EXTRACTION OF STRONTIUM AND BARIUM
BY NITROBENZENE SOLUTION OF DICARBOLIDE
IN THE PRESENCE OF POLYETHYLENE GLYCOLS
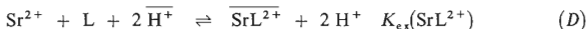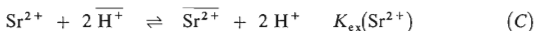
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Extraction of microamounts of Sr^{2+} and Ba^{2+} from $0.2-1.0$M-$HClO_4$ by the nitrobenzene solutions of dicarbolide $H^+[Co(C_2B_9H_{11})_2]^-$ in the presence of polyethylene glycols (PEG) ($\overline{M_r} = 200, 300, 400$) has been investigated. It has been found that the extraction of the protonated polyethylene glycol molecule $(\overline{H^+} + L \rightleftharpoons \overline{HL^+}$, where the bar denotes species present in the organic phase) and the extraction of the complex between the extracted ion and polyethylene glycol, *i.e.*, $M^{2+} + L + 2\overline{H^+} \rightleftharpoons \overline{ML^{2+}} + 2H^+$, are the predominant reactions in this system. The respective equilibrium constants have been determined. The hydration numbers of HL^+ and ML^{2+} ions in the organic phase have been obtained from the determination of water content by Karl Fischer titration method. The extraction constants and stability constants in the organic phase increase in the sequence $H^+ < Sr^{2+} < Ba^{2+}$ and PEG 200 < PEG 300 < PEG 400, while the hydration numbers decrease in the same sequence. Correlations between the hydration numbers and the extraction constants for these cations have been found.

In our previous paper[1] the extraction of microamounts of Sr^{2+} by nitrobenzene solutions of Co(III) dicarbolide — $H^+[Co(C_2B_9H_{11})_2]^-$ (henceforth H^+B^-) in the presence of polyethylene glycol PEG 400 (L) has been studied. The characteristic maxima on the dependence of the strontium distribution ratio (D_{Sr}) on the total concentration of polyethylene glycol have been explained by the competition between the charged strontium complex with PEG $(\overline{SrL^{2+}})$ and the protonated PEG $(\overline{HL^+})$ in the compensation of the negative charge of the dicarbolide anion in the organic phase[1]. The equilibrium constants of the following reactions have been determined

$$L \rightleftharpoons \overline{L} \qquad\qquad K_D \qquad\qquad (A)$$

$$\overline{H^+} + L \rightleftharpoons \overline{HL^+} \qquad\qquad K_{ex}(HL^+) \qquad\qquad (B)$$

$$Sr^{2+} + 2\overline{H^+} \rightleftharpoons \overline{Sr^{2+}} + 2H^+ \qquad K_{ex}(Sr^{2+}) \qquad (C)$$

$$Sr^{2+} + L + 2\overline{H^+} \rightleftharpoons \overline{SrL^{2+}} + 2H^+ \qquad K_{ex}(SrL^{2+}) \qquad (D)$$

(the bar denotes species in the organic phase). An equation, $C_L^{max} = C_B/2 + \beta$, has been derived[1] for the position of the maxima on the curves D_{Sr} vs C_L, where C_B is the dicarbolide concentration in the organic phase, $\beta = 1/K_{ex}(HL^+)$, and C_L^{max} is the ligand concentration corresponding to the maximum on the curve of log D_{Sr} vs log C_L.

In this paper we have studied whether the assumed extraction mechanism of Sr^{2+} extraction in the presence of PEG 400 can be extended also to the case of the extraction in the presence of lower polyethylene glycols (PEG 200 and 300) and to the extraction of Ba^{2+} ions; we intended to determine the respective equilibrium constants and hydration numbers of complexes in the organic phase. Because the proposed model does not explain the extraction in the presence of PEG 600 and 1 000, the results obtained for these polyethylene glycols will be published in one of our future communications.

EXPERIMENTAL

Reagents and the experimental procedures were identical with those used in our previous paper. Polyethylene glycols PEG 200, PEG 300, and PEG 400 (Koch-Light) with the average relative molecular weight 200, 300, and 400, respectively, were used without further purification. The solutions of Sr(II) and Ba(II) salts of dicarbolide were prepared by neutralization of the nitrobenzene solution of dicarbolide by the aqueous solution of strontium or barium hydroxide.

Microamounts of strontium and barium, labelled with ^{85}Sr and ^{133}Ba, respectively, were used for the extraction experiments. 2 ml of each phase were shaken for 30 min (2 min are sufficient for the equilibrium establishment) at the temperature of $25 \pm 1°C$. The activity was measured by the scintillation counter connected with the gamma analyzer NK 350/A (Gamma, Budapest). The concentration of water in the organic phase was determined by titration with the Fischer agent with the biamperometric indication using the "Dead-Stop Titrimeter" OP-402 (Radelkis, Budapest).

RESULTS AND DISCUSSION

Extraction Experiments

For the systems under study the dependences of the distribution ratios log D_{Sr} and log D_{Ba}, respectively, on the total concentration of PEG in the system (log C_L) were experimentally determined for various concentrations of dicarbolide in the organic phase and for various concentrations of $HClO_4$ in the aqueous phase. The concentrations of dicarbolide, polyethylene glycol, and $HClO_4$ are always related to the volume of one phase. Combinations of the concentrations C_B and C_{HClO_4} were chosen so that $-2 \leq \log D \leq 2$. The results are given in Tables I–VI. Figs 1 and 2 present the dependences log D vs log C_L for Sr^{2+} extraction in the presence of PEG 200, and for Ba^{2+} extraction in the presence of PEG 400, respectively.

Reactions of H^+ *and* M^{2+} *with Polyethylene Glycol*

Assuming that all systems under study can be described by the reactions $(A) - (D)$, together with the protonation of PEG in the aqueous phase,

$$L + H^+ \rightleftharpoons HL^+ \qquad (E)$$

TABLE I

Strontium distribution ratio as a function of the concentration of polyethylene glycol PEG 200 for the strontium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) = 0.001 — — 0.01 mol l^{-1}) from the aqueous solution of HClO$_4$ (c(HClO$_4$) = 0.2 — 1.0 mol l^{-1}). The values of log C_L and log D_{Sr} are given for all points

c(HClO$_4$) = 0.20 mol l^{-1}, c(dicarbolide) = 0.005 mol l^{-1}

−4.000, −0.323; −3.745, −0.031; −3.495, 0.196; −3.252, 0.456; −3.000, 0.709; −2.745, 0.956; −2.495, 1.174; −2.252, 1.373; −2.000, 1.541; −1.745, 1.659; −1.495, 1.673; −1.252, 1.607; −1.000, 1.395; −0.745, 1.179; −0.495, 0.931; −0.252, 0.647;

c(HClO$_4$) = 0.50 mol l^{-1}, c(dicarbolide) = 0.01 mol l^{-1}

−4.000, −0.735; −3.745, −0.468; −3.495, −0.213; −3.252, 0.012; −3.000, 0.252; −2.745, 0.500; −2.495, 0.732; −2.252, 0.939; −2.000, 1.145; −1.745, 1.288; −1.495, 1.344; −1.252, 1.315; −1.000, 1.211; −0.745, 0.990; −0.495, 0.756; −0.252, 0.485;

