

EXTRACTION OF STRONTIUM AND BARIUM SALTS
BY THE NITROBENZENE SOLUTION OF DICARBOLIDE
IN THE PRESENCE OF GLYMES

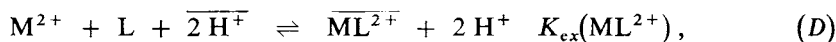
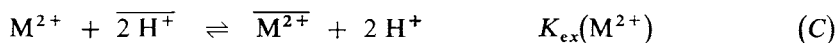
Petr VAŇURA and Emanuel MAKRLÍK

Nuclear Research Institute, 250 68 Řež

Received December 23rd, 1983

Extraction of microamounts of Sr^{2+} and Ba^{2+} (henceforth M^{2+}) from the aqueous solutions of perchloric acid (0.0125–1.02 mol/l) by means of the nitrobenzene solutions of dicarbolidate (0.004–0.05 mol/l of $\text{H}^+\{\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2\}^-$) was studied in the presence of monoglyme (only Ba^{2+}), diglyme, triglyme, and tetraglyme ($\text{CH}_3\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_n\text{CH}_3$, where $n = 1, 2, 3, 4$). The distribution of glyme between the aqueous and organic phases, the extraction of the protonized glyme molecule $\overline{\text{HL}}^+$ together with the extraction of $\overline{\text{M}^{2+}}$ ion and of the glyme complex with the M^{2+} ion, *i.e.*, $\overline{\text{ML}}^{2+}$ (where L is the molecule of glyme), were found to be the dominating reactions in the systems under study. In the systems with tri- and tetraglymes the extraction of H^+ and M^{2+} ions solvated with two glyme molecules, *i.e.*, the formation of $\overline{\text{HL}}_2^+$ and $\overline{\text{ML}}_2^{2+}$ species, can probably play a minor role. The values of the respective equilibrium constants, of the stability constants of complexes formed in the organic phase, and the theoretical separation factors $\alpha_{\text{Ba/Sr}}$ were determined. The effect of the ligand structure on the values of extraction and stability constants in the organic phase is discussed.

In our previous papers^{1,2} we studied the extraction of microamounts of Sr^{2+} or Ba^{2+} by means of the nitrobenzene solutions of Co(III)-dicarbolidate ($\text{H}^+\{\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2\}^-$, henceforth H^+ , B^-) in the presence of polyethylene glycols PEG 200, PEG 300, and PEG 400 (denoted by L in the equations). We have shown that the dominating reactions in the system are



where M^{2+} is the bivalent ion Sr^{2+} or Ba^{2+} , respectively; species present in the organic phase are denoted by a bar. Eq. (D) has been derived for the position of maxi-

mum on the curves of D_M vs C_L ,

$$C_L^{\max} = C_B/2 + 1/K_{ex}(HL^+), \quad (1)$$

where C_B is the dicarbolyde concentration in the organic phase, C_L^{\max} is the concentration of the ligand corresponding to the maximum on the curves of $\log D_M$ vs $\log C_L$. In the case that only one species (*e.g.*, \overline{ML}^{2+}) is extracted into the organic phase and the formation of the complex of the extracted metal with glyme in the aqueous phase is negligible it can be shown that the value of C_L^{\max} corresponds to the ratio $\overline{H}^+ : \overline{HL}^+ = 1 : 1$, *i.e.*, to the stoichiometric ratio for the reaction $M^{2+} + \overline{H}^+ + \overline{HL}^+ \rightleftharpoons \overline{ML}^{2+} + 2 H^+$.

The aim of this study is to find out whether the extraction of Sr^{2+} and Ba^{2+} by means of the nitrobenzene solutions of dicarbolyde in the presence of other types of oxyethylene compounds (organic polyethers of the general formula $CH_3O-(CH_2-CH_2-O)_n-CH_3$ with the trivial name of "glymes", where $n = 1$ for monoglyme \equiv 2,5-dioxahexane, $n = 2$ for diglyme \equiv 2,5,8-trioxanonane, $n = 3$ for triglyme \equiv 2,5,8,11-tetraoxadodecane, and $n = 4$ for tetraglyme \equiv 2,5,8,11,14-pentaioxapentadecane) can be explained by the same or similar mechanism and whether the separation factor values, $\alpha_{Ba/Sr}$, higher than those obtained in systems with polyethylene glycols, can be reached in the extraction in the presence of these ligands.

EXPERIMENTAL

The compound $Cs^+ \{[\pi-(3)-1,2-C_2B_9H_{11}]_2Co\}^-$ (abbreviated as CsDCC, the preparation of which is described in³) was transformed to the respective acid HDCC by two-fold shaking of the nitrobenzene solution of CsDCC (about 0.1 mol l^{-1}) with equal volumes of 15% (v/v) propanol in diluted H_2SO_4 of the concentration of about 1 mol l^{-1} . The complete removal of propanol from the organic phase required a ten-fold shaking of the nitrobenzene solution of HDCC with equal volumes of fresh aqueous solution of H_2SO_4 of the concentration of $1 \text{ mol} \cdot \text{l}^{-1}$. The small amount of extracted H_2SO_4 was removed from the organic phase by two-fold shaking of the nitrobenzene solution of HDCC with an equal volume of distilled water until the equilibrium was established. The HDCC concentration in the prepared nitrobenzene solution was determined by the neutralization titration diluting 2 ml of the original HDCC solution with 20–40 ml of ethanol or acetone and using the volumetric aqueous solution of NaOH and the bromocresol green as an acidobasic indicator.

The oxyethylene compounds of the type $CH_3O-(CH_2-CH_2O)_n-CH_3$ (where $n = 1, 2, 3, 4$) were supplied by Koch-Light. The isotopes ^{87}Sr and ^{133}Ba were of a standard radiochemical purity.

10 ml probes with polyethylene stoppers were used in the extraction experiments. The volume of each phase was 2 ml, the solutions were shaken for 30 min (under the conditions used 5 min is sufficient for the establishment of equilibrium) using a laboratory shaker at the temperature of $25 \pm 1^\circ C$. After centrifugation 0.5 ml were taken from each phase. The γ activity was measured

using a NaI(Tl) scintillation detector in combination with the NK 350 gamma analyzer (Gamma, Budapest, Hungary).

The distribution ratio of the microamounts of strontium or barium between the nitrobenzene and aqueous phases was determined as the ratio between the measured activities of the corresponding samples of the organic and aqueous phase.

RESULTS AND DISCUSSION

A series of dependences of $\log D_{\text{Sr}}$ (or $\log D_{\text{Ba}}$) on the total analytical concentration of glymes were measured for various concentrations of dicarbolidide in the organic phase and for various concentrations of HClO_4 in the aqueous phase. The concentrations of dicarbolidide, glyme, and HClO_4 are always related to the volume of one phase. The combinations of C_{B} and C_{HClO_4} values were chosen so that $-2.5 < \log D < 3$. The results are summarized in Tables I–VII and are partly illustrated in Fig. 1 (for the extraction of Sr^{2+} in the presence of triglyme).

