^{-1}$ $c(H^+, B^-) = 0.010 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, -0.090; -3.252, 0.110; -3.000, 0.297; -2.745, 0.461; -2.495, 0.588;
 -2.252, 0.604; -2.000, 0.460; -1.745, 0.226; -1.495, 0.024; -1.252, -0.191;
 -1.000, -0.388; -0.745, -0.658;

$c(\text{HClO}_4) = 0.20 \text{ mol} \cdot \text{l}^{-1}$ $c(H^+, B^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, 0.221; -3.252, 0.388; -3.000, 0.590; -2.745, 0.806; -2.495, 1.002;
 -2.252, 1.170; -2.000, 1.344; -1.745, 1.402; -1.495, 1.252; -1.252, 0.873;
 -1.000, 0.566; -0.745, 0.339;

$c(\text{HClO}_4) = 0.40 \text{ mol} \cdot \text{l}^{-1}$ $c(H^+, B^-) = 0.050 \text{ mol} \cdot \text{l}^{-1}$
 -3.495, -0.668; -3.252, -0.486; -3.000, -0.267; -2.745, -0.083; -2.495, 0.126;
 -2.252, 0.304; -2.000, 0.438; -1.745, 0.491; -1.495, 0.356; -1.252, 0.023;
 -1.000, -0.256; -0.745, -0.471

that the volumes of both aqueous and organic phases are equal)

$$[L]_{\text{org}} = \{r + (r^2 + 4c_L K_D s)^{1/2}\} / 2t, \quad (7)$$

$$[H^+]_{\text{org}} = [L]_{\text{org}} (1 + K_D^{-1}) + c_B - c_L, \quad (8)$$

where

$$r = K_{\text{ex}}(\text{HL}^+) \cdot (c_L - c_B) - 1 - K_D, \quad (9)$$

$$t = K_{\text{ex}}(\text{HL}^+) \cdot (1 + K_D^{-1}). \quad (10)$$

The assumptions under which these relations were derived¹, *i.e.*, the neglect of the proton concentration changes in the aqueous and organic phases due to metal extraction that is present in trace amounts, the neglect of the ligand concentration changes due to the formation of the complex with the extracted metal in the aqueous and organic phases, and the validity of the relations $[B^-]_{\text{org}} \approx c_B$ (all dicarbolidide remains in the organic phase⁶) and $[H^+]_{\text{aq}} \approx c(\text{HClO}_4)$ (perchloric acid remains in the aqueous phase), are valid also under the experimental conditions used in this study.

The most probable set of $\text{ML}_p\text{H}_{q\text{org}}^{(3+q)+}$ and $\text{ML}_p\text{H}_{q\text{aq}}^{(3+q)+}$ species in the organic and aqueous phases, respectively, was chosen by comparing various models acceptable from the chemical point of view. The "best" agreement between the theoretical and experimental values of the distribution ratios D_M was taken as the choice criterion. The following complexes were taken into consideration: $\text{ML}_{\text{org}}^{3+}$, $\text{ML}_{2\text{org}}^{3+}$, $\text{ML}_{3\text{org}}^{3+}$, $\text{ML}_{4\text{org}}^{3+}$ (only in the presence of PEG 200), $\text{MLH}_{-1\text{org}}^{2+}$, $\text{ML}_2\text{H}_{-1\text{org}}^{2+}$, and $\text{ML}_3\text{H}_{-1\text{org}}^{2+}$ in the organic phase, together with $\text{ML}_{\text{aq}}^{3+}$ and $\text{MLH}_{-1\text{aq}}^{2+}$ in the aqueous phase. The equilibrium constants of the reactions (B), (D), and (E) were obtained for every set under consideration using the computational procedure with the general least-square-minimizing programme LETAGROP⁽⁷⁻⁹⁾ including a special subroutine UBBE, based on the Eqs. (6-9) that contains also the subroutines for the graphical output. The difference between the measured and calculated logarithms of the distribution ratios of the extracted metal, D_M , were minimized, *i.e.*,

$$U = \sum (\log D_{M,\text{exp}} - \log D_{M,\text{calc}})^2. \quad (11)$$

The results are summarized in Table VII. It is evident from these results that for all systems under study (*i.e.*, for the extraction of Eu^{3+} and Ce^{3+} in the presence of PEG 200-400) the model considering the extraction of $\text{ML}_{\text{org}}^{3+}$, $\text{MLH}_{-1\text{org}}^{2+}$, $\text{ML}_{2\text{org}}^{3+}$, and $\text{ML}_{3\text{org}}^{3+}$ species together with the extraction of the protonized PEG (HL_{org}^+) fits best the experimental data. The existence of the complexes $\text{ML}_2\text{H}_{-1\text{org}}^{2+}$ and $\text{ML}_3\text{H}_{-1\text{org}}^{2+}$ was not proved as adding these complexes to the basic set of the