c(HClO$_4$) = 0.50 mol l^{-1}, c(dicarbolide) = 0.005 mol l^{-1}

−4.000, −1.137; −3.745, −0.843; −3.495, −0.582; −3.252, −0.364; −3.000, −0.143; −2.745, 0.110; −2.495, 0.331; −2.252, 0.527; −2.000, 0.684; −1.745, 0.785; −1.495, 0.788; −1.252, 0.723; −1.000, 0.589; −0.745, 0.354; −0.495, 0.110; −0.252, −0.136;

c(HClO$_4$) = 0.50 mol l^{-1}, c(dicarbolide) = 0.001 mol l^{-1}

−3.745, −1.799; −3.495, −1.719; −3.252, −1.508; −3.000, −1.287; −2.745, −1.056; −2.495, −0.897; −2.252, −0.722; −2.000, −0.621; −1.745, −0.594; −1.495, −0.649; −1.252, −0.731; −1.000, −0.916; −0.745, −1.146; −0.495, −1.370; −0.252, −1.682;

c(HClO$_4$) = 1.0 mol l^{-1}, c(dicarbolide) = 0.01 mol l^{-1}

−4.000, −1.382; −3.745, −1.187; −3.495, −0.982; −3.252, −0.729; −3.000, −0.486; −2.745, −0.237; −2.495, −0.013; −2.252, 0.193; −2.000, 0.377; −1.745, 0.524; −1.495, 0.606; −1.252, 0.612; −1.000, 0.499; −0.745, 0.277; −0.495, 0.063; −0.252, −0.174;

and with the reaction of Sr^{2+} (or Ba^{2+}) with PEG molecule in the aqueous phase

$$M^{2+} + L \rightleftharpoons ML^{2+}, \qquad (F)$$

the following set of equations can be used for their description[1]:

$$K_D = [\overline{L}]/[L] \qquad (1)$$

$$K_{ex}(HL^+) = [\overline{HL^+}]/[\overline{H^+}][L] \qquad (2)$$

$$K_{ex}(M^{2+}) = [\overline{M^{2+}}][H^+]^2/[M^{2+}][\overline{H^+}]^2 \qquad (3)$$

$$K_{ex}(ML^{2+}) = [\overline{ML^{2+}}][H^+]^2/[M^{2+}][L][\overline{H^+}]^2 \qquad (4)$$

$$K_{H,aq} = [HL^+]/[H^+][L] \qquad (5)$$
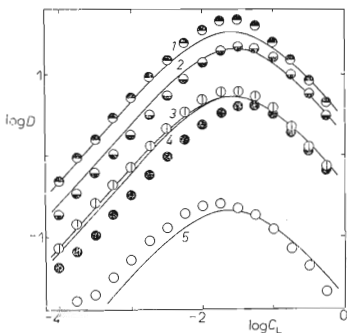
$$K_1(ML^{2+}) = [ML^{2+}]/[M^{2+}][L]. \qquad (6)$$

Fig. 1

Logarithm of the Sr^{2+} distribution ratio as a function of the total analytical concentration of PEG in the system $HClO_4$–Sr^{2+}–PEG 200–nitrobenzene–dicarbolide. $C(HClO_4)$/mol l^{-1}, $C(HB)$/mol l^{-1}: *1* 0·2, 5 . 10^{-3}; *2* 0·5, 1 . 10^{-2}; *3* 0·5, 5 . 10^{-3}; *4* 1·0, 1 . 10^{-2}; *5* 0·5, 1 . 10^{-3}. Solid curves were calculated for log $K_{ex}(HL^+) = 1\cdot65$ and log $K_{ex}(SrL^{2+}) = = 6\cdot97$
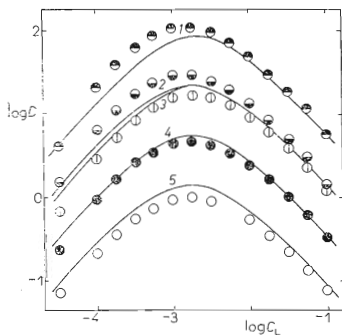

Fig. 2

Logarithm of the Ba^{2+} distribution ratio as a function of the total analytical concentration of PEG in the system $HClO_4$– –Ba^{2+}–PEG 400–nitrobenzene–dicarbolide. $C(HClO_4)$/mol l^{-1}, $C(HB)$/mol l^{-1}: *1* 0·5, 1 . 10^{-3}; *2* 0·5, 5 . 10^{-4}; *3* 1·0, 1 . 10^{-3}; *4* 1·0, 5 . 10^{-3}; *5* 1·0, 2·5 . 10^{-4}. Solid curves were calculated for log $K_{ex}(HL^+) = 2\cdot83$ and log $K_{ex}(BaL^{2+}) = 10\cdot76$

The electric neutrality condition for the organic phase

$$C_B = \overline{[H^+]} + \overline{[HL^+]} + 2\overline{[M^{2+}]} + 2\overline{[ML^{2+}]} \tag{7}$$

TABLE II

Barium distribution ratio as a function of the concentration of polyethylene glycol PEG 200 for the barium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) = 0·0005 — — 0·005 mol l^{-1}) from the aqueous solution of HClO$_4$ (c(HClO$_4$) = 0·5 — 1·0 mol l^{-1}). The values of log C_L and log D_{Ba} are given for all points

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

—4·000, —0·476; —3·745, —0·180; —3·495, 0·060; —3·252, 0·305; —3·000, 0·601;
—2·745, 0·833; —2·495, 1·045; —2·252, 1·205; —2·000, 1·325; —1·745, 1·354;
—1·495, 1·292; —1·252, 1·196; —1·000, 0·985; —0·745, 0·714; —0·495, 0·429;
—0·252, 0·054;

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

—4·000, —0·856; —3·745, —0·564; —3·495, —0·353; —3·252, —0·139; —3·000, 0·103;
—2·745, 0·333; —2·495, 0·515; —2·252, 0·655; —2·000, 0·743; —1·745, 0·743;
—1·495, 0·677; —1·252, 0·559; —1·000, 0·368; —0·745, 0·103; —0·495, —0·197;
—0·252, —0·519;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·005 mol l^{-1}

—4·000, —0·314; —3·745, —0·034; —3·495, 0·312; —3·252, 0·589; —3·000, 0·883;
—2·745, 1·178; —2·495, 1·439; —2·252, 1·633; —2·000, 1·812; —1·745, 1·933;
—1·495, 1·952; —1·252, 1·903; —1·000, 1·739; —0·745, 1·495; —0·495, 1·205;
—0·252, 0·893;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

—4·000, —1·114; —3·745, —0·835; —3·495, —0·634; —3·252, —0·363; —3·000, —0·137;
—2·745, 0·102; —2·495, 0·311; —2·252, 0·453; —2·000, 0·563; —1·745, 0·607;
—1·495, 0·582; —1·252, 0·473; —1·000, 0·310; —0·745, 0·046; —0·495, —0·226;
—0·252, —0·591;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

