THE EXTRACTION OF STRONTIUM AND BARIUM WITH A SOLUTION OF BIS-1,2-DICARBOLLYLCOBALTATE IN NITROBENZENE IN THE PRESENCE OF 18-CROWN-6

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A study has been made of the extraction of Sr and Ba in an aqueous solution of perchloric acid–18-crown-6–bis-1,2-dicarbollylcobaltate–nitrobenzene. It was found that the organic phase contains complexes of the ML^{2+}_{org} type ($M = Sr^{2+}$, Ba^{2+}) that are converted to $ML^{2+}_{2,org}$ when the concentration of crown (c_L) is greater than the concentration of bis-1,2-dicarbollylcobaltate (c_B). The values of the corresponding extraction constants, individual extraction constants and stability constants of the extracted species in the organic phase were determined. This system can be utilized for separation applications at concentrations where $c_L < c_B$.

Previous works that we have published[1–3] have described the extraction of the divalent ions of alkaline earths by solutions of bis-1,2-dicarbollylcobaltate (dicarbolide, the correct chemical name is 3,3′-commo-bis(undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate(-1)) in nitrobenzene in the presence of linear polyethylene glycols and polyethers. The presence of typical maxima on the curves of the dependence of the distribution ratio of the metal (D_M) on the total analytical concentration of the polyoxonium compound, i.e. the ligand, hereafter L) in the system was explained on the basis of the competition between the protonized ligand HL^+ and the metal–ligand complex ML^{2+} in compensating the negative charge of the dicarbollylcobaltate ion in the organic phase. We demonstrated that the concentration of ligand at the maximum point corresponds to the stoichiometric ratio of concentrations $[H^+_{org}]$ and $[HL^+_{org}]$ for the reaction

$$M^{2+}_{aq} + H^+_{org} + HL^+_{org} \rightleftharpoons ML^{2+}_{org} + 2\,H^+_{aq} \qquad (A)$$

(provided that $[ML^{2+}_{org}] >> [M^{2+}_{org}]$).

This work was carried out in order to determine whether this mechanism is also valid for the extraction of Sr^{2+} and Ba^{2+} solutions of bis-1,2-dicarbollylcobaltate in nitrobenzene in the presence of the cyclic polyether 18-crown-6, whether this system leads to better separation of Ba and Sr than linear polyethylene glycols and polyethers, or group separation of the alkaline earth metals and the rare earth metals, and also to determine the equilibrium constants of the given reactions in the aqueous and organic phases.

EXPERIMENTAL

The chemicals and experimental procedures were the same as in the previous work[3]. 18-crown-6 (Fluka) >98% pure, was used as received; its purity was checked by mass spectrometry in the central laboratories of the Prague Institute of Chemical Technology. The radionuclides ^{85}Sr and ^{133}Ba were of standard radiochemical purity. The extraction experiments were carried out in 10 ml glass test tubes fitted with polyethylene stoppers; 2 ml of each phase was shaken for 1 h, which preliminary experiments indicated is sufficient for establishment of equilibrium. The phases were separated in a centrifuge. The activities of the samples of the aqueous and organic phases were measured using a well-type NaI(Tl) detector in combination with an NK 350 gamma analyzer (Gamma, Budapest). The extractions were carried out at a temperature of 25 ± 1 °C.

RESULTS AND DISCUSSION

A study was made of the extraction of Sr^{2+} and Ba^{2+} from aqueous solutions of perchloric acid (c_{HClO_4} = 0.05 – 0.20 mol l^{-1} for Sr^{2+} and 0.05 – 0.40 mol l^{-1} for Ba^{2+}) using a solution of H^+B^- in nitrobenzene (c_B = 0.0025 – 0.0050 mol l^{-1} for Sr^{2+} and 0.0005 – 0.0050 mol l^{-1} for Ba^{2+}) in the presence of 18-crown-6 (c_L = 1.6 . 10^{-5} – 0.010 mol l^{-1}). The dependence of the logarithm of the distribution ratio of the extracted metal on the total analytical concentration of 18-crown-6 in the system (related to one phase) is given in Figs 1 and 2.

It is apparent from the figures that, similarly to the extraction in the presence of PEG's (refs[1,2]) and glym's (ref.[3]), typical maxima are present on the dependences of log D vs log c_L. The value of the synergic factor S, defined as the ratio of the values of the distribution ratio in the presence and absence of the crown is 3.5 orders in the extraction of strontium and 4.5 orders for the extraction of barium, which is less than in the extraction in the presence of PEG's, but more than in the extraction in the presence of glym's. The values of the Ba–Sr separation factor, $\log \alpha_{Sr}^{Ba} = 1.1$, is also lower than for extraction using PEG 400. In contrast, the group separation factors for the separation of Sr^{2+} and Ba^{2+} from the rare earth elements can also be higher for the extraction in the presence of 18-crown-6.