TABLE VII

Comparison of certain chosen models of europium and cerium extraction from the aqueous solutions of perchloric acid by the nitrobenzene solutions of dicarbollide in the presence of polyethylene glycols PEG 200, PEG 300, and PEG 400

Model ^a	$\log K_{\text{ex}}(\text{HL}^+)$	$\log K_{\text{ex}}(\text{ML}_p\text{H}_q)$ (resp. $\log K(\text{ML}_p\text{H}_q)$)	U	s^b
Eu-PEG 200, $n^c = 65$				
EuL _{org} , EuLH _{-1 org}	0.95 ± 0.09^d	$4.42 \pm 0.09, 1.54 (1.99)^d$	0.7928	0.1131
EuL _{org} , EuLH _{-1 org} , EuL _{2 org}	1.65 ± 0.15	$4.60 \pm 0.12, 2.40 (2.66),$ $6.71 (7.00)$	0.2906	0.0690
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org}	1.79 ± 0.12	$4.69 \pm 0.12, 2.45 (2.71),$ $6.99 (7.22), 7.13 (7.51)$	0.2309	0.0620
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org}	1.98 (2.20)	$4.84 (5.06), 2.55 (2.83),$ $7.27 (7.60), 8.62 (9.10),$ 0.78 ± 0.10	0.2037	0.0588
EuL _{aq} , EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org} , EuLH _{-1 aq}	1.79 ± 0.14	$4.69 \pm 0.13, 2.45 (2.71),$ $6.99 (7.23), 7.13 (7.55),$ < -2.00	0.2310	0.0626
Ce-PEG 200, $n = 60$				
CeL _{org} , CeLH _{-1 org}	1.10 ± 0.12	$4.92 \pm 0.11, 2.55 (2.88)$	1.0381	0.1350
CeL _{org} , CeLH _{-1 org} , CeL _{2 org}	1.58 ± 0.14	$5.10 \pm 0.11, 2.97 (3.20),$ $6.80 (7.08)$	0.4185	0.0864
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org}	1.68 ± 0.06	$5.17 \pm 0.09, 3.07 \pm 0.23,$ $6.92 \pm 0.26, 7.20 (7.46)$	0.3026	0.0742
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org}	1.88 ± 0.09	$5.34 \pm 0.08, 3.32 \pm 0.18,$ $7.03 (7.30), 9.03 (9.48),$ $1.15 (1.60)$	0.2058	0.0617
CeL _{aq} , CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org} , CeLH _{-1 aq}	1.70 ± 0.09	$5.16 \pm 0.09, 3.22 \pm 0.15,$ $6.87 \pm 0.25, 7.91 (8.16),$ -0.391 ± 0.10	0.1524	0.0531
Eu-PEG 300, $n = 60$				
EuL _{org} , EuLH _{-1 org}	1.85 ± 0.21	$5.36 \pm 0.05, 3.38 (3.72)$	1.1576	0.1425
EuL _{org} , EuLH _{-1 org} , EuL _{2 org}	2.27 ± 0.16	$5.65 \pm 0.14, 3.72 (3.94),$ $7.93 (8.23)$	0.4205	0.0867
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org}	2.46 ± 0.21	$5.79 \pm 0.17, 3.96 (4.19),$ $8.25 (8.62), 9.02 (9.50)$	0.2504	0.0675
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{2 H} -1 org	2.32 ± 0.19	$5.69 \pm 0.18, 3.75 (3.97),$ $8.04 (8.38), 4.02 (4.65)$	0.4129	0.0866
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org} , EuL _{aq}	2.49 ± 0.16	$5.81 \pm 0.14, 4.05 \pm 0.19,$ $8.18 (8.49), 9.77 (9.96),$ $0.85 (1.09)$	0.1932	0.0598
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org} , EuLH _{-1 aq}	2.46 ± 0.13	$5.79 \pm 0.12, 3.97 \pm 0.22,$ $8.27 (8.53), 9.05 (9.38),$ < -1.80	0.2504	0.0681

TABLE VII
 (Continued)