—4·000, —1·673; —3·745, —1·317; —3·495, —1·006; —3·252, —0·872; —3·000, —0·659;
—2·745, —0·422; —2·495, —0·234; —2·252, —0·098; —2·000, 0·003; —1·745, 0·034;
—1·495, —0·025; —1·252, —0·112; —1·000, —0·300; —0·745, —0·553; —0·495, —0·826;
—0·252, —1·138;

(practically all dicarbolide is present in the organic phase and in both phases it is fully dissociated so that $[\overline{B^-}] = C_B$, cf.[1]) and the mass balance of PEG in the system

$$C_L = [L] + [\overline{L}] + [HL^+] + [\overline{HL^+}] + [ML^{2+}] + [\overline{ML^{2+}}] \qquad (8)$$

must also be taken into consideration. The dependence of log D vs log C_L was studied using microamounts of Sr or Ba so that the concentration of the extracted metal was

TABLE III

Strontium distribution ratio as a function of the concentration of polyethylene glycol PEG 300 for the strontium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) $= 0.001 -$ $- 0.01$ mol l^{-1}) from the aqueous solution of $HClO_4$ (c($HClO_4$) $= 0.5 - 1.0$ mol l^{-1}). The values of log C_L and log D_{Sr} are given for all points

$$c(HClO_4) = 0.50 \text{ mol } l^{-1}, \ c(\text{dicarbolide}) = 0.01 \text{ mol } l^{-1}$$

$-3.745, 0.447; -3.495, 0.786; -3.252, 1.010; -3.000, 1.249;$
$-2.745, 1.483; -2.495, 1.677; -2.252, 1.821; -2.000, 1.849;$
$-1.745, 1.721; -1.495, 1.490; -1.252, 1.254; -1.000, 1.029;$
$-0.745, 0.701; -0.495, 0.411; -0.252, 0.127;$

$$c(HClO_4) = 0.50 \text{ mol } l^{-1}, \ c(\text{dicarbolide}) = 0.005 \text{ mol } l^{-1}$$

$-3.745, 0.109; -3.495, 0.369; -3.252, 0.593; -3.000, 0.813;$
$-2.745, 1.021; -2.495, 1.190; -2.252, 1.210; -2.000, 1.149;$
$-1.745, 0.981; -1.495, 0.770; -1.252, 0.555; -1.000, 0.313;$
$-0.745, 0.037; -0.495, -0.224; -0.252, -0.567;$

$$c(HClO_4) = 0.50 \text{ mol } l^{-1}, \ c(\text{dicarbolide}) = 0.001 \text{ mol } l^{-1}$$

$-3.745, -0.927; -3.495, -0.701; -3.252, -0.507; -3.000, -0.333;$
$-2.745, -0.217; -2.495, -0.184; -2.252, -0.209; -2.000, -0.343;$
$-1.745, -0.515; -1.495, -0.723; -1.252, -0.882; -1.000, -1.200;$
$-0.745, -1.497; -0.495, -1.705; -0.252, -1.787;$

$$c(HClO_4) = 1.00 \text{ mol } l^{-1}, \ c(\text{dicarbolide}) = 0.01 \text{ mol } l^{-1}$$

$-3.745, -0.201; -3.495, 0.055; -3.252, 0.248; -3.000, 0.519;$
$-2.745, 0.742; -2.495, 0.940; -2.252, 1.070; -2.000, 1.106;$
$-1.745, 0.997; -1.495, 0.814; -1.252, 0.608; -1.000, 0.377;$
$-0.745, 0.076; -0.495, -0.180; -0.252, -0.465;$

negligible in comparison with both C_B and C_L. The equations (7) and (8) then become

$$C_B = [\overline{H^+}] + [\overline{HL^+}] \tag{9}$$

$$C_L = [\overline{L}] + [L] + [HL^+] + [\overline{HL^+}]. \tag{10}$$

TABLE IV

Barium distribution ratio as a function of the concentration of polyethylene glycol PEG 300 for the barium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) = 0·0005 — — 0·005 mol l^{-1}) from the aqueous solution of HClO$_4$, (c(HClO$_4$) = 0·5 — 1·0 mol l^{-1}). The values of log C_L and log D_{Sr} are given for all points

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

−3·745, 1·084; −3·495, 1·325; −3·252, 1·524; −3·000, 1·757;
−2·745, 1·871; −2·495, 1·921; −2·252, 1·882; −2·000, 1·741;
−1·745, 1·554; −1·495, 1·345; −1·252, 1·103; −1·000, 0·801;

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

−4·000, 0·176; −3·745, 0·501; −3·495, 0·744; −3·252, 0·935;
−3·000, 1·106; −2·745, 1·203; −2·495, 1·223; −2·252, 1·174;
−2·000, 1·047; −1·745, 0·871; −1·495, 0·670; −1·252, 0·447;
−1·000, 0·156;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·0025 mol l^{-1}

−4·000, 0·442; −3·745, 0·709; −3·495, 0·927; −3·252, 1·143;
−3·000, 1·335; −2·745, 1·551; −2·495, 1·661; −2·252, 1·643;
−2·000, 1·600; −1·745, 1·453; −1·495, 1·252; −1·252, 1·000;
−1·000, 0·744;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

−3·745, 0·224; −3·495, 0·469; −3·252, 0·666; −3·000, 0·860;
−2·745, 1·005; −2·495, 1·064; −2·252, 1·030; −2·000, 0·921;
−1·745, 0·779; −1·495, 0·570; −1·252, 0·347; −1·000, 0·097;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

−4·000, −0·680; −3·745, −0·341; −3·495, −0·115; −3·252, 0·086;
−3·000, 0·246; −2·745, 0·360; −2·495, 0·392; −2·252, 0·381;
−2·000, 0·273; −1·745, 0·114; −1·495, −0·065; −1·252, −0·289;
−1·000, −0·539;

Using Eqs (1)–(6), (9), and (10), the following relation can be derived[1]

$$D_M = ([\overline{H^+}]^2/[H^+]^2) \cdot \{K_D \cdot K_{ex}(M^{2+}) + K_{ex}(ML^{2+}) \cdot [\overline{L}]\}/$$
$$/\{K_D + K_1(ML^{2+}) \cdot [\overline{L}]\}, \tag{11}$$

where

$$[\overline{L}] = \{r + (r^2 + 4C_L K_D s)^{1/2}\}/2s \tag{12}$$

$$[\overline{H^+}] = [\overline{L}] \{(K_{H,aq} \cdot [H^+]/K_D) + K_D^{-1} + 1\} + C_B - C_L \tag{13}$$

$$r = K_{ex}(HL^+) \cdot (C_L - C_B) - 1 - K_D - K_{H,aq} \cdot [H^+] \tag{14}$$

$$s = K_{ex}(HL^+) \cdot \{1 + K_D^{-1} + (K_{H,aq} \cdot [H^+]/K_D)\}. \tag{15}$$

TABLE V

Strontium distribution ratio as a function of the concentration of polyethylene glycol PEG 400 for the strontium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) = 0·001 – – 0·01 mol l^{-1}) from the aqueous solution of HClO$_4$ (c(HClO$_4$) = 0·5 – 1·0 mol l^{-1}). The values of log C_L and log D_{Sr} are given for all points