The values of K_{D} of glymes, required for the interpretation of the extraction equilibria, were determined by the method of concentration-dependent distribution

TABLE I

Distribution ratio of barium in dependence on the concentration of monoglyme for the barium extraction by the nitrobenzene solution of dicarbolidide ($c(\text{H}^+, \text{B}^-) = 0.025\text{--}0.050 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.0125\text{--}0.050 \text{ mol l}^{-1}$). The values of $\log c_{\text{L}}$ and $\log D_{\text{Ba}}$ are given for every point

$c(\text{HClO}_4) = 0.0125 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol l}^{-1}$
 - 2.796, 1.584; - 2.553, 1.602; - 2.301, 1.606; - 2.046, 1.619; - 1.796, 1.637; - 1.553, 1.656;
 - 1.301, 1.684; - 1.046, 1.745; - 0.796, 1.623; - 0.553, 1.524; - 0.301, 1.417; 0.000, 1.167

$c(\text{HClO}_4) = 0.025 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol l}^{-1}$
 - 2.796, 0.920; - 2.553, 0.946; - 2.301, 0.959; - 2.046, 0.974; - 1.796, 0.999; - 1.553, 1.023;
 - 1.301, 1.072; - 1.046, 1.154; - 0.796, 1.097; - 0.553, 0.957; - 0.301, 0.810; 0.000, 0.616

$c(\text{HClO}_4) = 0.025 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol l}^{-1}$
 - 2.796, 1.581; - 2.553, 1.601; - 2.301, 1.610; - 2.046, 1.616; - 1.796, 1.617; - 1.553, 1.621;
 - 1.301, 1.631; - 1.046, 1.736; - 0.796, 1.598; - 0.553, 1.567; - 0.301, 1.362; 0.000, 1.122

$c(\text{HClO}_4) = 0.050 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol l}^{-1}$
 - 2.796, 0.354; - 2.553, 0.366; - 2.301, 0.412; - 2.046, 0.452; - 1.796, 0.459; - 1.553, 0.497;
 - 1.301, 0.573; - 1.046, 0.564; - 0.796, 0.468; - 0.553, 0.340; - 0.301, 0.214; 0.000, - 0.059

$c(\text{HClO}_4) = 0.050 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.050 \text{ mol l}^{-1}$
 - 2.796, 0.931; - 2.553, 0.945; - 2.301, 0.961; - 2.046, 0.968; - 1.796, 0.977; - 1.553, 1.013;
 - 1.301, 1.045; - 1.046, 1.104; - 0.796, 1.021; - 0.553, 0.989; - 0.301, 0.788; 0.000, 0.547

TABLE II

Distribution ratio of barium in dependence on the concentration of diglyme for the barium extraction by the nitrobenzene solution of dicarbolyde ($c(\text{H}^+, \text{B}^-) = 0.025\text{--}0.050 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.050\text{--}0.20 \text{ mol l}^{-1}$). The values of $\log c_L$ and $\log D_{\text{Ba}}$ are given for every point

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

−3.046, 1.023; −2.796, 1.073; −2.553, 1.131; −2.301, 1.222; −2.046, 1.326; −1.796, 1.487;
−1.553, 1.654; −1.301, 1.785; −1.046, 1.784; −0.796, 1.698; −0.553, 1.440; −0.301, 1.225

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

−3.046, −0.256; −2.796, −0.171; −2.553, −0.114; −2.301, 0.071; −2.046, 0.159; −1.796, 0.258;
−1.553, 0.399; −1.301, 0.444; −1.046, 0.407; −0.796, 0.262; −0.553, 0.066; −0.301, −0.166

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

−3.046, 0.415; −2.796, 0.417; −2.553, 0.450; −2.301, 0.520; −2.046, 0.641; −1.796, 0.771;
−1.553, 0.918; −1.301, 1.067; −1.046, 1.095; −0.796, 0.950; −0.553, 0.752; −0.301, 0.469

$$c(\text{HClO}_4) = 0.20 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.025 \text{ mol l}^{-1}$$

−3.046, −0.659; −2.796, −0.631; −2.553, −0.571; −2.301, −0.513; −2.046, −0.411; −1.796,
−0.301; −1.553, −0.226; −1.301, −0.152; −1.046, −0.214; −0.796, −0.349; −0.553, −0.553;
−0.301, −0.723

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

−3.046, −0.217; −2.796, −0.190; −2.553, −0.101; −2.301, −0.033; −2.046, 0.094; −1.796,
0.230; −1.553, 0.343; −1.301, 0.432; −1.046, 0.465; −0.796, 0.338; −0.553, 0.157; −0.301;
−0.053

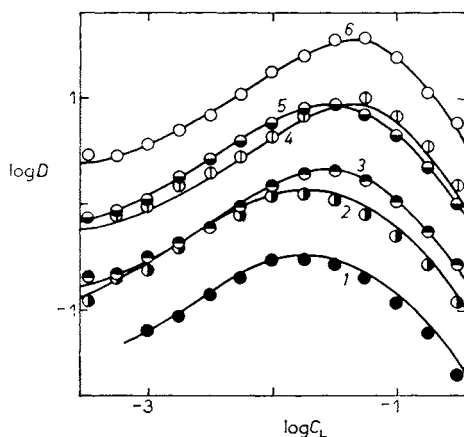


FIG. 1

Logarithm of the distribution ratio of Sr^{2+} as a function of the total analytical concentration of triglyme. $c(\text{HClO}_4)/\text{mol l}^{-1}$, $c(\text{H}^+, \text{B}^-)/\text{mol l}^{-1}$: Curve 1 0.102, 0.0085; 2 0.051, 0.0085; 3 0.102, 0.02125; 4 0.102, 0.0425; 5 0.051, 0.02125; 6 0.051, 0.0425. Solid curves were calculated for constants given in Table VIII (model $\overline{\text{Sr}^{2+}}$, $\overline{\text{SrL}_2^{2+}}$, $\overline{\text{SrL}_2^{2+}}$, $\overline{\text{HL}^+}$, $\overline{\text{HL}_2^+}$)

and the following values were obtained: $K_D = 0.22$ (for monoglyme), 0.25 (for diglyme), 0.30 (for triglyme), and 0.45 (for tetraglyme). The extraction constants $K_{ex}(Sr^{2+}) = 5$ and $K_{ex}(Ba^{2+}) = 7$ are taken from our previous study². However, the computations revealed that the concentrations of Sr^{2+} and Ba^{2+} ions in the organic phase (with the exception of Ba^{2+} extraction in the presence of triglyme and tetraglyme) are so high that these values can be obtained directly by the mathematical treatment of the experimentally obtained dependences of $\log D_M$ vs $\log C_L$. In these cases these more precise values were used for further computations.