Model ^a	$\log K_{ex}(HL^+)$	$\log K_{ex}(ML_pH_q)$ (resp. $\log K(ML_pH_q)$)	<i>U</i>	<i>s</i> ^b
Ce-PEG 300, <i>n</i> ^c = 60				
CeL _{org} , CeLH _{-1 org}	1.85 ± 0.18	5.83 ± 0.14, 3.61 (3.93)	1.1211	0.1402
CeL _{org} , CeLH _{-1 org} , CeL _{2 org}	2.22 ± 0.17	6.12 ± 0.14, 3.84 (4.09), 8.07 (8.41)	0.4354	0.0882
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org}	2.38 ± 0.15	6.27 ± 0.13, 4.07 (4.28), 8.29 (8.61) 9.16 (9.47)	0.2125	0.0622
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL ₂ H _{-1 org}	2.23 ± 0.18	6.21 ± 0.16, 3.84 (4.12), 8.25 (8.60), 4.62 (5.06)	0.3904	0.0843
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org} , CeL _{aq}	2.43 ± 0.13	6.30 ± 0.12, 4.23 ± 0.20, 7.97 (8.34), 10.17 (10.47), 1.17 ± 0.02	0.1319	0.0494
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org} , CeLH _{-1 aq}	2.36 (2.56)	6.23 ± 0.22, 4.13 (4.36), 8.06 (8.54), 9.44 (9.88), -0.43 (-0.14)	0.1436	0.0516
Eu-PEG 400, <i>n</i> = 60				
EuL _{org} , EuLH _{-1 org}	2.46 ± 0.23	6.10 ± 0.18, 4.43 (4.73)	1.0647	0.1367
EuL _{org} , EuLH _{-1 org} , EuL _{2 org}	2.62 ± 0.20	6.27 ± 0.18, 4.49 (4.75), 8.51 (8.92)	0.8154	0.1207
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org}	2.98 ± 0.06	6.55 ± 0.12, 4.98 ± 0.12, 8.69 (9.34) 10.90 ± 0.07	0.4556	0.0910
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org}	2.81 ± 0.10	6.39 ± 0.12, 4.91 ± 0.13, 8.17 (8.77), 10.46 (10.73)		
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL ₂ H _{-1 org}	2.78 (3.01)	6.42 (6.64), 4.65 (4.96), 8.83 (9.31), 5.63 (6.21)	0.7400	0.1160
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org} , EuL _{aq}	2.89 ± 0.16	6.48 ± 0.16, 4.88 ± 0.25, 8.17 (9.05), 10.69 (11.00), 0.15 ± 0.08	0.4089	0.0870
EuL _{org} , EuLH _{-1 org} , EuL _{2 org} , EuL _{3 org} , EuLH _{-1 aq}	2.87 ± 0.13	6.47 ± 0.14, 4.87 ± 0.23, 7.91 (9.07), 10.64 (10.97), -0.69 (-0.48)	0.4153	0.0877
Ce-PEG 400, <i>n</i> = 60				
CeL _{org} , CeLH _{-1 org}	2.46 ± 0.20	6.45 ± 0.16, 4.62 (4.89)	0.9050	0.1260
CeL _{org} , CeLH _{-1 org} , CeL _{2 org}	2.58 ± 0.19	6.58 ± 0.17, 4.65 (4.91), 8.56 (8.98)	0.7254	0.1138
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL _{3 org}	2.81 ± 0.09	6.79 ± 0.10, 4.97 ± 0.18, <9.01, 10.57 (10.78)	0.2784	0.0711
CeL _{org} , CeLH _{-1 org} , CeL _{2 org} , CeL ₂ H _{-1 org}	2.81 ± 0.24	6.81 ± 0.23, 4.87 (5.13), 8.97 (9.43), 6.08 (6.49)	0.5426	0.0993

TABLE VII
 (Continued)

model ^a	$\log K_{\text{ex}}(\text{HL}^+)$	$\log K_{\text{ex}}(\text{ML}_p\text{H}_q)$ (resp. $\log K(\text{ML}_p\cdot\text{H}_q)$)	U	s^b
CeL _{org} , CeLH _{-1org} , CeL _{2org} , CeL _{3org} , CeL _{aq}	2.84 ± 0.14	$6.81 \pm 0.13, 5.00 \pm 0.22,$ $<9.12, 10.88 (11.22),$ $0.62 (1.02)$	0.2475	0.0677
CeL _{org} , CeLH _{-1org} , CeL _{2org} , CeL _{3org} , CeLH _{-1aq}	2.83 ± 0.18	$6.80 \pm 0.16, 5.00 (5.22),$ $<9.02, 10.70 (11.01),$ $-0.83 (-0.52)$	0.2622	0.0697

