

EXTRACTION OF STRONTIUM WITH DICARBOLIDE IN THE PRESENCE OF POLYETHYLENE GLYCOL

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The extraction of microquantities of ^{85}Sr in the presence of $3 \cdot 10^{-4} - 0.25 \text{ mol l}^{-1}$ polyethylene glycol (PEG 400) (L) with solutions of dicarbolidide ($\{(\pi\text{-}(3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}\}^-$) in nitrobenzene ($10^{-3} - 10^{-2}\text{M}$) was investigated. The occurrence of the maxima (up to one order of magnitude) on the plots of the strontium distribution ratio *vs* the total PEG concentration was explained in terms of the competition between the charged strontium-PEG complex ($\overline{\text{SrL}^{2+}}$) and protonized PEG ($\overline{\text{HL}^+}$) during the balancing of the dicarbolidide electrostatic charge in the organic phase. Theoretical relations were derived for the shape of this dependence, for the effect of the acid concentration in the aqueous phase and that of the dicarbolidide concentration in the organic phase, as well as for the positions of the corresponding maxima. The theoretical dependences are in accordance with the experimental data. The values of the concentration equilibrium constants of the reactions $\text{Sr}^{2+} + \text{L} + 2 \text{H}^+ \rightleftharpoons \overline{\text{SrL}^{2+}} + 2 \text{H}^+$ ($K_{\text{ex}}(\text{SrL}^{2+})$) and $\text{H}^+ + \text{L} \rightleftharpoons \overline{\text{HL}^+}$ ($K_{\text{ex}}(\text{HL}^+)$) (for variable ionic strength) are $K_{\text{ex}}(\text{SrL}^{2+}) = 3.26 \cdot 10^8$ and $K_{\text{ex}}(\text{HL}^+) = 538$ at 25°C .

The published data^{1,2} suggest that extraction of alkali earth metals in the presence of polyethylene glycols (PEG) and bulky hydrophobic anions such as $\{(\pi\text{-}(3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_8\text{Br}_3)_2\text{Co}\}^-$ (see¹), dipyrylamines and tetraphenylborates may find application in analytical chemistry or radiochemistry.

The so far available data on the extraction with dicarbolidides indicate that the extraction of bivalent cations decreases in the order $\text{Ra} > \text{Ba} \approx \text{Pb} > \text{Sr} > \text{Ca} > \text{Mg}$. Only few other extracting agents are known that exhibit such a sequence of the extractability of cations; usually the extraction either decreases with increasing atomic weight of the alkaline earth metal, or it displays a maximum, for calcium for instance³.

It is peculiar to systems involving PEG that there is a pronounced maximum on the plot of the distribution ratio *versus* the total PEG concentration^{2,4}. This maximum appears at any concentration of the hydrophobic anion and for any molecular weight of the PEG; its position shifts toward higher PEG concentrations as the concentration of the hydrophobic anion increases⁵. An analogous effect has also been observed in the case of extraction of trivalent cations⁶.

One of the objectives of this work was to explain the origin of these maxima.

For a possible explanation of the increase in the distribution ratio on addition of PEG, the concept suggested by Yanagida and coworkers⁷ may be of importance; they assumed that in the organic phase the bivalent metal ions are surrounded by the PEG molecules so that the oxygen atoms are coordinatively bonded to the metal while the hydrophobic hydrocarbon groups are directed outwards, hence the structure of the complex is such as in the case of some crystalline compounds of PEG with alkali metals. The hydrophobic nature of such a complex is clearly much more pronounced than that of the original ion, its affinity towards the organic phase is therefore higher, too.

It is thus justified to assume that the original increase in the metal extraction with the increasing PEG concentration is due to the reaction $\text{Sr}^{2+} + \text{L} \rightleftharpoons \text{SrL}^{2+}$, leading to the formation of species which are better extracted. To account for the decrease in the distribution ratio with the further increase in the PEG concentration we introduce the assumption that, at higher concentrations of PEG, cations of the type $(\text{H}_n\text{L}_m)^{n+}$ are formed in the acidic range, these competing with the cations of the type $(\text{Sr}_x\text{L}_y)^{2x+}$ during the formation of the dissociated ion pairs with the hydrophobic anion — the extracting agent. This hypothesis is corroborated by the essential increase in the distribution ratio of PEG itself on addition of the acidic form of the extracting agent, found previously⁴; this can be interpreted simply in terms of the proton solvate formation in the organic phase.