In contrast to the extraction in the presence of PEG's, glym's and also dibenzo-18-crown-6 (ref.[4]), the decrease in the distribution ratio value for the extracted metal for $c_L \geq c_B$ is far sharper and the position of the maximum on the log D vs log c_L curves is shifted to $c_L \approx c_B/2$. This phenomenon can be qualitatively explained by the fact that the extraction constant $K_{ex}(HL)$ corresponding to the reaction

$$L_{aq} + H^+_{org} \rightleftharpoons HL^+_{org} \qquad (B)$$

defined as

$$K_{ex}(\mathrm{HL}) = [\mathrm{HL}^+_{org}]/[\mathrm{H}^+_{org}][\mathrm{L}_{aq}] \qquad (1)$$

is so large that practically all the crown in the system is present for $c_L < c_B$ in the form of HL^+_{org} species. As the extraction of the divalent metal using a solution of bis-1,2-dicarbollylcobaltate in nitrobenzene (where complete dissociation can be assumed in the organic phase) in the presence of polyoxonium compounds can be expressed to a first approximation by Eq. (*A*), it is apparent that, if the value of $K_{ex}(\mathrm{HL})$ approaches infinity, then, for $c_L \rightarrow c_B$, the value of the distribution ratio of the extracted metal must decrease to zero. Under these conditions, the value of $K_{ex}(\mathrm{HL})$ cannot be determined directly from the distribution of the extracted metal as described in ref.[1], but rather by independent methods. In this work, the value $K_{ex}(\mathrm{HL}) = 6.56$ is used. This value was determined on the basis of the extraction of perchloric acid into nitrobenzene in the presence of 18-crown-6 (see ref.[5]).

If the hydrated proton is assumed to be present in the organic phase in the form of the species H^+_{org} and HL^+_{org}, then the extraction of the metal can be described in terms of general equation (*A*) in the form

$$\mathrm{M}^{2+}_{aq} + (2-n)\,\mathrm{H}^+_{org} + n\,\mathrm{HL}^+_{org} \rightleftharpoons \mathrm{ML}^{2+}_{n,org} + 2\,\mathrm{H}^+_{aq}\,, \qquad (C)$$

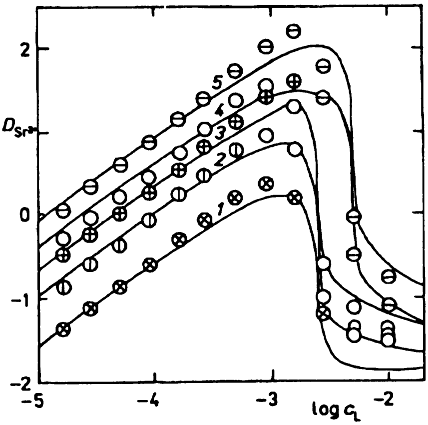

FIG. 1

Dependence of the logarithm of the distribution ratio of Sr^{2+} on the logarithm of the total analytical concentration of 18-crown-6. Curves ($c_{\mathrm{HClO_4},aq}$ and c_B in mol l^{-1}): *1* 0.2, 0.0025; *2* 0.1, 0.0025; *3* 0.1, 0.005; *4* 0.05, 0.0025; *5* 0.05, 0.005. The curves were calculated for constants $\log K_{ex}(\mathrm{HL}) = 6.563$, $\log K_{ex}(\mathrm{SrL}^{2+}) = 4.636$ and $\log K_{ex}(\mathrm{Sr}^{2+}_2) = 1.809$