^a the following values are given for each point: $\log K_{\text{ex}}(\text{HL}^+)$ — reaction (B), Eq. (2); $\log K_{\text{ex}}(\text{ML}_p\text{H}_q)$ — reaction (D), Eq. (4), and the stability constants of $\text{ML}_p\cdot\text{H}_q$ complexes in the aqueous phase — reaction (E), Eq. (5). The constants were calculated using the experimental data given in Tables I–VI and the equilibrium constants $K_{\text{ex}}(\text{Eu}) = 27$, $K_{\text{ex}}(\text{Ce}) = 33$, $K_{\text{D}} = 1.6 \cdot 10^{-3}$ (PEG 200), $1.5 \cdot 10^{-3}$ (PEG 300), and $1.3 \cdot 10^{-3}$ (PEG 400). The sequence of values corresponds to the sequence of complexes in the preceding column, the complex charges are not given in sake of simplicity.

^b s — the standard deviation of $\log D$ ($s = [U/(n - N)]^{1/2}$, where n is the number of experimental points and N is the number of unknown equilibrium constants).

^c n — number of experimental points.

^d the reliability interval or its maximum value were calculated by the procedure given in⁵.

^e values taken from ref.⁴.

species $\text{ML}_{\text{org}}^{3+}$, $\text{MLH}_{-1\text{org}}^{2+}$, $\text{ML}_{2\text{org}}^{3+}$, $\text{ML}_{3\text{org}}^{3+}$, and HL_{org}^+ led to the result that the minimum of the function U was found for the values of the constants $K_{\text{ex}}(\text{ML}_2\text{H}_{-1}^{2+})$ and $K_{\text{ex}}(\text{ML}_3\text{H}_{-1}^{2+})$ equal to zero. Not even under the assumption that the ions $\text{Eu}_{\text{org}}^{3+}$ or $\text{Ce}_{\text{org}}^{3+}$ can associate only with two PEG molecules the assumed existence of the $\text{ML}_{2\text{org}}^{3+}$ complex deprotonization does not lead to any substantial decrease of the value of U (cf. Table VII). Similarly, the existence of the species $\text{EuL}_{4\text{org}}^{3+}$ or $\text{CeL}_{4\text{org}}^{3+}$ in the organic phase (in the presence of PEG 200) could not be proved.

The existence of the complexes of the type $\text{ML}_{\text{aq}}^{3+}$ and $\text{MLH}_{-1\text{aq}}^{2+}$, respectively, in the aqueous phase (or the value of their stability constants) remains questionable. Though for certain systems (Ce — PEG 200 and 300, Eu — PEG 300) the addition of these complexes to the set mentioned above yields a rather substantial decrease of the function U , this is not the case for other systems. This fact can be hardly explained from the chemical point of view.

Therefore, it cannot be decided whether this composition of complexes represents species existing in reality or whether they mean only a mere correction for the non-ideality of one or both phases. Hence, the model considering the existence of $\text{ML}_{\text{org}}^{3+}$,

$ML_{2\text{org}}^{3+}$, $ML_{3\text{org}}^{3+}$, $MLH_{-1\text{org}}^{2+}$, and HL_{org}^{+} species seems to be a reasonable approximation of the behaviour of the systems under study in the given concentration range.

The extraction constants of HL_{org}^{+} species, calculated using this model (*cf.* Table VII), are in good agreement mutually as well as with the constants calculated in our previous study of the Sr and Ba extraction in analogous systems. As these constants were obtained by independent measurements (extractions of Ba^{2+} , Sr^{2+} , Ce^{3+} , and Eu^{3+}) this agreement can be taken for a proof of the correctness of the proposed mechanism (it should be noted that for oversimplified models that do not take into consideration the extraction of the higher complexes $ML_{2\text{org}}^{3+}$ and $ML_{3\text{org}}^{3+}$ the calculated value of $K_{\text{ex}}(HL^{+})$ are seriously in disagreement — *cf.* Table VII). From the knowledge of the extraction constants $K_{\text{ex}}(ML_p H_q^{(3+q)+})$, of the distribution constants K_D , and of the Ce^{3+} and Eu^{3+} extraction constants $K_{\text{ex}}(M^{3+})$ the consecutive and also the total stability constants of the species $ML_{p\text{org}}^{3+}$ and the protonization constants of the $MLH_{-1\text{org}}^{2+}$ species in nitrobenzene can be calculated. The results are summarized in Table VIII. The dependence of the logarithm of the total stability constants, $\log \beta(ML_{p\text{org}}^{3+})$, where

$$\beta(ML_{p\text{org}}^{3+}) = [ML_{p\text{org}}^{3+}]_{\text{org}} / [M^{3+}]_{\text{org}} [L]_{\text{org}}^p \quad (12)$$

on the PEG molecular weight is illustrated in Fig. 2.