At first sight, it might be argued against this explanation that the decrease in the strontium distribution ratio appears just in the PEG concentration range where the competition between the H^+ and Sr^{2+} ions in the reaction with PEG might be expected to slacken, as the PEG begins to be present "in excess". It must be pointed out, however, that our explanation is not based on the assumption of such competition, but on the assumption of the competition of already formed complex cations of protons and of strontium with respect to the anion type extracting agent. If the formation of the proton complexes is thermodynamically less easy than that of the complex cations of strontium, then their competition will obviously rise starting from such a concentration of PEG, at which the protons in the organic phase will apparently bond to PEG molecules.

The aim of the present work was to test this concept by quantitatively (or at least semiquantitatively) treating the equilibria in the extraction system Sr^{2+} -PEG-nitrobenzene-dicarbolide- HNO_3 , and to attempt to determine the equilibrium constants of the corresponding partial equilibrium reactions.

EXPERIMENTAL

The chemicals and the experimental procedure were the same as in the preceding work⁴. 2 ml of each phase were agitated at $25 \pm 1^\circ\text{C}$ for 30 min (2 min are sufficient for establishing the equilibrium). Microquantities of ^{85}Sr were employed for the extraction. All measurements were performed with polyethylene glycol PEG-400 (Koch-Light) with mean molecular weight 400. The commercial preparation contained also some fractions of lower and higher molecular weights, the constants obtained by us represent therefore also some average values pertaining to a mean molecule of PEG. However, as the dependence of the strontium extraction upon the mean molecular weight of PEG in the range of 400 is insignificant⁴, the values found can be supposed to approach closely those for a chemically uniform preparation.

RESULTS AND DISCUSSION

The dependences of the strontium distribution ratio were measured for three concentrations of dicarbolide, $c_B = 10^{-3}$, $5 \cdot 10^{-3}$, and $10^{-2} \text{ mol l}^{-1}$, and for three acidities, 0.1M, 0.5M, and 1M- HNO_3 , in the region of PEG concentrations $c_L = 3 \cdot 10^{-4} - 0.25 \text{ mol l}^{-1}$. The dependences measured are given in Table I and Fig. 1.

TABLE I

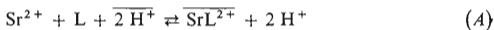
Dependence of the Strontium Distribution Ratio on the Concentration of Polyethylene Glycol for the Extraction of Strontium with 0.001–0.01M Solution of Dicarbolide in Nitrobenzene from 0.1–1.0M- HNO_3

$\log c_L$	$\log D_{Sr}$	$\log c_L$	$\log D_{Sr}$	$\log c_L$	$\log D_{Sr}$
0.5M- HNO_3 , 0.001M dicarbolide					
-3.523	-0.520	-2.523	-0.110	-1.618	-0.692
-3.218	-0.301	-2.223	-0.231	-1.523	-0.828
-3.044	-0.210	-2.034	-0.507	-1.413	-0.965
-2.823	-0.085	-1.823	-0.588	-1.315	-1.113
-2.618	-0.137				
0.5M- HNO_3 , 0.005M dicarbolide					
-3.523	0.450	-2.733	1.030	-1.618	0.670
-3.218	0.690	-2.618	1.092	-1.524	0.544
-3.043	0.754	-2.223	1.152	-1.414	0.420
-2.918	0.890	-2.038	1.050	-1.318	0.350
-2.823	0.954	-1.823	0.830		
0.5M- HNO_3 , 0.01M dicarbolide					
-3.523	0.809	-2.213	1.750	-1.222	1.145
-3.058	1.225	-1.922	1.742	-0.823	0.610
-2.824	1.410	-1.622	1.399	-0.624	0.351
-2.523	1.650				
0.1M- HNO_3 , 0.01M dicarbolide					
-3.523	2.280	-2.523	2.755	-2.073	2.570
-3.077	2.430	-2.208	2.625	-1.668	2.510
-2.828	2.550				
1.0M- HNO_3 , 0.01M dicarbolide					
-3.523	0.316	-2.523	1.185	-1.838	1.168
-3.053	0.750	-2.213	1.313	-1.673	0.905
-2.823	0.965	-2.058	1.310		