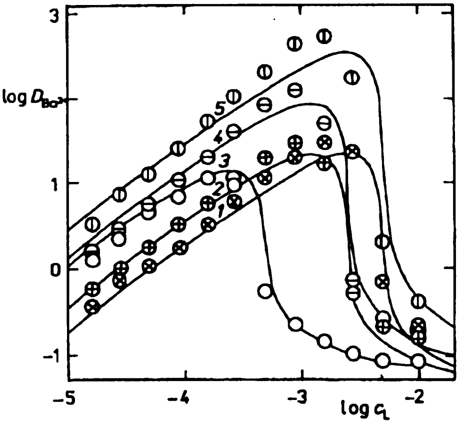

FIG. 2

Dependence of the logarithm of the distribution ratio of barium on the logarithm of the total analytical concentration of 18-crown-6. Curves ($c_{\mathrm{HClO_4},aq}$ and c_B in mol l^{-1}): *1* 0.4, 0.005; *2* 0.2, 0.0025; *3* 0.05, 0.0005; *4* 0.1, 0.0025; *5* 0.1, 0.005. The curves were calculated for constants $\log K_{ex}(\mathrm{HL}) = 6.563$, $\log K_{ex}(\mathrm{BaL}^{2+}) = 5.750$ and $\log K_{ex}(\mathrm{Ba}^{2+}_2) = 3.495$

whose equilibrium constant is given by the equation

$$K_{ex}(ML_n) = K_{ex,n} = [ML^{2+}_{n,org}][H^+_{aq}]^2/[M^{2+}_{aq}][H^+_{org}]^{2-n}[HL^+_{org}]^n . \qquad (2)$$

As the value of the distribution ratio is given by the relationship

$$D = \sum_0^N [ML^{2+}_{n,org}]/\sum_0^M [ML^{2+}_{m,aq}] \qquad (3)$$

and for $[L_{aq}] \rightarrow 0$, i.e. for $c_L < c_B$ it holds that $[M_{aq}] \cong c_{M,aq}$, then, for $N = 2$, Eq. (*3*) is converted to the form

$$D = \frac{[H^+_{org}]^2}{[H^+_{aq}]^2}\left(K_{ex,0} + K_{ex,1}\frac{[HL^+_{org}]}{[H^+_{org}]} + K_{ex,2}\frac{[HL^+_{org}]^2}{[H^+_{org}]^2}\right), \qquad (4)$$

where the value $K_{ex,0}$ is the equilibrium exchange constant of Sr^{2+} or Ba^{2+} in the water–nitrobenzene system, whose values $K^{Sr^{2+}}_{2H^+} = 5$ and $K^{Ba^{2+}}_{2H^+} = 7$ were taken from previous works[1,2].

If we introduce $x = [HL^+_{org}]/[H^+_{org}]$; $y = D\,([H^+_{aq}]/[H^+_{org}])^2$ and $z = (y - K_{ex,0})/x$, then Eq. (*4*) is converted to

$$z = K_{ex,1} + K_{ex,2}\, x . \qquad (5)$$

The dependence of z on x is then a straight line with a slope equal to $K_{ex,2}$ and intercept on the y-axis equal to $K_{ex,1}$. Assuming that it holds for $c_L < c_B$ that $[HL^+_{org}] \cong c_L$, then the values of x and y can be calculated using the relationships

$$x = c_L/(c_B - c_L) \qquad (6)$$

$$y = D\, c^2_{HClO_4,aq}/(c_B - c_L)^2 . \qquad (7)$$

In spite of the quite considerable scatter for various values of $c_{HClO_4,aq}$ and c_B, the dependences of z on x for the extraction of both Sr and Ba are linear so that the assumption that these metals are extracted in the form of the ML^{2+}_{org} and $ML^{2+}_{2,org}$ species is justified.

The final treatment of the experimental data was carried out by numerical computer calculation using a special version of the LETAGROP general minimization program[6 – 8], converted to Turbo Pascal. The calculation was carried out assuming that the metal is extracted according to Eq. (*C*). In addition, extraction of the protonated crown according to Eq. (*B*), separation of the crown between the aqueous and nitrobenzene phase

$$L_{aq} \rightleftharpoons L_{org} \tag{D}$$

$$K_D = [L_{org}]/[L_{aq}] \tag{8}$$

and the reaction of the H^+ and Sr^{2+} or Ba^{2+} ions with the crown in the aqueous phase

$$H^+_{aq} + L_{aq} \rightleftharpoons HL^+_{aq} \tag{E}$$

$$K(HL_{aq}) = [HL^+_{aq}]/[H^+_{aq}][L_{aq}] \tag{9}$$

$$M^{2+}_{aq} + L_{aq} \rightleftharpoons ML^{2+}_{aq} \tag{F}$$

$$K(ML_{aq}) = [ML^{2+}_{aq}]/[M^{2+}_{aq}][L_{aq}] \tag{10}$$

were also considered. The extraction system can then be described in terms of equilibrium equations (*2*), (*8*), (*9*) and (*10*) in combination with the mass balance of the crown

$$c_l = [L_{aq}] + [L_{org}] + \sum_{1}^{N'} n\,[HL^+_{n,org}] + \sum_{1}^{N''} n\,[HL^+_{n,aq}] \tag{11}$$

and the conditions of electroneutrality of both phases

$$[B^-_{org}] + [ClO^-_{4,org}] = \sum_{0}^{N'} [HL^+_{n,org}] \tag{12}$$

$$[ClO^-_{4,aq}] = [H^-_{aq}] + \sum_{1}^{N''} [HL^+_{n,aq}] \approx c_{HClO_4,aq}\,, \tag{13}$$

where $[B^-_{org}] \approx c_B$.