From this figure it follows that the dependence of $\log \beta(ML_{3\text{org}}^{3+})$ and $\log \beta(ML_{2\text{org}}^{3+})$ on the molecular weight of PEG are approximately linear; the differences can be ascribed to the fact that rather than the linear dependence of $\log \beta$ on the number of oxyethylene units (OEU) of PEG the linear dependence on the number of substituted molecules of water should be expected.

For complexes of the oxyethylene compounds with a higher number of OEU these two dependences are different because the rule that one OEU substitutes just one molecule of water is evidently no more valid^{2,3}. Figs. 3–5 present the dependences of the participation of individual complexes on the total (analytical) concentration of Ce in the organic phase for the extraction of cerium in the presence of PEG 200 and PEG 400. From the Tables VII and VIII and from Figs 3–5 certain conclusions on the stability of complexes in the organic phase can be deduced. While the values of the complex stability constants $K(EuL_{\text{org}}^{3+})$ are in all cases lower than the constants $K(CeL_{\text{org}}^{3+})$ (the stability constants of PEG complexes in nitrobenzene increase in the sequence $H^+ < Eu^{3+} < Ce^{3+} < Sr^{2+} < Ba^{2+}$) so that the ion with the higher diameter has a higher affinity towards PEG (similarly as in the group of alkaline earths), for the formation of higher complexes $ML_{3\text{org}}^{3+}$ we obtain already an inverse dependence. Deprotonization of ML_{org}^{3+} complexes increases with the molecular weight of PEG so that the deprotonized species is the most abundant in PEG 400. For the higher complexes $ML_{2\text{org}}^{3+}$ and $ML_{3\text{org}}^{3+}$ no deprotonization in a higher degree has

TABLE VIII

Stability constants of Eu-PEG and Ce-PEG complexes and the protonization constants of $\text{EuLH}_{-1\text{org}}^{2+}$ and $\text{CeLH}_{-1\text{org}}^{2+}$ complexes in nitrobenzene

Reaction	log <i>K</i>		
	PEG 200	PEG 300	PEG 400
$\text{Eu}_{\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{EuL}_{\text{org}}^{3+}$	6.05	7.18	8.00
$\text{Ce}_{\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{CeL}_{\text{org}}^{3+}$	6.45	7.58	8.16
$\text{EuL}_{\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{EuL}_{2\text{org}}^{3+}$	5.10	5.28	5.03
$\text{CeL}_{\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{CeL}_{2\text{org}}^{3+}$	4.55	4.84	— ^a
$\text{EuL}_{2\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{EuL}_{3\text{org}}^{3+}$	2.94	3.59	5.10
$\text{CeL}_{2\text{org}}^{3+} + \text{L}_{\text{org}} \rightleftharpoons \text{CeL}_{3\text{org}}^{3+}$	3.08	3.69	— ^a
$\text{Eu}_{\text{org}}^{3+} + 2\text{L}_{\text{org}} \rightleftharpoons \text{EuL}_{2\text{org}}^{3+}$	11.15	12.47	13.03
$\text{Ce}_{\text{org}}^{3+} + 2\text{L}_{\text{org}} \rightleftharpoons \text{CeL}_{2\text{org}}^{3+}$	10.99	12.42	— ^a
$\text{Eu}_{\text{org}}^{3+} + 3\text{L}_{\text{org}} \rightleftharpoons \text{EuL}_{3\text{org}}^{3+}$	14.09	16.06	18.13
$\text{Ce}_{\text{org}}^{3+} + 3\text{L}_{\text{org}} \rightleftharpoons \text{CeL}_{3\text{org}}^{3+}$	14.07	16.11	17.17
$\text{EuLH}_{-1\text{org}}^{2+} + \text{H}_{\text{org}}^{+} \rightleftharpoons \text{Eu}_{\text{org}}^{3+}$	2.24	1.83	1.57
$\text{CeLH}_{-1\text{org}}^{2+} + \text{H}_{\text{org}}^{+} \rightleftharpoons \text{Ce}_{\text{org}}^{3+}$	2.10	2.20	1.82

^a in the case of cerium extraction in the presence of PEG 400 the existence of $\text{CeL}_{2\text{org}}^{3+}$ species was not proved.