The extraction mechanism was interpreted using the model proposed in our previous studies. Because monoglyme, diglyme, triglyme, and even tetraglyme contain a lower number of oxyethylene units than the used polyethylene glycols also the solvation in the organic phase of H^+ ions or M^{2+} ions by two molecules of the glyme was taken into consideration, *i.e.*, the reactions

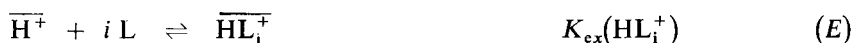


TABLE III

Distribution ratio of strontium in dependence on the concentration of diglyme for the strontium extraction by the nitrobenzene solution of dicarbollide ($c(H^+, B^-) = 0.025-0.050 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(HClO_4) = 0.0125-0.050 \text{ mol l}^{-1}$). The values of $\log C_L$ and $\log D_S$ are given for every point

$c(HClO_4) = 0.0125 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.050 \text{ mol l}^{-1}$
 -3.046, 1.729; -2.796, 1.770; -2.553, 1.802; -2.301, 1.815; -2.046, 1.897; -1.796, 2.000;
 -1.553, 2.057; -1.301, 2.125; -1.046, 2.022; -0.796, 1.829; -0.553, 1.635; -0.301, 1.412

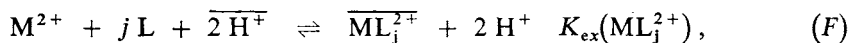
$c(HClO_4) = 0.025 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.025 \text{ mol l}^{-1}$
 -3.046, 0.527; -2.796, 0.535; -2.553, 0.561; -2.301, 0.612; -2.046, 0.662; -1.796, 0.752;
 -1.553, 0.781; -1.301, 0.768; -1.046, 0.623; -0.796, 0.448; -0.553, 0.262; -0.301, 0.100

$c(HClO_4) = 0.025 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.050 \text{ mol l}^{-1}$
 -3.046, 1.135; -2.796, 1.145; -2.553, 1.184; -2.301, 1.229; -2.046, 1.296; -1.796, 1.379;
 -1.553, 1.439; -1.301, 1.473; -1.046, 1.412; -0.796, 1.241; -0.553, 1.023; -0.301, 0.836

$c(HClO_4) = 0.050 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.025 \text{ mol l}^{-1}$
 -3.046, -0.022; -2.796, 0.003; -2.553, 0.023; -2.301, 0.077; -2.046, 0.099; -1.796, 0.126;
 -1.553, 0.218; -1.301, 0.140; -1.046, 0.059; -0.796, -0.177; -0.553, -0.367; -0.301,
 -0.506

$c(HClO_4) = 0.050 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.050 \text{ mol l}^{-1}$
 -3.046, 0.522; -2.796, 0.536; -2.553, 0.552; -2.301, 0.587; -2.046, 0.684; -1.796, 0.732;
 -1.553, 0.787; -1.301, 0.801; -1.046, 0.740; -0.796, 0.573; -0.553, 0.400; -0.301, 0.209

and



together with the possible solvation of H^+ or M^{2+} in the aqueous phase (*cf.*^{1,2}),

TABLE IV

Distribution ratio of barium in dependence on the concentration of triglyme for the barium extraction by the nitrobenzene solution of dicarbolidide ($c(H^+, B^-) = 0.00425-0.0425 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(HClO_4) = 0.098-1.02 \text{ mol l}^{-1}$). The values of $\log c_L$ and $\log D_{Ba}$ are given for every point

$c(HClO_4) = 0.098 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.00425 \text{ mol l}^{-1}$
 -3.252, -0.456; -3.000, -0.364; -2.745, -0.149; -2.495, -0.045; -2.252, 0.123; -2.000, 0.238; -1.745, 0.299; -1.495, 0.252; -1.252, 0.125; -1.000, -0.046; -0.745, -0.383; -0.495, -0.747; -0.252, -1.144

$c(HClO_4) = 0.098 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.0085 \text{ mol l}^{-1}$
 -3.000, 0.085; -2.745, 0.158; -2.495, 0.238; -2.252, 0.500; -2.000, 0.724; -1.745, 0.899; -1.495, 0.936; -1.252, 0.835; -1.000, 0.615; -0.745, 0.339; -0.495, -0.013; -0.252, -0.433

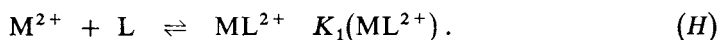
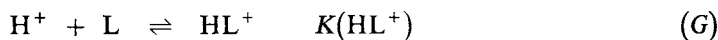
$c(HClO_4) = 0.49 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.0085 \text{ mol l}^{-1}$
 -3.495, -1.219; -3.252, -1.136; -3.000, -1.132; -2.745, -1.104; -2.252, -0.990; -2.000, -0.879; -1.745, -0.789; -1.495, -0.738; -1.252, -0.882; -1.000, -1.077; -0.745, -1.290; -0.495, -1.626; -0.252, -1.855

$c(HClO_4) = 0.49 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.02125 \text{ mol l}^{-1}$
 -3.000, -0.491; -2.495, -0.384; -2.252, -0.303; -2.000, -0.215; -1.745, -0.047; -1.495, 0.123; -1.252, 0.128; -1.000, -0.047; -0.745, -0.314; -0.495, -0.664; -0.252, -1.087

$c(HClO_4) = 0.098 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
 -3.495, 0.708; -3.252, 0.838; -3.000, 1.015; -2.745, 1.134; -2.495, 1.323; -2.252, 1.502; -2.000, 1.764; -1.745, 2.242; -1.495, 2.530; -1.252, 2.671; -1.000, 2.264; -0.495, 1.687; -0.252, 1.170

$c(HClO_4) = 0.49 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
 -3.000, -0.213; -2.495, 0.008; -2.000, 0.188; -1.745, 0.445; -1.495, 0.588; -1.252, 0.776; -1.000, 0.724; -0.745, 0.484; -0.495, 0.080; -0.252, -0.335

$c(HClO_4) = 1.02 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
 -2.745, -0.675; -2.495, -0.657; -2.252, -0.562; -1.745, -0.246; -1.495, -0.188; -1.252, -0.079; -1.000, -0.118; -0.745, -0.393; -0.495, -0.769; -0.252, -1.109



The possibility of the formation of species containing more molecules of glyme in the aqueous phase was not considered as the computations demonstrated that even the participation of HL^+ and ML^{2+} on the overall balance of H^+ , M^{2+} , and L is negligible.

TABLE V

Distribution ratio of strontium in dependence on the concentration of triglyme for the strontium extraction by the nitrobenzene solution of dicarbollide ($c(\text{H}^+, \text{B}^-) = 0.0085-0.0425 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(\text{HClO}_4) = 0.051-0.102 \text{ mol l}^{-1}$). The values of $\log C_L$ and $\log D_{Sr}$ are given for every point

$$c(\text{HClO}_4) = 0.051 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.0085 \text{ mol l}^{-1}$$

-3.495, -0.912; -3.000, -0.620; -2.745, -0.410; -2.495, -0.229; -2.252, -0.092; -2.000, 0.082; -1.745, 0.104; -1.495, 0.044; -1.252, -0.091; -1.000, -0.292; -0.745, -0.563; -0.495, -0.929

$$c(\text{HClO}_4) = 0.051 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.0425 \text{ mol l}^{-1}$$

-3.495, 0.466; -3.252, 0.460; -3.000, 0.572; -2.745, 0.706; -2.495, 0.843; -2.252, 1.036; -2.000, 1.255; -1.745, 1.400; -1.495, 1.552; -1.252, 1.569; -1.000, 1.389; -0.745, 1.057; -0.495, 0.771

$$c(\text{HClO}_4) = 0.102 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.0425 \text{ mol l}^{-1}$$

-3.495, -0.128; -3.252, -0.115; -3.000, -0.014; -2.745, 0.170; -2.495, 0.302; -2.252, 0.451; -2.000, 0.643; -1.745, 0.838; -1.495, 0.959; -1.252, 1.010; -1.000, 0.840; -0.745, 0.558; -0.495, 0.193

$$c(\text{HClO}_4) = 0.102 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.0085 \text{ mol l}^{-1}$$