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·01 mol l^{-1}

−4·000, 0·515; −3·745, 0·758; −3·495, 1·007; −3·252, 1·239; −3·000, 1·454; −2·745, 1·681; −2·495, 1·798; −2·252, 1·833; −2·000, 1·675; −1·745, 1·404; −1·495, 1·137; −1·252, 0·931;

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·005 mol l^{-1}

−4·000, 0·193; −3·745, 0·439; −3·495, 0·662; −3·252, 0·862; −3·000, 1·044; −2·745, 1·205; −2·495, 1·242; −2·252, 1·172; −2·000, 0·970; −1·745, 0·749; −1·495, 0·532; −1·252, 0·351;

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

−4·000, −0·614; −3·745, −0·449; −3·495, −0·314; −3·252, −0·197; −3·000, −0·119; −2·745, −0·080; −2·495, −0·136; −2·252, −0·244; −2·000, −0·368; −1·745, −0·509; −1·495, −0·646; −1·252, −0·767;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·01 mol l^{-1}

−4·000, −0·128; −3·745, 0·076; −3·495, 0·331; −3·252, 0·539; −2·745, 0·952; −2·495, 1·099; −2·000, 0·986; −1·746, 0·770; −1·495, 0·525; −1·252, 0·318; −1·000, 0·143;

These relations were incorporated in the program block UBBE[1] (as a part of the more general program LETAGROP[2]) which was used for the determination of the best values of the constants $K_{ex}(HL^+)$, $K_{ex}(ML^{2+})$, $K_{H,aq}$, and $K_1(ML^{2+})$. The sum of squares of the deviations of experimental values of log D_M from the theoretical values of log D_M, calculated on the basis of Eq. (*11*), was minimized so that the following relation can be written for the function U:

$$U = \sum (\log D_M^{exp} - \log D_M^{calc})^2 . \qquad (16)$$

TABLE VI

Barium distribution ratio as a function of the concentration of polyethylene glycol PEG 400 for the barium extraction by the nitrobenzene solution of dicarbolide (c(dicarbolide) = 0·00025 — — 0·001 mol l^{-1}) from the aqueous solution of HClO$_4$ (c(HClO$_4$) = 0·5 — 1·0 mol l^{-1}). The values of log C_L and log D_{Ba} are given for all points

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c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

—4·000, 1·309; —3·745, 1·576; —3·495, 1·787; —3·252, 1·928; —3·000, 2·026; —2·745, 2·028; —2·495, 1·976; —2·252, 1·841; —2·000, 1·673; —1·745, 1·449; —1·495, 1·243; —1·252, 1·032; —1·000, 0·721; —4·495, 0·607;

c(HClO$_4$) = 0·50 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

—4·495, 0·171; —4·000, 0·791; —3·745, 1·030; —3·495, 1·223; —3·252, 1·358; —3·000, 1·452; —2·745, 1·459; —2·495, 1·375; —2·252, 1·269; —2·000, 1·114; —1·745, 0·898; —1·495, 0·670; —1·252, 0·445; —1·000, 0·109;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·001 mol l^{-1}

—4·495, —0·186; —4·000, 0·442; —3·745, 0·701; —3·495, 0·902; —3·252, 1·052; —3·000, 1·171; —2·745, 1·208; —2·495, 1·178; —2·252, 1·082; —2·000, 0·933; —1·745, 0·759; —1·495, 0·558; —1·252, 0·320; —1·000, 0·037;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·0005 mol l^{-1}

—4·495, —0·649; —4·000, —0·048; —3·745, 0·199; —3·495, 0·398; —3·252, 0·517; —3·000, 0·622; —2·745, 0·643; —2·495, 0·603; —2·252, 0·501; —2·000, 0·358; —1·745, 0·180; —1·495, —0·028; —1·252, —0·251; —1·000, —0·530;

c(HClO$_4$) = 1·00 mol l^{-1}, c(dicarbolide) = 0·00025 mol l^{-1}

—4·495, —1·161; —4·000, —0·691; —3·745, —0·470; —3·495, —0·284; —3·252, —0·157; —3·000, —0·053; —2·745, —0·021; —2·495, —0·069; —2·000, —0·301; —1·745, —0·496; —1·495, —0·692; —1·252, —0·918; —1·000, —1·164;

The value $K_{ex}(Sr^{2+}) = 5.0$ was the same as that used in our previous paper, the value $K_{ex}(Ba^{2+}) = 7.0$ was determined by special extraction experiments. The constants K_D for PEG 200, PEG 300, and PEG 400 were determined (with the precision of $\pm 10\%$) by the method of the concentration dependent distribution[3] and their values are $K_D = 1.6 \cdot 10^{-3}$ (PEG 200), $1.5 \cdot 10^{-3}$ (PEG 300), and $1.3 \cdot 10^{-3}$ (PEG 400).

In spite of the fact that the used polyethylene glycols are not chemical species (individuals) as they contain oligomers with higher and lower relative molecular weight, their behaviour in the systems under study can be explained — as follows from the results of this paper — assuming the existence of a single hypothetical oligomer with a molecular weight equal to the average molecular weight.

The comparison of the experimental data with the calculated ones corroborates the assumption of the equilibrium mechanism in the systems under study as they are described above. Similarly as in Sr^{2+} extraction in the presence of PEG 400 the reactions $(A)-(D)$ predominate in the system while the participation of HL^+ and SrL^{2+} (or BaL^{2+}) species on the total concentration of polyethylene glycol and strontium (or barium) is evidently negligible under the given conditions. The resulting values of equilibrium constants are listed in Table VII. The values of $K_{ex}(SrL^{2+})$ and $K_{ex}(BaL^{2+})$ are substantially higher than the values of $K_{ex}(HL^+)$. For each of the two studied cations the increase of $\log K_{ex}$ is roughly twice higher if going from PEG 200 to PEG 300 than from PEG 300 to PEG 400. The absolute differences are higher for Sr^{2+} and Ba^{2+} than for H^+. As it is evident from Table VII the values of $K_{ex}(HL^+)$ are practically identical if the calculation is done for the respective PEG and Sr^{2+} or Ba^{2+}. As these values were obtained by the analysis of independent data (extraction of Sr^{2+} and Ba^{2+}), this agreement indicates the reliability of the assumed extraction model. Similarly to our previous paper, the values of the extraction constants for various acidities of the aqueous phase have been calculated. As we have demonstrated earlier[1] it can be assumed that the differences in the extraction constants measured at various acidities of the aqueous phase are first of all given by the changes of the activity coefficients, particularly of H^+ and M^{2+} ions in the aqueous phase. For the same reason also the constants $K_{ex}(ML^{2+})$ are affected more by the changes of acidity than the constants $K_{ex}(HL^+)$ that consider only reactions of charged species present in the organic phase and of the uncharged polyethylene glycol species in the aqueous phase. However, the changes of K_{ex} with acidity are generally small and they permit the evaluation of mean values of these constants for 2 (eventually 3) values of acidity.* These are the values given for each element in the last row of Table VII.