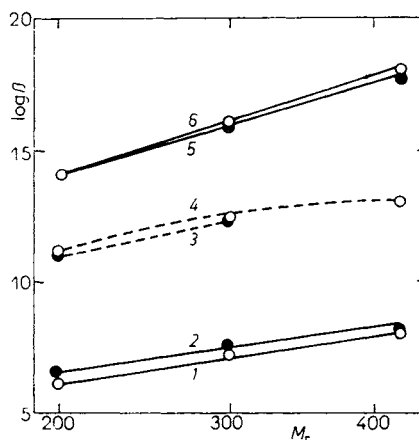


FIG. 2

Stability constants of $\text{EuL}_{\text{porg}}^{3+}$ and $\text{CeL}_{\text{porg}}^{3+}$ species in nitrobenzene in dependence on the molecular weight of PEG. 1 $\text{EuL}_{\text{org}}^{3+}$, 2 $\text{CeL}_{\text{org}}^{3+}$, 3 $\text{CeL}_{2\text{org}}^{3+}$, 4 $\text{EuL}_{2\text{org}}^{3+}$, 5 $\text{CeL}_{3\text{org}}^{3+}$, 6 $\text{EuL}_{3\text{org}}^{3+}$

been proved. The increasing trend for the formation of higher complexes with the increasing molecular weight of PEG seems rather interesting. Analogous results were obtained also in our previous paper³ for the Sr^{2+} and Ba^{2+} extraction by dicarbolides in the presence of linear polyethers of the type $\text{CH}_3\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{CH}_3$ ($n = 1-4$). While in the extraction in the presence of monoglyme and diglyme ($n = 1$ or 2 , respectively) only the existence of the $\text{ML}_{\text{org}}^{2+}$ species in the organic phase was proved, in the extraction in the presence of triglyme and tetraglyme ($n = 3$ or 4 , respectively) the higher complexes $\text{ML}_{2\text{org}}^{2+}$ are probably formed. This behaviour

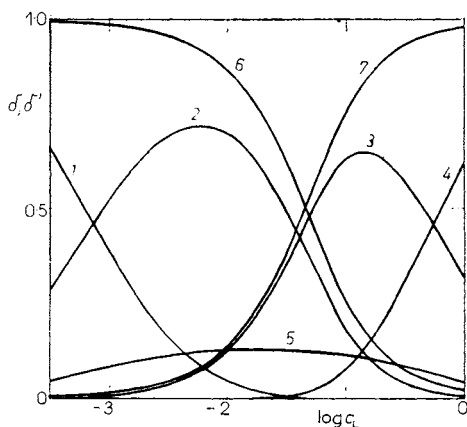


FIG. 3

Abundance of species present in the organic phase during the extraction in the system $\text{Ce}^{3+}-\text{HClO}_4$ -PEG 200-dicarbolide-nitrobenzene. The following values are given: the ratios of the extracted $\text{Ce}_{\text{org}}^{3+}$ and of the complexes $\text{CeL}_p\text{H}_q^{(3+q)+}$ on the total concentration of Ce^{3+} in the organic phase (δ) and the ratios of H_{org}^+ and HL_{org}^+ on the total concentration of dicarbolide in the system (δ'); practically all dicarbolide is present in the organic phase. $c(\text{HClO}_4) = 0.1 \text{ mol} \cdot \text{l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.05 \text{ mol} \cdot \text{l}^{-1}$. The values of δ , δ' were calculated using the constants given in Table VII for the model considering the extraction of the species $\text{Ce}_{\text{org}}^{3+}$, $\text{CeL}_{\text{org}}^{3+}$, $\text{CeLH}_{\text{org}}^{2+}$, CeL_2^{3+} , CeL_3^{3+} , and HL_{org}^+ . Curves: 1 $\delta(\text{Ce}_{\text{org}}^{3+})$, 2 $\delta(\text{CeL}_{\text{org}}^{3+})$, 3 $\delta(\text{CeL}_2^{3+})$, 4 $\delta(\text{CeL}_3^{3+})$, 5 $\delta(\text{CeLH}_{\text{org}}^{2+})$, 6 $\delta'(\text{H}_{\text{org}}^+)$, 7 $\delta'(\text{HL}_{\text{org}}^+)$