3.000, -1.181; -2.745, -1.040; -2.495, -0.841; -2.252, -0.674; -2.000, -0.512; -1.745, 0.508; -1.495, -0.558; -1.252, -0.682; -1.000, -0.915; -0.745, -1.201; -0.495, -1.604

$$c(\text{HClO}_4) = 0.102 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.02125 \text{ mol l}^{-1}$$

-3.495, -0.685; -3.252, -0.653; -3.000, -0.498; -2.745, -0.350; -2.495, -0.206; -2.252, 0.007; -2.000, 0.192; -1.745, 0.307; -1.495, 0.334; -1.252, 0.244; -1.000, 0.040; -0.745, 0.235; 0.495, -0.544

$$c(\text{HClO}_4) = 0.051 \text{ mol l}^{-1}, c(\text{H}^+, \text{B}^-) = 0.02125 \text{ mol l}^{-1}$$

-3.495, -0.119; -3.252, -0.053; -3.000, 0.051; -2.745, 0.270; -2.495, 0.434; -2.252, 0.605; -2.000, 0.774; -1.745, 0.922; -1.495, 0.958; -1.252, 0.854; -1.000, 0.665; -0.745, 0.365; -0.495, 0.025

The extraction system can be then described by the equations

$$K_D = \overline{[L]}/[L] \quad (2)$$

$$K_{ex}(HL_i^+) = \overline{[HL_i^+]}/\overline{[H^+]}\overline{[L]}^i \quad (3)$$

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

$$K_{ex}(ML_j^{2+}) = \overline{[ML_j^{2+}]}\overline{[H^+]^2}/\overline{[M^{2+}]}\overline{[L]}^j\overline{[H^+]^2} \quad (5)$$

$$K(HL^+) = \overline{[HL^+]}/\overline{[H^+]}\overline{[L]} \quad (6)$$

$$K_1(ML^{2+}) = \overline{[ML^{2+}]}/\overline{[M^{2+}]}\overline{[L]} \quad (7)$$

$$(i, j = 1, 2, \dots)$$

TABLE VI

Distribution ratio of barium in dependence on the concentration of tetraglyme for the barium extraction by the nitrobenzene solution of dicarbollide ($c(H^+, B^-) = 0.005-0.025 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(HClO_4) = 0.10-0.50 \text{ mol l}^{-1}$). The values of $\log C_L$ and $\log D_{Ba}$ are given for every point

$c(HClO_4) = 0.10 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.010 \text{ mol l}^{-1}$
 -3.301, 0.636; -3.046, 0.956; -2.796, 1.192; -2.553, 1.303; -2.301, 1.404; -2.046, 1.522;
 -1.796, 1.455; -1.553, 1.255; -1.301, 0.860; -1.046, 0.702; -0.796, 0.483; -0.553, 0.235

$c(HClO_4) = 0.10 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.005 \text{ mol l}^{-1}$
 -3.301, 0.206; -3.046, 0.504; -2.796, 0.672; -2.553, 0.796; -2.301, 0.945; -2.046, 0.821;
 -1.796, 0.630; -1.553, 0.472; -1.301, 0.250; -1.046, 0.105; -0.796, -0.100; -0.553, -0.380

$c(HClO_4) = 0.20 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.010 \text{ mol l}^{-1}$
 -3.301, 0.132; -3.046, 0.310; -2.796, 0.515; -2.553, 0.710; -2.301, 0.937; -2.046, 1.023;
 -1.796, 0.822; -1.553, 0.630; -1.301, 0.410; -1.046, 0.212; -0.796, -0.032; -0.553, -0.230

$c(HClO_4) = 0.20 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.005 \text{ mol l}^{-1}$
 -3.301, -0.355; -3.046, -0.125; -2.796, 0.123; -2.553, 0.220; -2.301, 0.388; -2.046, 0.330;
 -1.796, 0.150; -1.553, -0.030; -1.301, -0.160; -1.046, -0.420; -0.796, -0.605; -0.553,
 -0.850

$c(HClO_4) = 0.50 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.025 \text{ mol l}^{-1}$
 -3.301, -0.262; -3.046, -0.020; -2.796, 0.195; -2.553, 0.450; -2.301, 0.653; -2.046, 0.820;
 -1.796, 1.020; -1.553, 0.855; -1.301, 0.530; -1.046, 0.140; -0.796, -0.084; -0.553, -0.327

together with the mass balance of glyme in the system (for the phase volume ratio 1 : 1)

$$C_L = [L] + [\bar{L}] + [HL^+] + \sum_i [\overline{HL_i^+}] + \sum_j [\overline{ML_j^{2+}}] + [ML^{2+}], \quad (8)$$

with the conditions of electroneutrality of both the aqueous

$$[B^-] + [ClO_4^-] = [H^+] + [HL^+] + 2[ML^{2+}], \quad (9)$$

and organic phases

$$[\bar{B}^-] + [\overline{ClO_4^-}] = [\overline{H^+}] + \sum [\overline{HL_i^+}] + 2 \sum [\overline{ML_j^{2+}}]. \quad (10)$$

TABLE VII

Distribution ratio of strontium in dependence on the concentration of tetraglyme for the strontium extraction by the nitrobenzene solution of dicarbide ($c(H^+, B^-) = 0.0085-0.0425 \text{ mol l}^{-1}$) from the aqueous solutions of perchloric acid ($c(HClO_4) = 0.051-0.51 \text{ mol l}^{-1}$). The values of $\log C_L$ and $\log D_{Sr}$ are given for every point

$c(HClO_4) = 0.051 \text{ mol l}^{-1}, c(H^+, B^-) = 0.02125 \text{ mol l}^{-1}$
- 3.495, 0.078; - 3.252, 0.201; - 3.000, 0.399; - 2.745, 0.585; - 2.495, 0.838; - 2.252, 0.989;
- 2.000, 1.073; - 1.745, 0.983; - 1.495, 0.567; - 1.252, 0.370; - 1.000, 0.208; - 0.745, -0.002
$c(HClO_4) = 0.051 \text{ mol l}^{-1}, c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
- 3.495, 0.541; - 3.252, 0.657; - 3.000, 0.808; - 2.745, 0.998; - 2.495, 1.223; - 2.252, 1.421;
- 2.000, 1.615; - 1.745, 1.776; - 1.495, 1.655; - 1.252, 1.235; - 1.000, 0.969; - 0.745, 0.714
$c(HClO_4) = 0.051 \text{ mol l}^{-1}, c(H^+, B^-) = 0.0085 \text{ mol l}^{-1}$
- 3.495, -0.532; - 3.252, -0.362; - 3.000, -0.080; - 2.745, 0.009; - 2.495, 0.173; - 2.252,
0.184; - 2.000, -0.009; - 1.745, -0.275; - 1.495, -0.469; - 1.252, -0.607; - 1.000, -0.751;
- 0.745, -0.915
$c(HClO_4) = 0.51 \text{ mol l}^{-1}, c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
- 3.000, -1.387; - 2.745, -1.119; - 2.495, -0.991; - 2.252, -0.778; - 2.000, -0.584; - 1.745,
- 0.429; - 1.495, -0.510; - 1.252, -0.948; - 1.000, -1.245; - 0.745, -1.437; - 0.495, -1.750;
- 0.252, -2.015
$c(HClO_4) = 0.098 \text{ mol l}^{-1}, c(H^+, B^-) = 0.0425 \text{ mol l}^{-1}$
- 3.495, 0.071; - 3.000, 0.230; - 2.745, 0.419; - 2.495, 0.585; - 2.252, 0.810; - 2.000, 1.004;
- 1.745, 1.121; - 1.495, 1.096; - 1.252, 0.639; - 1.000, 0.378; - 0.745, 0.115; - 0.495, -0.162
$c(HClO_4) = 0.098 \text{ mol l}^{-1}, c(H^+, B^-) = 0.02125 \text{ mol l}^{-1}$
- 3.495, -0.440; - 3.000, -0.116; - 2.745, 0.036; - 2.495, 0.259; - 2.252, 0.399; - 2.000, 0.511;
- 1.745, 0.402; - 1.495, 0.005; - 1.252, -0.199; - 1.000, -0.379; - 0.745, -0.609; - 0.495,
-0.863; -0.252, -1.163