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* Mean values of constants in Table VII are not arithmetic means of values measured at the individual values of acidity but the values calculated by the least-square method from all experimental data of Tables I—VI.

TABLE VII

Constants of the reactions (B), (D), (G), and (H) for the Sr^{2+} and Ba^{2+} extraction by the polyethylene glycols PEG 200, PEG 300, and PEG 400 for various concentrations of nitric acid in the aqueous phase

$[H^+]$ mol l^{-1}	C_B mol l^{-1}	$\log K_{ex}(HL^+)$	$\log K_{ex}(ML^{2+})$	$\log K_{H,org}$	$\log K(\overline{ML^{2+}})$	U	n^a
			Sr–PEG 200				
0·2	$5 \cdot 10^{-3}$	1·65 ± 0·07	7·04 ± 0·07	4·44 ± 0·07	9·14 ± 0·07	0·05455	16
0·5	$10^{-3}–10^{-2}$	1·69 ± 0·08	7·03 ± 0·08	4·48 ± 0·08	9·12 ± 0·08	0·5850	47
1·0	10^{-2}	1·50 ± 0·04	6·68 ± 0·04	4·30 ± 0·04	8·77 ± 0·04	0·01887	16
0·2–1·0	$10^{-3}–10^{-2}$	1·65 ± 0·07	6·96 ± 0·07	4·44 ± 0·07	9·06 ± 0·07	1·4084	79
			Ba–PEG 200				
0·5	$5 \cdot 10^{-4}–10^{-3}$	1·85 ± 0·06	9·13 ± 0·07	4·65 ± 0·06	11·09 ± 0·07	0·2467	32
1·0	$5 \cdot 10^{-4}–5 \cdot 10^{-3}$	1·74 ± 0·10	8·87 ± 0·11	4·54 ± 0·10	10·82 ± 0·11	1·1663	48
0·5–1·0	$5 \cdot 10^{-4}—5 \cdot 10^{-3}$	1·79 ± 0·08	8·98 ± 0·08	4·59 ± 0·08	10·93 ± 0·08	2·081	80
			Sr–PEG 300				
0·5	$10^{-3}–10^{-2}$	2·53 ± 0·04	8·34 ± 0·05	5·35 ± 0·04	10·47 ± 0·05	0·1076	45
1·0	10^{-2}	2·38 ± 0·03	8·09 ± 0·04	5·20 ± 0·03	10·21 ± 0·04	0·00546	15
0·5–1·0	$10^{-3}–10^{-2}$	2·50 ± 0·04	8·29 ± 0·06	5·32 ± 0·04	10·41 ± 0·06	0·2386	60

TABLE VII
(Continued)

$[H^+]$ mol l^{-1}	C_B mol l^{-1}	log $K_{ex}(HL^+)$	log $K_{ex}(ML^{2+})$	log $K_{H,org}$	log $K(ML^{2+})$	U	n^a
			Ba-PEG 300				
0·5	$5 . 10^{-4} — 10^{-3}$	2·57 ± 0·05	10·41 ± 0·06	5·39 ± 0·05	12·39 ± 0·06	0·06753	25
1·0	$5 . 10^{-4} — 2·5 . 10^{-3}$	2·48 ± 0·07	10 05 ± 0·08	5·31 ± 0·07	12·03 ± 0·08	0·26415	38
0·5–1·0	$5 . 10^{-4} — 2·5 . 10^{-3}$	2·52 ± 0·09	10·19 ± 0·11	5·34 ± 0·09	12·17 ± 0·11	1·4445	63
			Sr-PEG 400				
0·5	$10^{-3} — 10^{-2}$	2·91 ± 0·12	8·87 ± 0·15	5·80 ± 0·12	11·05 ± 0·15	0·4347	36
1·0	10^{-2}	2·88 ± 0·19	8·72 ± 0·26	5·76 ± 0·19	10·91 ± 0·26	0·08469	11
0·5–1 0	$10^{-3} — 10^{-2}$	2·91 ± 0·10	8·84 ± 0·14	5·80 ± 0·10	11·03 ± 0·14	0 6095	47
			Ba-PEG 400				
0·5	$5 . 10^{-4} — 10^{-3}$	2·89 ± 0·05	10·95 ± 0·07	5·78 ± 0·05	12·99 ± 0·07	0·08733	28
1·0	$2·5 . 10^{-4} — 10^{-3}$	2·79 ± 0·03	10·63 ± 0·04	5·67 ± 0·03	12·68 ± 0·04	0·08426	41
0·5–1·0	$2·5 . 10^{-4} — 10^{-3}$	2·83 ± 0·06	10·76 ± 0·08	5·71 ± 0·06	12·80 ± 0·08	0·8814	69

^{a} Number of experimental points.

Along with the extraction constants Table VII gives also the values of the protonation constant of polyethylene glycol in the organic phase $K_{H,org}$ and the stability constants of ML^{2+} complexes in the organic phase $K_1(\overline{ML^{2+}})$, *i.e.*, the equilibrium constants of the reactions

$$\overline{H^+} + \overline{L} \;\rightleftharpoons\; \overline{HL^+} \quad K_{H,org} \tag{G}$$

$$K_{H,org} = [\overline{HL^+}]/[\overline{H^+}]\,[\overline{L}] = K_{ex}(HL^+)/K_D \tag{17}$$

$$\overline{M^{2+}} + \overline{L} \;\rightleftharpoons\; \overline{ML^{2+}} \tag{H}$$

$$K_1(\overline{ML^{2+}}) = [\overline{ML^{2+}}]/[\overline{M^{2+}}]\,[\overline{L}] = K_{ex}(ML^{2+})/K_D K_{ex}(M^{2+}), \tag{18}$$

Hydration of Complexes in the Organic Phase

To elucidate the behaviour of the given system it is useful to know the hydration numbers of ions present in the organic phase. However, these numbers are not always constant for various solvents, temperatures, and activities of water in the aqueous phase[4], nevertheless the values measured under similar conditions are well comparable.

The hydration numbers of H^+, Ba^{2+}, and Sr^{2+} ions were determined by the titration of water in nitrobenzene in solutions with a various content of cations and their values are in good agreement with the published data[4-6].

To determine the hydration numbers of complexes in the organic phase the concentration of water in the organic phase was followed under the condition when simultaneously a known concentration of HL^+ or ML^{2+} is present in the solution. Because the dicarbolide anion in nitrobenzene is evidently not hydrated[4], the concentration of water in the organic phase is given only by the hydration of cations and cationic complexes and by the physical solubility of water.

If — along with water, dicarbolide, polyethylene glycol, and nitrobenzene — only acid is present in the extraction system, the following relation can be written:

$$C_{H_2O}^{org} = h_{H^+} \cdot [\overline{H^+}] + h_{HL^+} \cdot [\overline{HL^+}] + [\overline{H_2O}] + h_L \cdot [\overline{L}], \tag{19}$$

where h_{H^+}, h_{HL^+}, and h_L mean the hydration numbers of H^+ and HL^+ ions and polyethylene glycol, respectively.