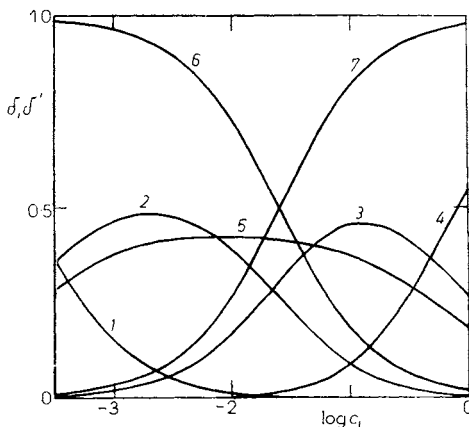


FIG. 4

The same dependences as in Fig. 3 for $c(\text{HClO}_4) = 0.1 \text{ mol} \cdot \text{l}^{-1}$ and $c(\text{H}^+, \text{B}^-) = 0.01 \text{ mol} \cdot \text{l}^{-1}$. Curves: 1-7: cf. caption to Fig. 3

can be evidently ascribed to the fact that the affinity of polyethylene glycol to the metal ion increases with the increasing length of the oxyethylene chain; at the same time the number of coordination sites (*e.g.*, of water molecules in the hydration shell¹⁰ that are substituted by the oxyethylene groups of PEG) is sufficient for the coordination of several molecules of PEG 200, 300, and even 400 (*cf.*³).

The values of the separation factors $\alpha_{\text{Ce/Eu}}$ ($= D_{\text{Ce}}/D_{\text{Eu}}$) increase after the addition of polyethylene glycol to the extraction system from the initial value of $\alpha_{\text{Ce/Eu}} = 1.2$ to 1.5–3. The highest values of separation factors were obtained for the extraction in the presence of PEG 200 under the conditions that the species $\text{ML}_{\text{org}}^{3+}$ predominates in the organic phase, but due to the experimental errors the obtained dependences are not unambiguous (*cf.* also¹¹).

Similarly as in the case of alkaline earth metals even here (in contrast to the majority of other extraction systems) the value of $\log \alpha_{\text{Ce/Eu}}$ corresponding to the difference of the extraction constants can be added to the value of $\log \alpha_{\text{Ce/Eu}}$ obtained by the addition of a common masking agent (*e.g.*, EDTA salts at an appropriate pH value) to the aqueous phase.

In contrast to the separation of alkaline earths¹² the separation effect in rare earths, achieved by the extraction into the nitrobenzene phase, is about one order of magnitude lower than the effect achieved in the aqueous phase by masking by the complex formation with the amino polycarboxylic acid. This fact follows from the comparison of the differences of the extraction constants of the species $\text{EuL}_p\text{H}_q^{(3+q)+}$ and $\text{CeL}_p\text{H}_q^{(3+q)+}$ (*cf.* Table VII) with the stability constants of Eu^{3+} and Ce^{3+} complexes with common amino polycarboxylic acids^{13,14}. In spite of this shortcomings the analytical application of such systems can bring some advantages in certain special cases.