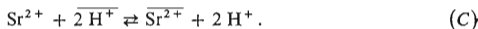
The suggested hypothesis concerning the origin of the maxima on the plots $\log D_{\text{Sr}}$ vs c_L can be summarized as follows: 1) The increase of the distribution ratio accompanying that of the concentration of PEG is due to a higher extraction of the SrL^{2+} complex by the hydrophobic anion in the organic phase as compared with the "free" Sr^{2+} cation. 2) The drop of the distribution ratio appearing as the PEG concentration is additionally increased is a result of the competitive extraction of the protonized molecule LH^+ .

Since nitrobenzene was employed as the solvent, the dissociation can be supposed to be complete both in the aqueous and in the organic phases⁴. The extraction constant of dicarbolide itself is so high that virtually all the dicarbolide is only present in the organic phase ($[\text{B}^-] = c_B$).

The system can be then described by the equations



(the bar denotes species present in the organic phase) in conjunction with the equation of extraction of "free" strontium cations with dicarbolide (extraction ion exchange)



In this set of equations, the species SrL^{2+} and HL^+ do not appear in the aqueous phase, for reasons explained below.

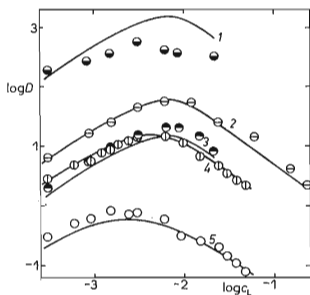


FIG. 1

Dependence of the Distribution Ratio of ^{85}Sr on the Total Analytical Concentration of PEG in the System HNO_3 -Sr-PEG 400-Nitrobenzene-Dicarbolide

1 0.1M- HNO_3 , 0.01M dicarbolide; 2 0.5M- HNO_3 , 0.01M dicarbolide; 3 1.0M- HNO_3 , 0.01M dicarbolide; 4 0.5M- HNO_3 , 0.005M dicarbolide; 5 0.5M- HNO_3 , 0.001M dicarbolide. The solid lines are calculated for $\log K'_{\text{ex}}(\text{HL}^+) = 2.73$ and $\log K_{\text{ex}}(\text{SrL}^{2+}) = 8.51$.

Assuming that the activity coefficients are constant, the corresponding equilibrium constants can be expressed as

$$K_{ex}(\text{SrL}^{2+}) = [\overline{\text{SrL}^{2+}}] [\text{H}^+]^2 / [\text{Sr}^{2+}] [\text{L}] [\overline{\text{H}^+}]^2 \quad (1)$$

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

$$K_{ex}(\text{Sr}^{2+}) = [\overline{\text{Sr}^{2+}}] [\text{H}^+]^2 / [\text{Sr}^{2+}] [\overline{\text{H}^+}]^2. \quad (3)$$

As has been found in our laboratory⁴, the distribution constant of PEG itself between water and pure nitrobenzene, hence the constant of the reaction



$$K_D = [\overline{\text{L}}] / [\text{L}] \quad (4)$$

is so low ($K_D = 1.1 \cdot 10^{-3}$) that for a first approximation, unprotonized PEG can be assumed to be present in the aqueous phase only. Taking into account only the reactions (A)–(C), we can set up the PEG mass balance equation for a negligible strontium concentration,

$$c_L = [\text{L}] + [\overline{\text{HL}^+}]. \quad (5)$$

Analogously, the condition of electroneutrality in the organic phase leads to the equation

$$c_B = [\overline{\text{HL}^+}] + [\overline{\text{H}^+}]. \quad (6)$$

For the strontium distribution ratio we have then

$$D_{\text{Sr}} = K_{ex}(\text{SrL}^{2+}) \cdot \beta \cdot [\overline{\text{H}^+}] \cdot (c_B - [\overline{\text{H}^+}]) / [\text{H}^+]^2 + K_{ex}(\text{Sr}^{2+}) \cdot [\overline{\text{H}^+}]^2 / [\text{H}^+]^2, \quad (7)$$