Because the distribution ratios of the used polyethylene glycols in the system water–nitrobenzene are very low, the equilibrium concentration $[\overline{L}]$ does not reach values higher than $1 \cdot 10^{-3}$ mol l^{-1}. For the same reason also no increase of $C_{H_2O}^{org}$ has been observed in the system water–nitrobenzene after the addition of PEG, even at $C_L = 0.20$ mol l^{-1}. Due to this fact the term $h_L[\overline{L}]$ can be neglected and the

relation (19) is constricted to

$$C_{H_2O}^{org} = h_{H^+} \cdot [\overline{H^+}] + h_{HL^+} \cdot [\overline{HL^+}] + [\overline{H_2O}] . \tag{20}$$

If the concentration C_L is not too high, the value of the water solubility in nitrobenzene at the given temperature can be directly substituted for $[\overline{H_2O}]$ so that $[\overline{H_2O}] = 0.16$ mol l^{-1} (ref.[7,8]). Because it was impossible to create conditions under which only negligible amount of H^+ was present in the organic phase, the amount of polyethylene glycol in the system was chosen so that the concentration ratio $[\overline{H^+}]/[\overline{HL^+}]$ in the organic phase was equal to 1.

If the extraction constant of dicarbolide between the aqueous and organic phases is expressed in the form (in contrast to systems in which the distribution of metals has been followed, no mineral acid was present)

$$K_{ex}(H^+, B^-) = [\overline{H^+}] [\overline{B^-}]/[H^+] [B^-] \tag{21}$$

and the mass balance equation for dicarbolide is given by (in absence of M^{2+})

$$C_B = [\overline{H^+}] + [\overline{HL^+}] + [H^+] \tag{22}$$

and the same relation for polyethylene glycol by

$$C_L = [L] + [\overline{L}] + [\overline{HL^+}] \tag{23}$$

and also, taking into account the conditions of electric neutrality of the aqueous and organic phases

$$[H^+] = [B^-] \tag{24}$$

$$[\overline{H^+}] + [\overline{HL^+}] = [\overline{B^-}] \tag{25}$$

it is possible to derive this relation for the required concentration of polyethylene glycol

$$C_L(m) = (1 + 1/K_D) \, m/K_{H,org} + m \, C_B/\{(m + 1) + [(m + 1)/K_{ex}(H^+, B^-)]^{1/2}\} , \tag{26}$$

where $C_L(m)$ is such a concentration of PEG that the concentration ratio $[\overline{HL^+}]/[\overline{H^+}]$ is equal to m.

For $m = 1$ Eq. (26) can be simplified to

$$C_L(1) = (1 + 1/K_D)/K_{H,org} + C_B/(2 + v), \quad (27)$$

where $v = \{2/K_{ex}(H^+, B^-)\}^{1/2}$.

Under this condition (*i.e.*, $m = 1$) the following relation was derived for the water concentration in the organic phase

$$C_{H_2O}^{org} = [\overline{H_2O}] + C_B(h_{H^+} + h_{HL^+})/(2 + v). \quad (28)$$

The dependence of $C_{H_2O}^{org}$ *vs* C_B is a straight line with the slope $(h_{H^+} + h_{HL^+})/(2 + v)$ if the value C_L is chosen so that $m = 1$. This dependence for PEG 200, PEG 300, and PEG 400 is given in Fig. 3. It is evident that this dependence is indeed a straight line and knowing the value of h_{H^+} and $K_{ex}(H^+, B^-)$ $(= 10^{+3.18}$, ref.[7]$)$ the value of h_{HL^+} can be calculated from its slope (due to the high value of the constant $K_{ex}(H^+, B^-)$ the value of v participates on the nominator in Eqs (27) and (28) by less than 2% so that it could be neglected). The results for polyethylene glycols with the average relative molecular weight 200, 300, and 400 are presented in Table VIII together with the values of h_{H^+}. The hydration of PEG complexes with strontium and barium was studied under the condition that the only charged species in the organic phase is the complex of the ML^{2+} type, which can be easily achieved because the extraction constant of the complex ML^{2+} is — contrary to the constant

TABLE VIII
Hydration numbers of H^+, Sr^{2+}, and Ba^{2+} ions and of the complexes HL^+, SrL^{2+}, and BaL^{2+} (L = PEG 200, PEG, 300, and PEG 400) in the nitrobenzene solution

L	Ion			Ref.
	H^+	Sr^{2+}	Ba^{2+}	
—	5·5	12·3	10·8	—[a]
—	—	12·1	10·5	6
—	5·5	—	—	4
—	—	—	11·5 ± 1	5
PEG 200	3·7	2·8	1·7	—[a]
PEG 300	2·9	2·0	1·3	—[a]
PEG 400	2·3	1·6	1·0	—[a]

[a] This paper.

for HL$^+$ species — sufficiently high. Assuming that the system contains only strontium (or barium) salt of dicarbolide, water, and nitrobenzene, the concentration of water in the organic phase is given by Eq. (29), analogous to Eq. (19):

$$C_{H_2O}^{org} = h_{M^{2+}} . [\overline{M^{2+}}] + h_{ML^{2+}} . [\overline{ML^{2+}}] + h_L . [\overline{L}] + [\overline{H_2O}] . \qquad (29)$$

As mentioned above, the participation of $h_L . [\overline{L}]$ on the total concentration of water in the organic phase is negligible and the concentration $[\overline{H_2O}]$ for low concentrations of PEG is given with sufficient precision by the solubility of water in nitrobenzene.

Under the assumption of a complete dissociation in both phases the system water––dicarbolide salt of a bivalent metal–nitrobenzene can be described by the equilibrium extraction constant,

$$K_{ex}(M^{2+}, B^-) = ([\overline{M^{2+}}] [\overline{B^-}]^2 / [M^{2+}] [B^-]^2) , \qquad (30)$$
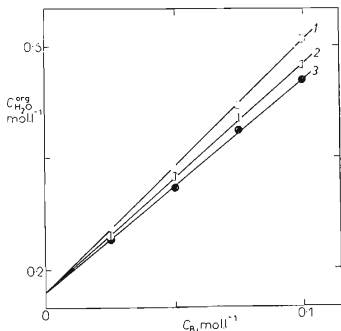

Fig. 3

Equilibrium concentration of water in the organic phase as a function of the initial concentration of dicarbolide in the organic phase for the system water–nitrobenzene––polyethylene glycol-dicarbolide ($[\overline{H^+}] = [\overline{HL^+}]$). 1 PEG 200; 2 PEG 300; 3 PEG 400
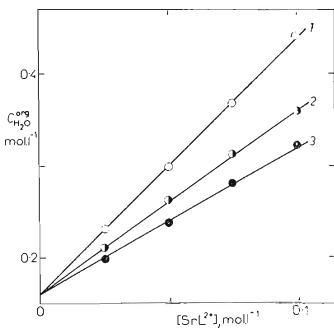