Because the dependences of $\log D$ vs $\log C_L$ were studied for microamounts of Sr or Ba the concentration of the extracted metal is negligible in comparison with C_L and even C_B . At the same time practically all dicarbonyl is present in the organic phase² while the perchloric acid remains during the extraction in the aqueous phase. Under these conditions the Eqs (8) and (10) turn into

$$C_L = [L] + [\overline{L}] + [HL^+] + \sum i[\overline{HL_i^+}] \quad (11)$$

and

$$C_B = [\overline{H^+}] + \sum [\overline{HL_i^+}]. \quad (12)$$

Eq. (15) can be obtained from Eq. (9). Under the assumptions mentioned above the following relations can be derived from Eqs (2)–(6), (9), (11) and (12):

$$D_M = \frac{([\overline{H^+}]^2/[H^+]^2) \{K_{ex}(M^{2+}) + \sum K_{ex}(ML_j^{2+}) [L]^j\}}{1 + K_1(ML^{2+})} \quad (13)$$

and

$$C_L = [L] \{1 + K_D + K(HL^+) [H^+]\} + [H^+] \sum i K_{ex}(HL_i^+) [L]^i, \quad (14)$$

where

$$[H^+] = C_{HClO_4} / (1 + K(HL^+) [L]) \quad (15)$$

$$[\overline{H^+}] = C_B / (1 + \sum K_{ex}(HL_i^+) [L]^i). \quad (16)$$

The unknown value of $[L]$ can be evaluated by a numerical solution of Eq. (14), e.g., using the procedure described in the paper by Arnek, Sillén, and Wahlberg⁴.

A subroutine UBBE, based on the relations given above, was formulated and inserted into the more general least-squares minimizing programme LETAGROP (ref.⁵) that was used for the evaluation of the "best" values of the constants $K_{ex}(HL^+)$, $K_{ex}(HL_2^+)$, $K_{ex}(ML^{2+})$, $K_{ex}(ML_2^{2+})$, $K_1(ML^{2+})$, $K(HL^+)$, and $K_{ex}(M^{2+})$. The sum of squares of the deviations of the experimental values of $\log D_M^{exp}$ from the theoretical values of $\log D_M^{calc}$, evaluated on the basis of Eqs (13)–(16), was minimized so that for the function U we get the relation

$$U = \sum (\log D_M^{exp} - \log D_M^{calc})^2. \quad (17)$$

For the interpretation of Ba extraction in the presence of triglyme and tetraglyme, when the extraction of free Ba^{2+} is already very small, the value of $K_{ex}(Ba^{2+}) = 7$ was used, the value being taken from our preceding paper². The results are summarized in Table VIII.

It has been found that the course of Sr^{2+} extraction in the presence of diglyme and that of Ba^{2+} extraction in the presence of monoglyme and diglyme are in agreement with the assumption that only the reactions (A)–(D) proceed in the systems under study. If the formation of HL_2^+ and ML_2^+ species is assumed no decrease or a very insignificant decrease of the function U is obtained. On the other hand, in the Ba^{2+} extraction and particularly in the Sr^{2+} extraction in the presence of triglyme and tetraglyme the reactions (E) and (F) play a certain role even though it cannot be proven with such a certainty as for the reactions (A)–(D). Using similar arguments it can be deduced that there is no evidence for the reaction (H), *i.e.*, for the formation of complexes of the metal with glyme in the aqueous phase, and for the reaction (G), *i.e.*, for the protonization of glyme in the aqueous phase, in any of the systems under study.

A seemingly contradictory increase of the number of ligands in the molecule with the chain length can be probably explained by the increase of the ligand affinity to the M^{2+} ion in the organic phase with the increasing chain length, while at the same time the number of coordination sites is still sufficient for bonding of two glyme molecules.

It is advantageous to compare the extraction in the presence of tetraglyme with the extraction in the presence of polyethylene glycol PEG 200 which contains an approximately equal number of oxyethylene units (henceforth OEU) but instead of the terminal methoxy group $\text{CH}_3\text{—O—}$ it contains hydroxyl groups —OH . The protonization constant of glyme in the organic phase is by 1.5 orders of magnitude lower and the stability constants $K(\text{SrL}^{2+})$ and $K(\text{BaL}^{2+})$ even by 3.5 and 4 orders of magnitude, respectively, lower than those found in the presence of polyethylene glycol PEG 200. These results could probably indicate a much higher affinity of terminal hydroxyl groups towards H^+ , Sr^{2+} , and Ba^{2+} ions if compared with the methoxy group. On the other hand, the higher solubility of glyme in the organic phase affects positively the extraction of complexes with glyme ($K_D(\text{PEG 200}) = 1.6 \cdot 10^{-3}$ while $K_D = 0.45$ for tetraglyme). Due to the partial compensation of these three antagonistic factors ($K(\text{HL}^+)$ vs $K(\text{ML}^{2+})$ and K_D) the extraction of Sr and Ba in the presence of tetraglyme is by about 2 orders of magnitude less effective than in the presence of PEG 200. The theoretical values of separation factors $\alpha_{\text{Ba/Sr}}$, defined by the relation $\alpha_{\text{Ba/Sr}} = D_{\text{Ba}}/D_{\text{Sr}}$, where D_{Ba} and D_{Sr} are the distribution ratios of Ba and Sr, respectively, under the same conditions (for the evaluation of $\alpha_{\text{Ba/Sr}}$ the ligand concentration at the maximum on the curves of $\log D$ vs $\log C_L$ was chosen), for the extraction of Sr and Ba in the presence of glymes are always lower than in the presence of PEG 200–600. The values of $\log \alpha_{\text{Ba/Sr}} = 0.9$ (for diglyme), 1.3 (for triglyme), and 1.7 (for tetraglyme) can be compared with the respective values of $\log \alpha_{\text{Ba/Sr}} = 2.0$ (for PEG 200), 2.1 (for PEG 300 and 400), 1.9 (for PEG 600), and 1.5 (for PEG 1 000) (*cf.*^{2,6}). From the point of view of separation

TABLE VIII

Values of the logarithms of constants for the reactions (D), (C), (B); (D), (C), (F), (B); and (D), (C), (F), (B), (E) respectively, of the function U and the standard deviations s of the logarithm of the metal distribution ratio calculated for the Sr^{2+} and Ba^{2+} extraction from the aqueous solutions of perchloric acid by the nitrobenzene solutions of dicarbolide in the presence of monoglyme, diglyme, triglyme and tetraglyme