where

$$[\overline{\text{H}^+}] = -0.5(c_L - c_B + \beta) + [0.25(c_L - c_B + \beta)^2 + \beta c_B]^{1/2} \quad (8)$$

and $\beta = 1/K_{ex}(\text{HL}^+)$ (the solution with the negative root is of no physical meaning). The position of the maximum, *i.e.* the concentration $c_L(\text{max})$, can be solved from Eqs (7) and (8). For the resulting $c_L(\text{max})$ value we obtain

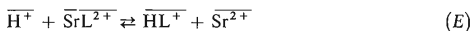
$$c_L(\text{max}) = \{(c_B/2) [K_{ex}(\text{SrL}^{2+}) \cdot \beta - 2K_{ex}(\text{Sr}^{2+})] / [K_{ex}(\text{SrL}^{2+}) \cdot \beta -$$

$$- K_{\text{ex}}(\text{Sr}^{2+})] + [K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta - 2K_{\text{ex}}(\text{Sr}^{2+})]/K_{\text{ex}}(\text{SrL}^{2+}). \quad (9)^*$$

From Eq. (9) it is obvious that there always is a maximum on the D_{Sr} vs c_{L} plots, if only $K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta > 2K_{\text{ex}}(\text{Sr}^{2+})$. The maximum shifts to higher PEG concentrations with increasing concentration of dicarbolid, which is in accordance with the experiment. From Fig. 1 it is apparent that the value of the distribution ratio D_{Sr} in the maximum is by orders of magnitude higher than in the absence of PEG. The term $2K_{\text{ex}}(\text{Sr}^{2+})$ can be then neglected with respect to $K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta$, and Eq. (9) takes on the very simple form

$$c_{\text{L}}(\text{max}) = c_{\text{B}}/2 + \beta. \quad (10)$$

That the neglecting of the term $2K_{\text{ex}}(\text{Sr}^{2+})$ against $K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta$ is warranted can be verified also by calculating the ratio of these two terms, which, in fact, represents the equilibrium constant of the reaction



Thus, *e.g.* for $K_{\text{ex}}(\text{Sr}^{2+}) = 5$, $K_{\text{ex}}(\text{SrL}^{2+}) = 10^{8.51}$, and $\beta = 10^{-2.73}$ (Table II), $K_{\text{ex}}(\text{Sr}^{2+})/[K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta] = 10^{-5.08}$.

The equations (A) and (B) account thus for the occurrence of the maxima and, moreover, for their shift towards higher PEG concentrations with increasing concentration of dicarbolid in the organic phase.

* The general form for the reactions (A)–(D) and (F)–(G) (see the subsequent text) is

$$c_{\text{L}}(\text{max}) = c_{\text{B}} - \varepsilon + \varepsilon c_{\text{B}}/[\overline{\text{H}^+}]_{\text{max}} - [\overline{\text{H}^+}]_{\text{max}},$$

where

$$\begin{aligned} [\overline{\text{H}^+}]_{\text{max}} &= \{-3yt + xz + [(3yt - xz)^2 + 16xyzt]^{1/2}\}/4yz; \\ \varepsilon &= \beta(1 + K_{\text{H,aq}}[\overline{\text{H}^+}] + K_{\text{D}}); \quad x = K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta \cdot c_{\text{B}}; \\ y &= K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta - K_{\text{ex}}(\text{Sr}^{2+}); \quad z = 1 - K(\text{SrL}^{2+}) \cdot \beta; \\ t &= K(\text{SrL}^{2+}) \cdot \beta \cdot c_{\text{B}}. \end{aligned}$$

For $K(\text{SrL}^{2+}) = 0$ this relation becomes appreciably simplified to

$$c_{\text{L}}(\text{max}) = \{(c_{\text{B}}/2) [K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta - 2K_{\text{ex}}(\text{Sr}^{2+})]/[K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta - K_{\text{ex}}(\text{Sr}^{2+})]\} + \varepsilon [K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta - 2K_{\text{ex}}(\text{Sr}^{2+})]/K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta,$$

so that here, too, a maximum exists always when

$$K_{\text{ex}}(\text{SrL}^{2+}) \cdot \beta > 2K_{\text{ex}}(\text{Sr}^{2+}).$$

The experimental data were finally computer processed by minimizing the squares of the deviations between the experimental and calculated strontium distribution ratio logarithms applying the program LETAGROP (ref.⁸⁻¹⁰).