Fig. 4

Equilibrium concentration of water in the organic phase as a function of the $[\overline{SrL^{2+}}]$ concentration for the system water–nitrobenzene–polyethylene glycol–SrL^{2+}–dicarbolide 1 PEG 200; 2 PEG 300; 3 PEG 400

by the stability constant for the complex of the bivalent metal with PEG (Eq. *18*), by the conditions of electric neutrality of both phases,

$$2([\overline{M^{2+}}] + [\overline{ML^{2+}}]) = [\overline{B^-}] \quad \text{and} \tag{31}$$

$$2[M^{2+}] = [B^-] \tag{32}$$

and by the mass balance equations for dicarbolide and the ligand

$$C_B = 2([M^{2+}] + [\overline{ML^{2+}}] + [\overline{M^{2+}}]) \tag{33}$$

$$C_L = [L] + [\overline{ML^{2+}}] + [\overline{L}] . \tag{34}$$

For the concentration C_L, at which $k = [\overline{ML^{2+}}]/[\overline{M^{2+}}]$ the following relation can be derived,

$$C_L = \{(1 + 1/K_D)\, k/K_1(\overline{ML^{2+}})\} + kC_B/2\{(1 + k) +$$
$$[(1 + k)^2/K_{ex}(M^{2+}, B^-)]^{1/3}\} . \tag{35}$$

In our case the concentrations C_L were chosen so that $k \geqq 1\,000$. The concentrations of polyethylene glycol were $C_L = 0.15 \text{ mol } l^{-1}$ for PEG 200, and $C_L = 0.12 \text{ mol } l^{-1}$ for PEG 300 and PEG 400. Under this condition Eq. (*29*) is reduced to a simple relation

$$C_{H_2O}^{org} = [\overline{H_2O}] + h_{ML^{2+}} . [\overline{ML^{2+}}] . \tag{36}$$

It can be shown that for the given values of $K_{ex}(M^{2+}, B^-)$ and $K_1(\overline{ML^{2+}})$ and in the given concentration range $[\overline{ML^{2+}}]$ is practically equal to the analytical concentration of the dicarbolide salt so that $[\overline{ML^{2+}}] \approx C_B/2$ and

$$C_{H_2O}^{org} = [\overline{H_2O}] + h_{ML^{2+}} . C_B/2 . \tag{37}$$

The dependence $C_{H_2O}^{org}$ *vs* $C_B/2$ is then a straight line with the ordinate on the *y* axis equal to $[\overline{H_2O}]$ and with the slope $h_{ML^{2+}}$.

For Sr^{2+} ion Fig. 4 presents the dependence $C_{H_2O}^{org}$ *vs* $[\overline{SrL^{2+}}]$ for the polyethylene glycols PEG 200, PEG 300, and PEG 400. From Fig. 4 it is again evident that the dependence $C_{H_2O}^{org}$ *vs* $C_B/2$ is really a straight line so that the value of $h_{ML^{2+}}$ can be evaluated using the Eq. (*37*). The resulting values $h_{BaL^{2+}}$ and $h_{SrL^{2+}}$ are given in Table VIII for the polyethylene glycols PEG 200, PEG 300, and PEG 400. This table

demonstrates that the effective hydration number in the organic phase for H^+ as well as for Sr^{2+} and Ba^{2+} decreases (in agreement with the previous assumptions[1]) in the reactions with polyethylene glycol what evidently indicates that the oxyethylene groups replace water in the hydration of a free cation and at the same time increase the hydrophobic properties of the formed complex ion.

The relative change of hydration of the three mentioned cations in the nitrobenzene phase due to the formation of a complex with the polyethylene glycol species is the most remarkable conclusion derived from this table. In spite of the fact that the free cations are hydrated in the sequence $Sr^{2+} > Ba^{2+} \gg H^+$, the hydration of complex cations follows the sequence $H^+ \gg Sr^{2+} > Ba^{2+}$. In this case it can be assumed that the small dimensions of proton cause probably the decrease of the hydration number by one third in the case of complexes with PEG 200 while in the case of strontium it decreases by about 77% and in the case of barium by about 84%. In other words, it can be assumed that the higher hydration of HL^+ in comparison with the hydration of SrL^{2+} and BaL^{2+} species is due to the fact that the energy required for the deformation of a PEG molecule that gives spatially favourable configuration for the coordination bond of the $H^+ \ldots O$ type (O from PEG) is so high due to the small dimensions of proton that the energy gain from the formation of these bonds cannot counterbalance it. Probably only some of the possible $H^+—O$ bonds are formed or the bonds H—O are formed not with the free proton but rather with a hydrogen from one of the water molecules participating on the hydration. In the case of Ba or Sr cations both these effects either do not take place at all or in much lesser extent what can explain the substantial decrease of the hydration number due to the formation of the complex cation.

It may be assumed that the substitution of one water molecule in the solvation shell of the ion by one oxyethylene group should cause a constant increment of $\log K_{ex}$ which we shall denote by δ. The value of δ is principally given by the increase of the cation hydrophobic properties due to the substitution of water molecules in the solvation shell by the oxyethylene group, the hydrophobic CH_2 groups of which are directed towards the surface of the solvation shell[3]. Considering the results of this paper the values of δ can be evaluated only approximately using the following simplifying assumptions: (1) one water molecule in the solvation shell of the ion is replaced by one oxyethylene group; 2) the number of accessible coordination positions for the solvation by oxyethylene groups is equal to the hydration number of the cation in absence of polyethylene glycol, and 3) the solvation of cations is not accompanied by any conformation effects that would increase the relative advantage of the solvation of the given cation by the respective PEG.

Evaluating for every cation and PEG the values of $h_{H^+} - h_{HL^+}$, or $h_{M^{2+}} - h_{ML^{2+}}$, respectively, we obtain the theoretical numbers e_{HL} and e_{ML} of the oxyethylene units in the solvation shell. The mean values of $\log K_{ex}(H^+)$ and $\log K_{ex}(ML^{2+})$ were plotted *versus* the values of e_{HL} and e_{ML}. The resulting dependences (cf. Fig. 5) are

straight lines and the derived values of δ are given by $\delta_{HL} = 0{\cdot}9 \log K_{ex}/e_{HL}$, $\delta_{SrL} = 1{\cdot}6 \log K_{ex}/e_{SrL}$, and $\delta_{BaL} = 2{\cdot}4 \log K_{ex}/e_{BaL}$. These results corroborate the correctness of our previous assumptions as well as the correlation between the values K_{ex} found in this study and the hydration numbers h_{HL^+}, $h_{SrL^{2+}}$, and $h_{BaL^{2+}}$.