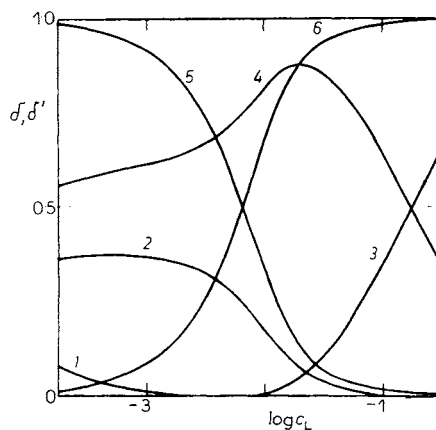


FIG. 5

The same dependences as in Fig. 3 for Ce^{3+} extraction in the system Ce^{3+} – HClO_4 –PEG–dicarbolide–nitrobenzene. $c(\text{HClO}_4) = 0.1 \text{ mol} \cdot \text{l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.01 \text{ mol} \cdot \text{l}^{-1}$. The values of δ , δ' were calculated using the constants given in Table VII for the model considering the extraction of the species $\text{Ce}_{\text{org}}^{3+}$, $\text{CeL}_{\text{org}}^{3+}$, $\text{CeLH}_{\text{org}}^{2+}$, $\text{CeL}_2_{\text{org}}^{3+}$, $\text{CeL}_3_{\text{org}}^{3+}$, and HL_{org}^+ . Curves: 1 $\delta(\text{Ce}_{\text{org}}^{3+})$, 2 $\delta(\text{CeL}_{\text{org}}^{3+})$, 3 $\delta(\text{CeL}_2_{\text{org}}^{3+})$, 4 $\delta(\text{CeLH}_{\text{org}}^{2+})$, 5 $\delta'(\text{H}_{\text{org}}^+)$, 6 $\delta'(\text{HL}_{\text{org}}^+)$

It can be summarized that the Eu and Ce extraction in the presence of polyethylene glycols with the average molecular weight 200–300 proceeds in agreement with the mechanism described in our previous papers^{2,4}. This mechanism (similarly as in the case of Sr^{2+} and Ba^{2+} extraction) is independent of the molecular weight of PEG within the limits studied and comprises the extraction of the complexes $\text{EuL}_{\text{org}}^{3+}$, $\text{EuL}_{2\text{org}}^{3+}$, and $\text{EuL}_{3\text{org}}^{3+}$, and $\text{CeL}_{\text{org}}^{3+}$, $\text{CeL}_{2\text{org}}^{3+}$, and $\text{CeL}_{3\text{org}}^{3+}$, respectively. Moreover, the complexes of the $\text{ML}_{\text{org}}^{3+}$ type can split off one proton in the organic phase and form the species $\text{EuLH}_{-1\text{org}}^{2+}$ and $\text{CeLH}_{-1\text{org}}^{2+}$, respectively. The values of the extraction constants increase in the sequence $\text{PEG 200} < \text{PEG 300} < \text{PEG 400}$ and in the same sequence increases also the ability to form the complexes $\text{EuL}_{3\text{org}}^{3+}$ and $\text{CeL}_{3\text{org}}^{3+}$ at the expense of the species $\text{EuL}_{2\text{org}}^{3+}$ and $\text{CeL}_{2\text{org}}^{3+}$, respectively.

LIST OF SYMBOLS

B^-	dicarbolyde anion $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$
c_{B}	total (analytical) concentration of dicarbolyde (the initial concentration of dicarbolyde in the organic phase)
$c(\text{H}^+\text{B}^-)$	concentration of dicarbolyde (in the form of the acid H^+B^-) in the organic phase
$c(\text{HClO}_4)$	concentration of perchloric acid in the aqueous phase
c_{L}	total (analytical) concentration of polyethylene glycol
D	distribution ratio of the species specified by the index
K_{D}	distribution constant of polyethylene glycol in the system water – nitrobenzene; Eq. (1)
$K_{\text{ex}}(\text{HL}^+)$	extraction constant of polyethylene glycol – Eq. (2)
$K_{\text{ex}}(\text{M}^{3+})$	extraction constant of europium or cerium – Eq. (3)
$K_{\text{ex}}(\text{ML}_p\text{H}_q^{(3+q)+})$	extraction constant of the species of the general formula $\text{ML}_p\text{H}_q^{(3+q)+}$ – Eq. (4)
$K(\text{ML}_p\text{H}_q^{(3+q)+})$	stability constant of the species of the general formula $\text{ML}_p\text{H}_q^{(3+q)+}$ – Eq. (5)
L	polyethylene glycol (in formulas and equations)
M^{2+}	cation of a bivalent metal (Sr^{2+} or Ba^{2+})
M^{3+}	cation of a trivalent metal (Eu^{3+} or Ce^{3+})
M_r	(relative) molecular weight
N	number of complexes of the type $\text{ML}_p\text{H}_q^{(3+q)+}$ assumed to exist in the organic phase
N'	number of complexes of the type $\text{ML}_p\text{H}_q^{(3+q)+}$ assumed to exist in the aqueous phase
s	standard deviation
U	sum of squares of the deviations of the experimental and theoretical values of $\log D$ – Eq. (11)
V_{aq}	volume of the aqueous phase
V_{org}	volume of the organic phase
$\alpha_{\text{Ce/Eu}}$	separation factor of cerium and europium ($\alpha_{\text{Ce/Eu}} = D_{\text{Ce}}/D_{\text{Eu}}$)
$\beta(\text{ML}_p^{3+})$	total stability constant of the species ML_p^{3+} in nitrobenzene – Eq. (12)

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