In addition to the relations (A)–(D), we considered also the protonation of PEG in the aqueous phase,



$$K_{H,aq} = [HL^+]/[L][H^+], \quad (11)$$

and the formation of the complex of strontium with PEG,



$$K(SrL^{2+}) = [SrL^{2+}]/[Sr^{2+}][L]. \quad (12)$$

From the equilibrium constants of the reactions (A)–(D), (F), and (G), in conjunction with the requirement of electroneutrality of the organic phase (Eq. 6) and the equation of mass balance of PEG,

$$c_L = [L] + [\bar{L}] + [HL^+] + [\overline{HL^+}] \quad (13)$$

(which again holds for negligible concentration of strontium), the following relations are derived:

$$[\bar{L}] = [r + (r^2 + 4c_L K_D s)^{1/2}]/2s \quad (14)$$

$$[\overline{HL^+}] = [\bar{L}] \{ (K_{H,aq} \cdot [H^+]/K_D) + (1/K_D) + 1 \} + c_B - c_L \quad (15)$$

and

$$D_{Sr} = ([\overline{HL^+}]^2/[H^+]^2) \{ K_D \cdot K_{ex}(Sr^{2+}) + K_{ex}(SrL^{2+}) [\bar{L}] \} / \{ K_D + K(SrL^{2+}) [\bar{L}] \}, \quad (16)$$

where

$$r = K_{ex}(HL^+) \cdot (c_L - c_B) - 1 - K_D - K_{H,aq} \cdot [H^+]$$

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

Based on these relations, a special block „UBBE” was set up as a supplement to the program LETAGROP. From our previous works^{4,11} we took the values of the constants $K_D = 1 \cdot 10^{-3}$ and $K_{ex}(Sr^{2+}) = 5$.

The calculations showed a good agreement between the theoretical and experimental curves even under the original assumption that in addition to the reactions

(C) and (D), protonation of PEG in the organic phase (reaction (B)) and extraction of the complex of strontium with PEG (reaction (A)) proceed. The U value is 1.326 (52 points) for $\log K_{ex}(\text{HL}^+) = +2.73 \pm 0.14$ and $\log K_{ex}(\text{SrL}^{2+}) = 8.51 \pm 0.18$. If another complex, $\text{HL}^+(\text{aq})$, is taken into account, the U value decreases further down to 1.257, the standard deviation of the corresponding equilibrium constant is, however, so high, $\sigma(k) > k$, that the existence of protonized polyethylene glycol in the aqueous phase cannot be regarded as proved ($\log K_{ex}(\text{HL}^+) = 3.35$ max. 3.97, $\log K_{H, \text{aq}} = 0.78$ max. 1.50, $\log K_{ex}(\text{SrL}^{2+}) = 9.13$ max. 9.76).

Introducing into the two above models the complex $\text{SrL}^{2+}(\text{aq})$ does not affect the value of the U function, inasmuch as the minimum was attained for zero value of the constant $K(\text{SrL}^{2+})$ in both cases.

It is noteworthy that when assuming complete protonation of PEG in the aqueous phase we arrive at a model, which fits the experimental data equally well as that based on the assumption that the protonation does not take place at all ($U = 1.310$). In order to decide between the two models, we calculated the equilibrium constants for each concentration of the acid in the aqueous phase.

If PEG occurs in the aqueous phase in the protonized form solely, then the values of the two equilibrium constants are directly proportional to the acidity, whereas if, on the contrary, neutral molecules predominate, the constants are considerably less dependent upon the acidity. It can be thus stated that the reactions dominating in the system correspond to the equations (A) and (B).