For $c_L > c_B$, when the concentration of the free crown in the aqueous phase is not negligible, it is also necessary to consider the passage of the perchlorate anion into the nitrobenzene, i.e. extraction of perchloric acid in the form of the species HL^+_{org} and $ClO^-_{4,org}$. Here we employed the formerly measured values of the extraction constants of perchloric acid[5] in the water–nitrobenzene system, defined by the relationship

$$K_{ex}(H^+, ClO^-_4) = [H^+_{org}][ClO^-_{4,org}]/[H^+_{aq}][ClO^-_{4,aq}] = 3.78 \,.\, 10^{-8}\,. \tag{14}$$

As the extraction of perchloric acid into nitrobenzene is small compared to $c_{ClO_4,aq}$ under our conditions (but not compared to c_B), the consequent change in the acidity of the aqueous phase is negligible. The concentration of perchloric acid in the organic phase is then given by the relationship

$$[\mathrm{ClO}^-_{4,\mathrm{org}}] = 0.5\,(-c_\mathrm{B} + (c^2_\mathrm{B} + 4\sum_0^N K_\mathrm{ex}(\mathrm{HL_n})\,[\mathrm{L}]^n\,K_\mathrm{ex}\,(\mathrm{H}^+, \mathrm{ClO}^-_4)\,a^2_{\mathrm{HClO_4,aq}})^{1/2})\,, \qquad (15)$$

where $a_{\mathrm{ClO_4,aq}}$ is the activity of perchloric acid in the aqueous phase, given by the relationship

$$a_{\mathrm{HClO_4,aq}} = c_{\mathrm{HClO_4,aq}}\ \gamma_\pm\,, \qquad (16)$$

where $\gamma_\pm$ is the mean activity coefficient of perchloric acid in water.

Equations (*2*) and (*8*) – (*16*) were then used to set up a special "UBBE" block for the general LETAGROP program, with a graphic output. The difference in the logarithms of the measured (D_exp) values was minimized and the (D_calc) values of the distribution ratios of the extracted metals were calculated from the equilibrium constants, so that

$$U = \sum (\log D_\mathrm{exp} - \log D_\mathrm{calc})^2\,. \qquad (17)$$

The value of the equilibrium constant for the protonation of crown in water, required for this calculation, $K(\mathrm{HL_{aq}}) = 5.83$ was taken from an earlier work[5], the stability constant of the complexes of strontium and barium with 18-crown-6 in water, $\log K(\mathrm{SrL}) = 2.72$ and $\log K(\mathrm{BaL}) = 3.87$ are taken from ref.[9], the distribution constant for crown between water and nitrobenzene $K_\mathrm{D} = 0.1$ from ref.[10] and the activity coefficients of perchloric acid in water from the book by Marcus and Kertes[11].

The calculation was carried out using the extraction constant of the HL^+ species, determined in an earlier work[5], $\log K_\mathrm{ex}(\mathrm{HL}) = 6.56$, and this constant was also calculated using the LETAGROP program, together with the extraction constants of the metal, from the distribution of Sr^{2+} and Ba^{2+} in the test system.

The results are given in Tables I and II. It can be seen that the extraction of Sr^{2+} and Ba^{2+} can be satisfactorily explained assuming that, in addition to the hydrated ions $\mathrm{Sr}^{2+}_\mathrm{org}$ and $\mathrm{Ba}^{2+}_\mathrm{org}$, whose extraction is practically negligible at the concentrations employed here, the organic phase also contains species of the $\mathrm{ML}^{2+}_\mathrm{org}$ and $\mathrm{ML}^{2+}_{2,\mathrm{org}}$ type, while the crown passes into the organic phase as the uncharged species $\mathrm{L_{org}}$ and protonated form $\mathrm{HL}^+_\mathrm{org}$. The differences in the values of function U, obtained by calculation using the formerly determined protonation constant values for crown in nitrobenzene $\log K(\mathrm{HL_{org}}) = 7.563$, i.e. $\log K_\mathrm{ex}(\mathrm{HL}) = 6.563$, are very similar to the results of the calculations where the magnitude of $\log K_\mathrm{ex}(\mathrm{HL})$ was determined from the extraction of Sr^{2+} or Ba^{2+}. The calculated values of $K_\mathrm{ex}(\mathrm{HL})$ are 0.6 or 1 order of magnitude larger (respectively) than the value found by independent measurement, which is acceptable agreement, considering that the magnitude of $K_\mathrm{ex}(\mathrm{HL})$ cannot be determined directly from the extraction of Sr or Ba.