Model	$\log K_{\text{ex}}$	U	s
	Ba-monoglyme, $i^a = 60$		
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{HL}^+}$, ^b	0.94 ± 0.03 ^c , 2.64 ± 0.11, 1.05 ± 0.07	0.07046	0.03516
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}, \overline{\text{HL}_2^+}$	0.94, 2.63 ± 0.12, < 2.65, 1.03 ± 0.10, -0.52 (0.82)	0.07017	0.03540
	Ba-diglyme, $i = 60$		
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{HL}^+}$	0.93 ± 0.07, 3.69 ± 0.10, 1.45 ± 0.07	0.2089	0.06053
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}, \overline{\text{HL}_2^+}$	0.93, 3.89 (4.33), 5.43 ± 0.05, 1.82 (2.38), 2.38 (2.96)	0.1850	0.05748
	Ba-triglyme, $i = 82$		
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{HL}^+}$	0.85, 5.50 ± 0.16, 2.00 ± 0.12	3.222	0.20068
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}$	0.85, 5.50 ± 0.16, < 5.85, 2.01 ± 0.12	3.222	0.20194
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}, \overline{\text{HL}_2^+}$	0.85, 5.88 (6.16), 8.20 (8.66), 2.60 (2.91), 3.53 (3.84)	2.466	0.17780
	Ba-tetraglyme, $i = 60$		
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{HL}^+}$	0.85, 6.72 ± 0.06, 2.60 ± 0.05	0.2111	0.06034
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}$	0.85, 6.77 ± 0.07, 6.96 (7.31), 2.65 ± 0.06	0.1825	0.05658
$\overline{\text{Ba}^{2+}}, \overline{\text{BaL}^{2+}}, \overline{\text{BaL}_2^{2+}}, \overline{\text{HL}^+}, \overline{\text{HL}_2^+}$	0.85, 6.79 ± 0.11, 7.66 (8.25), 2.67 ± 0.12, 2.92 (3.52)	0.1805	0.05677

TABLE VIII
(Continued)

Model	$\log K_{ex}$	U	s
	Sr-diglyme, $i = 60$		
$\overline{Sr^{2+}}$, $\overline{SrL^{2+}}$, $\overline{HL^+}$	0.51 ± 0.05 , 2.96 ± 0.12 , 1.61 ± 0.07	0.1362	0.04887
Sr^{2+} , SrL^{2+} , SrL_2^{2+} , HL^+ , HL_2^+	0.51 , 3.08 ± 0.15 , 3.68 (4.16), 1.74 ± 0.16 , 1.71 (2.16)	0.1259	0.04741
	Sr-triglyme, $i = 75$		
$\overline{Sr^{2+}}$, $\overline{SrL^{2+}}$, $\overline{HL^+}$	0.41 ± 0.12 , 4.23 ± 0.08 , 1.97 ± 0.06	0.3904	0.07364
Sr^{2+} , SrL^{2+} , SrL_2^{2+} , HL^+	0.41 , 4.23 ± 0.08 , <4.37 , 1.97 ± 0.06	0.3904	0.07364
$*Sr^{2+}$, SrL^{2+} , SrL_2^{2+} , HL^+ , HL_2^+	0.41 , 4.36 ± 0.03 , 6.26 ± 0.04 , 2.23 ± 0.06 , 3.28 (3.57)	0.1799	0.05034
	Sr-tetraglyme, $i = 73$		
$\overline{Sr^{2+}}$, $\overline{SrL^{2+}}$, $\overline{HL^+}$	0.58 ± 0.22 , 5.14 ± 0.16 , 2.73 ± 0.10	0.8306	0.10893
Sr^{2+} , SrL^{2+} , SrL_2^{2+} , HL^+	0.58 , 5.28 ± 0.17 , 5.87 (6.25), 2.88 ± 0.15	0.6689	0.09775
$*Sr^{2+}$, SrL^{2+} , SrL_2^{2+} , HL^+ , HL_2^+	0.58 , 5.91 ± 0.23 , 8.19 (8.52), 3.52 ± 0.23 , 4.33 (4.56)	0.3229	0.06838

^a i The number of experimental points; ^b the models considered are denoted by an asterisk; ^c the reliability interval is given in agreement with⁵ as three times the values of the standard deviation of the respective equilibrium constant ($s(K)$). If $s(K) > 0.2$ K only the maximum limit of $\log \cdot (K + 3s(K))$ is given in parentheses. If the computation yields a zero value, the maximum possible value of the constant is given in the form $<\log(3s(K))$. If no reliability interval is given for $K_{ex}(M^{2+})$, the value is either taken from ref.² or calculated for the simpler model.

factors the glymes under study are therefore less suitable for the separation of Ba from Sr than the polyethylene glycols PEG 200–600. Their greater extraction into the organic phase is another fact that can be taken for a disadvantage.

The increase of the value of the distribution constant K_D with the increase of the oxyethylene chain length is rather unexpected; in the case of polyethylene glycols PEG 200–1 500 a reverse dependence has been observed: $K_D = 1.6 \cdot 10^{-3}$ (PEG 200), $1.5 \cdot 10^{-3}$ (PEG 300), $1.3 \cdot 10^{-3}$ (PEG 400), $1 \cdot 10^{-3}$ (PEG 600), $6.4 \cdot 10^{-4}$ (PEG 1 000), and $\leq 5 \cdot 10^{-4}$ (PEG 1 500) (ref.^{2,6}).

Figs 2 and 3 present the participation of $\overline{H^+}$ and $\overline{HL^+}$ species ($\overline{H^+}$, $\overline{HL^+}$, and $\overline{HL_2^+}$, respectively) on the total concentration of dicarbolide in the organic phase and the participation of $\overline{Ba^{2+}}$ and $\overline{BaL^{2+}}$ species ($\overline{Sr^{2+}}$, $\overline{SrL^{2+}}$, and $\overline{SrL_2^{2+}}$, respectively) on the total concentration of the metal in the organic phase for the Ba^{2+} extraction in the presence of monoglyme (or for the Sr^{2+} extraction in the presence of triglyme).