The resulting values of the constants for the reactions are given in Table II. In addition to the constants of the reactions (A) and (B) as mentioned, the table includes also the stability constants of the complex $\overline{\text{SrL}^{2+}}$ in the organic phase and the protonation constant of PEG in the organic phase, hence the equilibrium constants of

TABLE II

Dependence of the Constants of the Equations (B), (A), (I), (H) on the Acidity of the Aqueous Phase

$[\text{H}^+]$ mol l^{-1}	$\log K_{ex}(\text{HL}^+)$	$\log K_{ex}(\text{SrL}^{2+})$	$\log K_{H, \text{org}}$	$\log K(\overline{\text{SrL}^{2+}})$	U	n^a
0.1	2.922 (3.409)	8.417 (8.942)	5.881 (6.368)	10.68 (11.20)	0.3147	7
0.5	2.747 ± 0.07	8.562 ± 0.10	5.706 ± 0.07	10.82 ± 0.10	0.1902	37
1.0	2.781 ± 0.08	8.701 ± 0.09	5.740 ± 0.08	10.96 ± 0.09	0.0030	8
0.1–1.0	2.73 ± 0.14	8.51 ± 0.18	5.69 ± 0.14	10.77 ± 0.18	1.326	52

^a Number of experimental points.

the reactions



$$K(\overline{\text{SrL}^{2+}}) = \frac{[\overline{\text{SrL}^{2+}}]}{[\overline{\text{Sr}^{2+}}][\overline{\text{L}}]} = K_{\text{ex}}(\text{SrL}^{2+}) / \{K_{\text{D}}K_{\text{ex}}(\text{Sr}^{2+})\} \quad (17)$$



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

The model presented accounts well for the shape of the extraction isotherms as well as the positions of their maxima. The dependences of the distribution ratio on the acidity (and on the ionic strength) of the aqueous phase show some departures for 0.1M and 1M nitric acid. Comparing the values of the constants calculated for the various acid concentrations (ionic strengths) we find a pronounced dependence particularly in the case of the constant $K_{\text{ex}}(\text{SrL}^{2+})$, while the constant $K_{\text{ex}}(\text{HL}^+)$ changes only slightly (Table II).

Regarding that unlike the constant $K_{\text{ex}}(\text{HL}^+)$, the constant $K_{\text{ex}}(\text{SrL}^{2+})$ reflects the reactions of charged species in the aqueous phase, we can deduce that the activities of the species H^+ and Sr^{2+} depend to an extent on the ionic strength, which brings about a change of $\log K_{\text{ex}}(\text{SrL}^{2+})$ by approximately 0.284 if $\log [\text{H}^+]$ is changed by a unit.

On the other hand, the dependences of the distribution ratio on the dicarbolide concentration in the organic phase are in accordance with the theory, which evidences that in the organic phase the activity coefficients of the components are nearly constant; this is probably also due to the narrower span of the concentration changes in this phase.

Another explanation of the dependence of the constant $K_{\text{ex}}(\text{SrL}^{2+})$ on the acidity of the aqueous phase lies in the existence of additional complexes, some of which, H_2L^{2+} for instance, have been observed by some authors¹¹. Investigation of models comprising a greater number of complex species, however, necessarily leads — particularly if the changes of the activity coefficients are not known with certainty — to constants which represent either an average composition of the system in question rather than the actually occurring species, or only empirical corrections of the non-ideality of the system. Thus, with the current state-of-the-art, a model which is capable of accounting for the existence, positions, and to an extent also the absolute magnitudes of the maxima based on the assumption of two complexes only seems to present the best available description of the strontium extraction in the system under study.

As far as we know, a theoretical model of extraction, where the dependence of the distribution ratio of the extracted element on the concentration of the extraction

promoting agent exhibits a maximum has not been so far suggested. It is peculiar to such systems that the reagent that enhances the extraction of the cation extracted simultaneously is able with a lower affinity to form extractable competitive ions with another cation or with H^+ ions, which displace then the complex (solvate) of the cation in question from the organic phase. Analogous systems are being under study in our laboratory.

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