TABLE I
Comparison of various models for the extraction of $^{85}Sr^{2+}$ from an aqueous solution of perchloric acid by a solution of bis-1,2-dicarbollylcobaltate in nitrobenzene in the presence of 18-crown-6

Species in the organic phase	$\log K_{ex}(HL)$[a]	$\log K_{ex}(HL_2)$	$\log K_{ex}(SrL)$	$\log K_{ex}(SrL_2)$	U	δ
HL^+, SrL^{2+}	6.563[b]	–	4.801 ± 0.17	–	11.000	0.4318
HL^+, SrL_2^{2+}	6.563[b]	–	–	4.637 (5.111)	159.33	1.6433
HL^+, SrL^{2+}, SrL_2^{2+}	6.563[b]	–	4.636 ± 0.08	1.809 ± 0.20	1.8408	0.1782
HL^+, HL_2^+, SrL^{2+}, SrL_2^{2+}	6.563[b]	converted to HL^+, SrL^{2+}, SrL_2^{2+}				
HL^+, SrL^{2+}	5.510 (5.790)	–	4.633 ± 0.14	–	5.7855	0.3157
HL^+, SrL_2^{2+}	3.810 (4.164)	–	–	4.637 ± 0.01	146.79	1.5909
HL^+, SrL^{2+}, SrL_2^{2+}	7.140 (7.463)	–	4.650 ± 0.07	1.669 ± 0.23	1.4770	0.1610
HL^+, HL_2^+, SrL^{2+}, SrL_2^{2+}	7.475 (7.939)	10.119 (10.897)	4.647 ± 0.07	1.773 (1.985)	1.3539	0.1555

[a] The interval of reliability is equal to three times the standard deviation[6] and is converted to the logarithmic scale using the approximate relationship $\log K \approx \log \{(K + 1.5\, s(K)) - \log (K - 1.5\, s(K))\}$, where $s(K)$ is the standard deviation of constant K. For $s(K) > 0.2\, K$, this relationship is no longer valid and the brackets contain only the upper limit in the form $\log K$ ($\log (K + 3\, s(K))$. [b] Calculation carried out for $\log K_{ex}(HL) = 6.563$, taken from ref.[5].

TABLE II

Comparison of various models for the extraction of $^{133}Ba^{2+}$ from an aqueous solution of perchloric acid by a solution of bis-1,2-dicarbollylcobaltate in nitrobenzene in the presence of 18-crown-6

Species in the organic phase	$\log K_{ex}(HL)$[a]	$\log K_{ex}(HL_2)$	$\log K_{ex}(BaL)$	$\log K_{ex}(BaL_2)$	U	δ
HL^+, BaL^{2+}	6.563[b]	–	6.047 ± 0.26	–	25.485	0.6572
HL^+, BaL_2^{2+}	6.563[b]	–	–	5.959 (6.371)	156.98	1.6312
HL^+, BaL^{2+}, BaL_2^{2+}	6.563[b]	–	5.750 ± 0.09	3.495 ± 0.18	2.4891	0.2072
HL^+, HL_2^+, BaL^{2+}, BaL_2^{2+}	6.563[b]	converted to HL^+, BaL^{2+}, BaL_2^{2+}				
HL^+, BaL^{2+}	4.474 (4.792)	–	5.728 ± 0.17	–	9.3562	0.4016
HL^+, BaL_2^{2+}	6.470 (6.958)	–	–	3.478 (4.053)	118.19	1.4275
HL^+, BaL^{2+}, BaL_2^{2+}	7.551 (7.908)	–	5.765 ± 0.07	2.910 (3.206)	1.6256	0.1689
HL^+, HL_2^+, BaL^{2+}, BaL_2^{2+}	7.741 (8.154)	10.231 (11.044)	5.765 ± 0.07	2.858 (3.157)	1.5699	0.1674

For explanations, see Table I.