To interprete on the molecular level the rather different values of δ for H^+, Sr^{2+}, and Ba^{2+}, that obviously determine the high selectivity of this system towards Sr and Ba, is difficult. The measured values of K_{ex} are always a product of the complex extraction constant with the stability constant of the given cation with polyethylene glycol in the aqueous phase (it can be easily proved that $K_{ex}(ML^{2+}) = K_{2H}^{ML}$. $K(ML^{2+})$ and $K_{ex}(HL^+) = K_H^{HL}$. $K_{H,aq}$, where K_{2H}^{ML} and K_H^{HL} are the equilibrium constants of the reactions $2\,\overline{H^+} + ML^{2+} = \overline{ML^{2+}} + 2\,H^+$ and $\overline{H^+} + HL^+ = \overline{HL^+} + H^+$, respectively, so that one more factor appears in the value of δ — the increase of the stability constant in the aqueous phase due to the unit increase of oxyethylene groups. Because the constants $K_{H,aq}$ and $K_{M,aq}$ are not known (in the interpretation of the extraction curves these constants were neglected; however, in the mentioned comparison we are more interested in their relative growth in the sequence PEG 200, PEG 300, PEG 400 rather than in their absolute values), it can be hardly decided whether the differences in δ values are caused by the changes in the aqueous phase (a higher increase of $K_1(SrL^{2+})$ in comparison with $K_1(BaL^{2+})$ and $K_{H,aq}$) or by other factors, e.g., by the already mentioned conformation differences that might cause a better compatibility of the given complex with the given spatial structure of the respective polyethylene glycol.
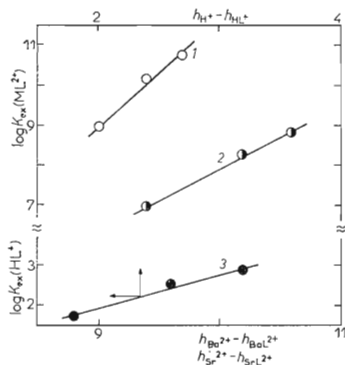

FIG. 5

Extraction constant $K_{ex}(ML^{2+})$ as a function of the hydration number of the free cation and cationic complex with PEG 200, 300, and 400. Used values of h_{H^+}, $h_{Ba^{2+}}$, and $h_{Sr^{2+}}$: 5·5, 10·7, and 12·2, respectively. The values of K_{ex} are the mean values from Table VII. 1 Ba, 2 Sr, 3 H

Values of the extraction constants $K_{ex}(ML^{2+})$ and of the stability constants $K_1(\overline{ML^{2+}})$ of the metal–polyethylene glycol complex in the organic phase increase therefore in the sequence PEG 200 < PEG 300 < PEG 400. An analogous dependence was found also for the constants $K_{ex}(HL^+)$ and $K_{H,org}$ (Table VII) what can evidently be explained by the increasing number of the oxyethylene units in the ligand solvating the ion and simultaneously expelling water molecules. This is in agreement with the fact that the values of metal extraction constants (in the extraction one PEG species replaces more water molecules) increase with the increasing molecular weight more rapidly than the constants $K_{ex}(HL^+)$. The increase of the values of the distribution ratios D_{Sr} and D_{Ba} in the same sequence, i.e., PEG 200 < < PEG 300 < PEG 400, is due to the same fact, as the metal distribution ratio for systems containing PEG is directly proportional to the ratio of the extraction constants $K_{ex}(ML^{2+})/K_{ex}(HL^+)$; this is always so if $[L] \ll [\overline{HL}]$ and $K_{ex}(M^{2+}) \ll$ $\ll K_{ex}(ML^{2+})/K_{ex}(HL^+)$ (ref.[1]). It can be demonstrated from the values of extraction constants (Table VII) that in the region of maxima on the curves of log D_M vs log C_L this condition is fulfilled in the concentration limits under study for PEG 200, 300, and 400.

Rather remarkable is the increase of the theoretical separation factors $\alpha_{Ba/Sr} =$ $= D_{Ba}/D_{Sr}$, the values of which reach in the systems containing PEG the value of $\alpha_{Ba/Sr} \approx 100$ (these separation factors were denoted as theoretical because they were calculated from the results obtained in the extraction systems in the presence of only one metal; any eventual interaction between metals might change this separation ratio). Preliminary experiments that are not described in this paper indicate that the theoretical separation factors do not substantially differ from the actual values obtained for the mixture Sr + Ba.

The dependence of $\alpha_{Ba/Sr}$ on the relative molecular weight of PEG in the region from PEG 200 to PEG 1 000 (ref.[9]) has a nondistinct maximum for PEG 400. This would also indicate a rather strong effect of a low amount of hydration water in the complex on its hydrophobic properties. It also confirms the assumption that about $8-9$ ethylene units contained in PEG 400 are just sufficient to occupy the coordination positions of Sr^{2+} or Ba^{2+} cations.

LIST OF SYMBOLS

B^-	anion of Co(III) dicarbolide $Co(C_2B_9H_{11})_2^-$
C_B	total analytical concentration of Co(III) dicarbolide (the initial concentration of dicarbolide in the organic phase)
C_L	total analytical concentration of polyethylene glycol
$C_{H_2O}^{org}$	total analytical concentration of water in the organic phase
D	the distribution ratio of the species given in index
e_{HL}	the average number of oxyethylene units in the solvation shell of H^+ ion in the organic phase

e_{ML}	the average number of oxyethylene units in the solvation shell of M^{2+} ion in the organic phase
h	hydration number of the species given in index
m	$[\overline{HL^+}]/[\overline{H^+}]$
k	$[\overline{ML^{2+}}]/[\overline{M^{2+}}]$
L	polyethylene glycol (in equations and formulas)
PEG	polyethylene glycol (in the text)
M^{2+}	cation of a bivalent metal (Sr^{2+} or Ba^{2+})
M_r	relative molecular weight
U	sum of squares of deviations of the experimental and theoretical values of log D – cf. Eq. (16)
$\alpha_{Ba/Sr}$	separation factor for Ba and Sr ($\alpha_{Ba/Sr} = D_{Ba}/D_{Sr}$)
δ	increment of log K_{ex} in the dependence of log K_{ex} on the number of bound oxyethylene units in polyethylene glycol
K_D	distribution constant of polyethylene glycol in the system water–nitrobenzene, Eq. (1)
$K_{ex}(HL^+)$	extraction constant of polyethylene glycol by the nitrobenzene solution of dicarbolide, Eq. (2)
$K_{ex}(M^{2+})$	extraction constant of strontium or barium by the nitrobenzene solution of dicarbolide, Eq. (3)
$K_{ex}(ML^{2+})$	extraction constant of strontium or barium by the nitrobenzene solution of dicarbolide in the presence of polyethylene glycol, Eq. (4)
$K_{ex}(H^+, B^-)$	extraction constant of dicarbolide in the system water–nitrobenzene, Eq. (21)
$K_{ex}(M^{2+}, B^-)$	extraction constant of metal salt of dicarbolide in the system water–nitrobenzene, Eq. (30)
$K_{H,aq}$	protonation constant of polyethylene glycol in water, Eq. (5)
$K_{H,org}$	protonation constant of polyethylene glycol in nitrobenzene, Eq. (19)
$K_1(ML^{2+})$	stability constant of the strontium or barium complex with polyethylene glycol in water, Eq. (16)
$K_1(\overline{ML^{2+}})$	stability constant of the strontium or barium complex with polyethylene glycol in nitrobenzene, Eq. (18)
$K_H^{HL} = [\overline{HL^+}] [H^+]/[HL^+] [\overline{H^+}]$,	the constant for the extraction exchange of the protonized molecule of PEG for H^+ ion
$K_{2H}^{ML} = [\overline{ML^{2+}}] [H^+]^2/[ML^{2+}] [\overline{H^+}]^2$,	the constant for the extraction exchange of the PEG complex with strontium or barium for H^+ ion
$\beta = 1/K_{ex}(HL^+) \; (= [\overline{H^+}] [L]/[\overline{HL^+}])$	

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