From Fig. 3 it follows that HL_2^+ species is present in significant concentrations only at relatively high concentrations of glyme in the system ($>0.1 \text{ mol l}^{-1}$) when the

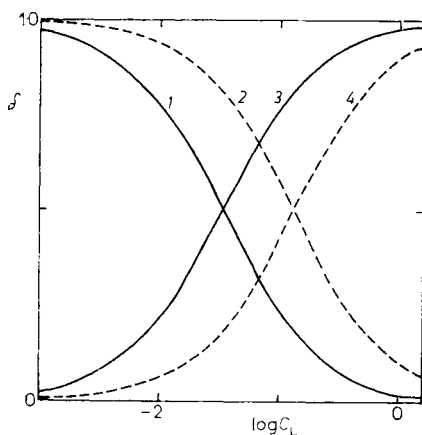


FIG. 2

Participation of species present in the organic phase during the extraction in the system Ba^{2+} – $HClO_4$ –monoglyme–dicarbolide–nitrobenzene. The portions δ of the extracted Ba^{2+} and of the complex $\overline{BaL^{2+}}$ on the total Ba^{2+} concentration in the organic phase are given (solid curves) as well as the portions δ' of $\overline{H^+}$ and $\overline{HL^+}$ on the total concentration of dicarbolide in the system (practically all dicarbolide is present in the organic phase—dashed curves). $c(HClO_4) = 0.25 \text{ mol l}^{-1}$, $c(H^+, B^-) = 0.05 \text{ mol l}^{-1}$. The values of δ and δ' were calculated using the constants $\log K_{ex}(HL^+) = 1.05$, $\log K_{ex}(Ba^{2+}) = 0.95$, $\log K_{ex}(BaL^{2+}) = 2.64$ and $K_D = 0.22$. The curves 1 $\delta(\overline{Ba^{2+}})$, 2 $\delta'(\overline{H^+})$, 3 $\delta(\overline{BaL^{2+}})$, 4 $\delta'(\overline{HL^+})$

constant values of the activity coefficients in the aqueous phase cannot be vaunched for. In the numerical interpretation of the experimental data it has been found that under the assumption that $K_{\text{ex}}(\overline{\text{ML}}_2^{2+})$ constant is equal to zero, during the computations either the value of zero is ascribed to $K_{\text{ex}}(\overline{\text{ML}}_2^{2+})$ (triglyme) or the calculated value of $K_{\text{ex}}(\overline{\text{ML}}_2^{2+})$ is substantially lower than that obtained for models comprising also the extraction of $\overline{\text{HL}}_2^+$ and $\overline{\text{ML}}_2^{2+}$ species (Table VIII). For this reason it cannot be stated with certainty whether these species actually exist in the system under study.

The dependence of extraction constants of the species $\overline{\text{HL}}^+$, $\overline{\text{SrL}}^{2+}$, and $\overline{\text{BaL}}^{2+}$ on the number of OEU in the glyme is given in Fig. 4 (using the constants calculated for simpler models in which the extraction of $\overline{\text{HL}}_2^+$ and $\overline{\text{ML}}_2^{2+}$ species is not assumed). These dependences are linear and the average values of the slopes $\Delta \log K_{\text{ex}}/\Delta n(\text{OEU})$ are 0.53 (for $\overline{\text{HL}}^+$), 1.11 (for $\overline{\text{SrL}}^{2+}$), and 1.39 (for $\overline{\text{BaL}}^{2+}$), respectively. This dependence is in certain degree analogous to the previously obtained results when for the Sr^{2+} and Ba^{2+} extractions in the presence of PEG 200–400 a linear dependence of $\log K_{\text{ex}}$ on the number of replaced water molecules has been found. As far as we can assume that one OEU replaces always an approximately equal

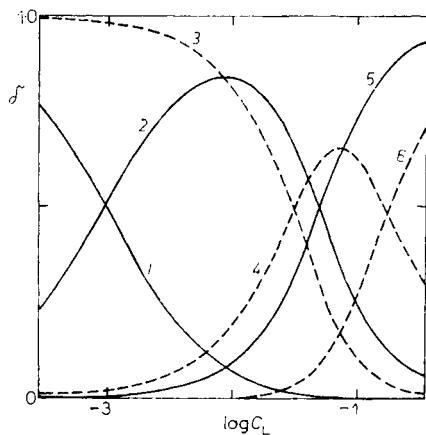
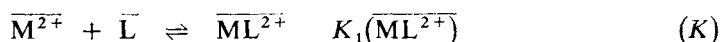
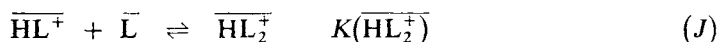
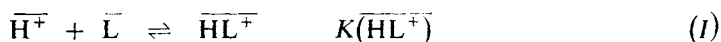


FIG. 3

Participation of species present in the organic phase during the extraction in the system Sr^{2+} – HClO_4 –triglyme–dicarbolide–nitrobenzene. Curves 1 $\delta(\overline{\text{Sr}}^{2+})$, 2 $\delta(\overline{\text{SrL}}^{2+})$, 3 $\delta'(\overline{\text{H}}^+)$, 4 $\delta'(\overline{\text{HL}}^+)$, 5 $\delta(\overline{\text{SrL}}_2^{2+})$, 6 $\delta'(\overline{\text{HL}}_2^+)$, where δ is the portion of species containing strontium atoms on the total concentration of Sr in the organic phase and δ' is the portion of species containing H^+ on the total concentration of dicarbolide in the organic phase. $c(\text{HClO}_4) = 0.51 \text{ mol l}^{-1}$, $c(\text{H}^+, \text{B}^-) = 0.0425 \text{ mol l}^{-1}$. The values of δ and δ' were calculated using the constants $\log K_{\text{ex}}(\overline{\text{HL}}^+) = 2.23$, $\log K_{\text{ex}}(\overline{\text{HL}}_2^+) = 3.28$, $\log K_{\text{ex}}(\overline{\text{Sr}}^{2+}) = 0.41$, $\log K_{\text{ex}}(\overline{\text{SrL}}^{2+}) = 4.36$, $\log K_{\text{ex}}(\overline{\text{SrL}}_2^{2+}) = 6.26$, and $K_{\text{D}} = 0.30$.

number of water molecules, which is quite probably for glymes containing 2–5 oxygen atoms, both these dependences are equivalent.

The knowledge of constants of the reactions (A)–(F) allows us to calculate also the protonization constants and stability constants of the species extracted into nitrobenzene, *i.e.*, the equilibrium constants of the reactions



using the following relations

$$K(\overline{\text{HL}}) = \frac{[\overline{\text{HL}^+}]}{[\overline{\text{L}}][\text{H}^+]} = K_{\text{ex}}(\text{HL}^+)/K_{\text{D}} \quad (18)$$

$$K(\overline{\text{HL}_2^+}) = \frac{[\overline{\text{HL}_2^+}]}{[\overline{\text{HL}^+}][\overline{\text{L}}]} = K_{\text{ex}}(\text{HL}_2)/K_{\text{ex}}(\text{HL})K_{\text{D}} \quad (19)$$

$$K_1(\overline{\text{ML}^{2+}}) = \frac{[\overline{\text{ML}^{2+}}]}{[\overline{\text{M}^{2+}}][\overline{\text{L}}]} = K_{\text{ex}}(\text{ML}^{2+})/K_{\text{ex}}(\text{M}^{2+})K_{\text{D}} \quad (20)$$

$$K_2(\overline{\text{ML}_2^{2+}}) = \frac{[\overline{\text{ML}_2^{2+}}]}{[\overline{\text{ML}^{2+}}][\overline{\text{L}}]} = K_{\text{ex}}(\text{ML}_2^{2+})/K_{\text{ex}}(\text{ML}^{2+})K_{\text{D}} \quad (21)$$

The results are summarized in Table IX.