The assignment of the $HL_{2,org}^{2+}$, $HL_{3,org}^{+}$, $H_2L_{org}^{2+}$ and $ML_{3,org}^{2+}$ species to a model describing the extraction of the ML_{org}^{2+}, $ML_{2,org}^{2+}$ complexes and of the protonated crown HL_{org}^{+} does not lead to any further great decrease in the value of function U. It thus follows that, in the given concentration range, these species are probably not important; in addition, it is difficult to imagine the chemical nature of the bonding between the ion and three crown molecules.

The determined values of the extraction constants $\log K_{ex}(SrL) = 4.64 \pm 0.08$ and $\log K_{ex}(BaL) = 5.75 \pm 0.09$ are practically independent of the complexity of the model employed to describe the given extraction system. As the given complexes completely predominate in the test concentration interval for $c_L < c_B$, it follows that these complexes are well defined by our experimental data and the corresponding extraction constant can be calculated with high reliability. This situation is not as simple for complexes of the $ML_{2,org}$ type. The extraction constant values determined graphically for $x < 0.25$ are $\log K_{ex,2} = 4.6$ for $SrL_{2,org}$ and $\log K_{ex,2} = 6.2$ for $BaL_{2,org}$ and the same values can be obtained through numerical calculation using the LETAGROP program in this concentration region. In contrast, if the calculation is carried out for the whole concentration region of interest, much lower values are obtained, $\log K_{ex}(SrL_2) = 1.809$ and $\log K_{ex}(BaL_2) = 3.495$. Although it is apparent that this complex is formed during extraction in the test system, the determination of its extraction constant is less reliable as a consequence of the presence of a number of competing reactions. The errors in the constants of the competing reactions are incorporated in the final K_{ex} value and neglecting of any changes in the activity coefficients in the organic phase also affects the reliability of the values found.

It can be added that mathematical treatment of the extraction equilibria together with the balance equations can demonstrate that, provided that the extraction occurs according to Eq. (C) with $n = 1$, i.e. the organic phase contains only complex ML^{2+}, then the curves of the dependence of D on c_L will contain a maximum for $[HL_{org}^{+}] = [H_{org}^{+}]$, see refs[1-3]. If only a complex of the $ML_{2,org}^{2+}$ type is present, then a maximum is not observed and the magnitude of the distribution ratio of the metal increases monotonously with increasing crown concentration, or limits towards a certain value.

Figures 3 and 4 depict the dependence of the fractions of species H_{org}^{+} and HL_{org}^{+} in the total acid concentration (i.e. H^+B^- and $HClO_4$) in the organic phase (δ), the fractions of species Sr_{org}^{2+}, SrL_{org}^{2+} and $SrL_{2,org}^{2+}$ or Ba_{org}^{2+}, BaL_{org}^{2+} and $BaL_{2,org}^{2+}$ in the total concentration of metal in the organic phase (δ') and the fractions of species SrL_{aq}^{2+} or BaL_{aq}^{2+} in the total metal concentration in the aqueous phase (δ'') on the logarithm of the total analytical concentration of crown in the system.

It is apparent from the figure that, as mentioned above, for $c_L < c_B$, the extracted metal passes into the organic phase practically only in the form of the ML_{org}^{2+} species, while species of the $ML_{2,org}^{2+}$ type are formed only at crown concentrations greater than the concentration of bis-1,2-dicarbollylcobaltate. The fact that a complex of the

$ML^{2+}_{2,org}$ type is practically not formed at $c_L < c_B$ can be explained on the basis of competition from free H^+_{org} in the organic phase, which has higher affinity for 18-crown-6 than the complexes SrL^{2+}_{org} and BaL^{2+}_{org}. In addition, the SrL^{2+}_{aq} and BaL^{2+}_{aq} complexes are formed in the aqueous phase only when the concentration of crown in the extraction system is higher than the concentration of dicarbolide (for a phase ratio of 1 : 1; otherwise it is necessary to relate the concentration to the given phase irregardless of the phase in which the given component predominates) because, at $c_L < c_B$, the concentration of free ligand in the aqueous phase is too low.

The individual extraction constants of the SrL^{2+} or BaL^{2+} species in the water–nitrobenzene system can be calculated from the $K_{ex}(ML)$, $K_{ex}(HL)$ and $K(ML_{aq})$ values.