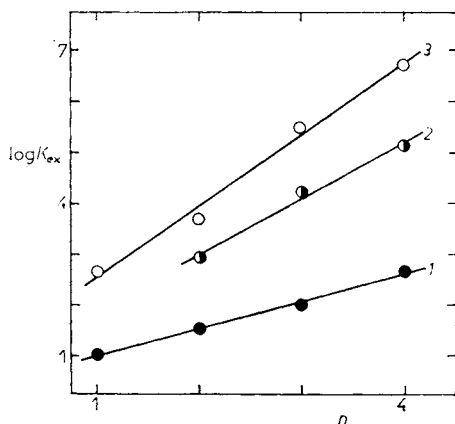


FIG. 4

Values of the extraction constants $K_{\text{ex}}(\text{HL}^+)$, $K_{\text{ex}}(\text{SrL}^{2+})$ and $K_{\text{ex}}(\text{BaL}^{2+})$ in dependence on the number of oxyethylene units in the ligand. The values from Table VIII, calculated for models assuming the extraction of $\overline{\text{HL}^+}$ and $\overline{\text{ML}^{2+}}$ species were used. 1 HL^+ , 2 SrL^{2+} , 3 BaL^{2+}

TABLE IX
Values of protonization constants or of the stability constants of the species \overline{HL}_2^+ , \overline{HL}_2^+ , \overline{ML}_2^{2+} , \overline{ML}_2^{2+} , \overline{ML}_2^{2+} in nitrobenzene

Ligand	$\log K(\overline{HL}_2^+)$	$\log K(\overline{HL}_2^+)$	$\log K(\overline{BaL}_2^{2+})$	$\log K(\overline{BaL}_2^{2+})$	$\log K(\overline{SrL}_2^{2+})$	$\log K(\overline{SrL}_2^{2+})$
Monoglyme	1.70 ^a	—	2.35	—	—	—
Diglyme	2.06 ^a	—	3.37	—	3.06	—
	2.21 ^b					
Triglyme	2.53 ^a	1.45 ^a	5.18	2.85	4.34	2.43
	2.44 ^b	1.58 ^b				
Tetraglyme	2.94 ^a	0.59 ^a	6.23	1.12	4.90	2.62
	3.06 ^b	1.15 ^b				

^a Value calculated for the interpretation of the Ba extraction, ^b value calculated for the interpretation of Sr extraction. *Footnote:* All values of the constants $K(\overline{HL}_2^+)$ and $K(\overline{ML}_2^{2+})$ were calculated from the extraction constants obtained under the assumption that no species \overline{HL}_2^+ and \overline{ML}_2^{2+} are extracted into the organic phase. Because the errors of individual constants can cancel each other during the computation, the stability constants calculated by this procedure are more reliable.

The agreement between the values of the constants $K_{\text{ex}}(\text{HL}^+)$ and $K(\overline{\text{HL}^+})$ as obtained during the interpretation of Sr^{2+} and Ba^{2+} extractions is quite evident from the Tables VIII and IX. Because these values were calculated from independent data (extraction of Sr^{2+} and Ba^{2+} , respectively), this fact can be supposed to be a confirmation of the correctness of the proposed mechanism. A good agreement was found also between the values of $K_{\text{ex}}(\text{HL}_2^+)$ and $K(\overline{\text{HL}_2^+})$ calculated for the Sr^{2+} and Ba^{2+} extractions in the presence of triglyme while larger differences were found in the case of tetraglyme.

This corresponds again to the fact that the existence of $\overline{\text{HL}_2^+}$ and $\overline{\text{ML}_2^{2+}}$ species, particularly in the case of tetraglyme, is less probable than the existence of $\overline{\text{HL}^+}$ and $\overline{\text{ML}^{2+}}$ species.

The extraction of Sr and Ba in the presence of glymes proceeds therefore with an analogous mechanism as the extraction in the presence of PEG 200–400. The existence of $\overline{\text{HL}^+}$ and $\overline{\text{ML}^{2+}}$ species in the organic phase has been proven and the value of the extraction constants $K_{\text{ex}}(\text{HL}^+)$ and $K_{\text{ex}}(\text{ML}^{2+})$ has been found to be proportional to the number of OEU in the ligand (in the case of PEG 200–400 a linear dependence on the number of replaced water molecules has been obtained). However, in the extraction of Ba^{2+} and particularly Sr^{2+} in the presence of triglyme and tetraglyme the existence of the species $\overline{\text{HL}_2^+}$, $\overline{\text{BaL}_2^{2+}}$, and $\overline{\text{SrL}_2^{2+}}$ in the organic phase cannot be excluded.

LIST OF SYMBOLS

B^-	anion of Co(III)-dicarbollide — $\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$
C_{B}	total analytical concentration of Co(III)-dicarbollide; (the initial concentration of dicarbollide in the organic phase)
C_{HClO_4}	total analytical concentration of perchloric acid (the concentration of perchloric acid in the aqueous phase)
C_{L}	total analytical concentration of polyethylene glycol
D	distribution ratio of the species given by the index
L	glyme or polyethylene glycol, respectively (in equations and formulas)
M^{2+}	cation of the bivalent metal (Sr^{2+} or Ba^{2+})
s	standard deviation
$s(K)$	standard deviation of the constant K
U	sum of squares of deviations of the experimental and theoretical values of $\log D$ — Eq. (17)
$\alpha_{\text{Ba/Sr}}$	separation factor of barium and strontium ($\alpha_{\text{Ba/Sr}} = D_{\text{Ba}}/D_{\text{Sr}}$)
K_{D}	distribution constant of the glyme (PEG, respectively) in the system water-nitrobenzene, Eq. (2)
$K_{\text{ex}}(\text{HL}_i^+)$	extraction constant of the species HL_i^+ (proton solvated by i molecules of glyme) by the nitrobenzene solution of dicarbollide, Eq. (3)
$K_{\text{ex}}(\text{M}^{2+})$	extraction constant of strontium or barium by the nitrobenzene solution of dicarbollide, Eq. (4)

- $K_{ex}(ML_j^{2+})$ extraction constant of the species ML_j^{2+} (strontium or barium ion solvated by j molecules of glyme) by the nitrobenzene solution of dicarbollide, Eq. (5)
- $K(HL^+)$ protonization constant of glyme in water, Eq. (6)
- $K(\overline{HL^+})$ protonization constant of glyme in nitrobenzene, Eq. (18)
- $K(\overline{HL_2^+})$ solvation constant of the $\overline{HL^+}$ species in nitrobenzene by another molecule of glyme, Eq. (19)
- $K_1(ML^{2+})$ stability constant of the strontium or barium complex with glyme in water, Eq. (7)
- $K_1(\overline{ML^{2+}})$ the first-step stability constant of the strontium or barium complex with glyme in nitrobenzene, Eq. (20)
- $K_2(\overline{ML_2^{2+}})$ the second-step stability constant of the strontium or barium complex with glyme in nitrobenzene, Eq. (21)

REFERENCES

1. Vaňura P., Rais J., Selucký P., Kytš M.: This Journal 44, 157 (1979).
2. Vaňura P., Makrlík E., Rais J., Kytš M.: This Journal 47, 1444 (1982).
3. Hawthorne M. F., Young D. C., Andrews T. D., Howe D. V., Pilling R. L., Pitts A. D., Rejntjes M., Warren, L. F., jr, Wegner P. A.: J. Amer. Chem. Soc. 90, 879 (1968).
4. Arnek R., Sillén L. G., Wahlberg O.: Arkiv Kemi 31, 353 (1969).
5. Sillén L. G., Warnqvist B.: Arkiv Kemi 31, 315 (1969).
6. Makrlík E., Selucký P., Vaňura P.: Unpublished results.

Translated by Z. Prašil.