If extraction constant $K_{ex}(ML^{2+}, B^-)$ is written in the form

$$K_{ex}(ML^{2+}, B^-) = [ML^{2+}_{org}][B^-_{org}]^2/[ML^{2+}_{aq}][B^-_{aq}]^2 \qquad (18)$$

then it follows from the definition of the individual extraction constant[12] that

$$\log K_{ex}(ML^{2+}, B^-) = \log K_i(ML^{2+}) + 2 \log K_i(B^-) , \qquad (19)$$

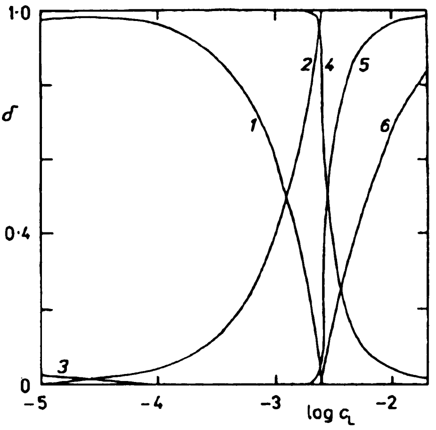

FIG. 3

Fractions of species present in the organic and aqueous phases in the extraction of the Sr^{2+}–$HClO_4$–18-crown-6–bis-1,2-dicarbollylcobaltate–nitrobenzene system. $c_{HClO_4,aq} = 0.1$ mol l^{-1}, $c_B = 0.0025$ mol l^{-1}; $\log K_{ex}(HL) = 6.563$, $\log K_{ex}(Sr^{2+}) = 0.699$, $\log K_{ex}(SrL) = 4.636$, $\log K_{ex}(SrL_2^{2+}) = 1.809$, $\log K(SrL^{2+}_{aq}) = 2.72$, $K(HL^{2+}_{aq}) = 5.83$, $K_D = 0.1$. Curves: *1* $\delta(H^+_{org})$, *2* $\delta(HL^+_{org})$, *3* $\delta(Sr^{2+}_{org})$, *4* $\delta'(SrL^{2+}_{org})$, *5* $\delta'(SrL^{2+}_{2,org})$, *6* $\delta''(SrL^{2+}_{aq})$

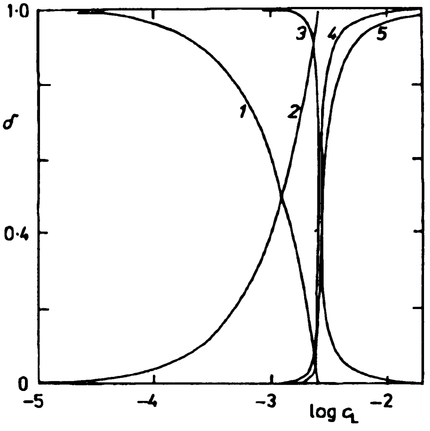

FIG. 4

Fractions of species present in the organic and aqueous phases in the extraction of the Ba^{2+}–$HClO_4$–18-crown-6–bis-1,2-dicarbollylcobaltate – nitrobenzene system. $c_{HClO_4,aq} = 0.1$ mol l^{-1}, $c_B = 0.0025$ mol l^{-1}; $\log K_{ex}(HL) = 6.563$, $\log K_{ex}(Ba) = 0.845$, $\log K_{ex}(BaL) = 5.750$, $\log K_{ex}(BaL_2) = 3.495$, $\log K(BaL_{aq}) = 3.87$, $K(HL_{aq}) = 5.83$, $K_D = 0.1$. Curves: *1* $\delta(H^+_{org})$, *2* $\delta(HL^+_{org})$, *3* $\delta'(BaL^{2+}_{org})$, *4* $\delta'(BaL^{2+}_{2,org})$, *5* $\delta''(BaL^{2+}_{aq})$. $\delta(Ba^{2+}_{org})$ is negligible where K_i denotes the individual extraction constant. The value of $\log K_i(ML^{2+})$ can be calculated from the value of the individual extraction constant of the H^+ ion, given in the literature[12], $\log K_i(H^+) = -5.7$, as it holds that

$$\log K_{2H^+}^{ML^{2+}} = \log K_i(ML^{2+}) - 2 \log K_i(H^+) , \qquad (20)$$

where $K_{2H^+}^{ML^{2+}}$ is the exchange constant of species ML^{2+} for ion H^+ in the water–nitrobenzene system, defined as

$$K_{2H^+}^{ML^{2+}} = [ML_{org}^{2+}][H_{aq}^+]^2/[ML_{aq}^{2+}][H_{org}^+]^2 . \qquad (21)$$

The values of constants $K_{2H^+}^{ML^{2+}}$ can be calculated from the extraction constants $K_{ex}(ML)$, $K_{ex}(HL)$, determined in this work, and the stability constant $K(ML)$, taken from the literature, using the relationship

$$K_{2H^+}^{ML^{2+}} = K_{ex}(ML)\, K_{ex}(HL)/K(ML_{aq}) . \qquad (22)$$

The value of $K_i(ML^{2+})$ can be used to calculate the value of the standard Gibbs energy for the transfer of species ML^{2+} from the aqueous to the nitrobenzene phase

$$\Delta G_{tr,\, ML^{2+}}^{0} = -RT \ln K_i(ML^{2+}) \qquad (23)$$

and the difference in the standard Galvani potentials for the ML^{2+} ion between the aqueous and organic phases

$$\Delta_{aq}^{org} \varphi_{ML^{2+}}^{0} = - \Delta G_{tr,\, ML^{2+}}^{0} /2 F , \qquad (24)$$

where F is the Faraday constant.

The values obtained are listed in Table III, together with the consecutive stability constants for the SrL_{org}^{2+}, $SrL_{2,org}^{2+}$ and BaL_{org}^{2+}, $BaL_{2,org}^{2+}$ complexes, calculated using the relationships

$$\log K(ML_{org}) = \log K_{ex}(ML) + \log K(HL_{org}) - \log K_{2H^+}^{M^{2+}} \qquad (25)$$

$$\log K(ML_{2,org}) = \log K_{ex}(ML_2) + \log K(HL_{org}) - \log K_{ex}(ML) . \qquad (26)$$

It is apparent from the table that the values of the individual extraction constants of the SrL^{2+} and BaL^{2+} ions are practically identical and even differ less than for the Sr^{2+} and Ba^{2+} ions. This is apparently a result of the fact that the formation of large complexes of the ML^{2+} type considerably masks differences resulting from the size of the central ion. Thus, the selectivity of the Ba–Sr extraction is almost completely a consequence of difference in the stability constants of the SrL^{2+} and BaL^{2+} complexes and not of their extractabilities. The stability of complexes of the ML^{2+} type is apparently a result of the compatibility of the size of the crown cavity, with a radius of 0.134 – 0.143 nm (see ref.[13]), with the radius of the given ion. For complexes of the ML_2^{2+} type, which apparently have sandwich structure, this factor has a smaller effect, corresponding to the smaller differences in the stability constants of the SrL_2^{2+} and BaL_2^{2+} complexes in nitrobenzene (see Table III).

The lower value of the separation factor $\log \alpha_{Sr}^{Ba} = 1.1$ than that for analogous systems containing PEG or some glym's is a disadvantage for the utilization of the system of a solution of a strong mineral acid–18-crown-6–bis-1,2-dicarbollylcobaltate–nitrobenzene for the extraction separation of Sr and Ba. If this system was to be used, e.g. for group separation or because of the better separation of some other ions, it is preferable to work at crown concentrations lower than the concentration of bis-1,2-dicarbollylcobaltate. If $c_B < c_L$, the value of the distribution ratios of Sr and Ba in the concentration range employed are relatively low. In some cases, it may also be significant that, if the extraction is carried out under conditions where $c_L < c_B$, practically no crown remains in the aqueous phase after the extraction; this substance is practically all extracted into the organic phase. The extractant can then be regenerated by washing with a solution of strong mineral acid.

TABLE III
Some thermodynamic constants of the complexes SrL^+, SrL_2^{2+}, BaL^{2+} and BaL_2^{2+} in the water–nitrobenzene system[a]

Constants	Sr^{2+}	Ba^{2+}
Ionic radius, nm	0.118	0.135
$\log K_{2H^+}^{M^{2+}}$ (refs[1,2])	0.699	0.845
$\log K_{ex}(ML^{2+})$	4.636 ± 0.08	5.750 ± 0.09
$\log K_{ex}(ML_2^{2+})$	1.809 ± 0.20	3.495 ± 0.18
$\log K(ML_{aq})$ (ref.[9])	2.72	3.87
$\log K(ML_{org})$	11.50	12.47
$\log K(ML_{2,org})$	4.74	5.31
$\log K_i(ML^{2+})$	-2.921	-2.957
$\Delta G_{tr,ML^{2+}}^0$, kJ mol^{-1}	16.67	16.88
$\Delta_{aq}^{org}\varphi_{ML^{2+}}^0$, mV	-86.4	-87.5

[a] The extraction constant values were calculated for $\log K(HL_{org}) = 7.563$, $K_D = 0.1$, $K(HL_{aq}) = 5.83$.

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