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Studies on the Solvent Extraction of Metal Perchlorates III. Extraction Equilibria of Alkaline Earth Ions with Trioctylphosphine Oxide as Perchlorate and Thiocyanate

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Solvent extraction of alkaline earth metal ions in 1 mol dm^{-3} sodium perchlorate or thiocyanate aqueous solution with trioctylphosphine oxide (TOPO) in hexane was studied at 25 °C. The extraction in both systems improved in the order: beryllium(II)>calcium(II)>strontium(II)$\simeq$magnesium(II)$\simeq$barium(II). When the TOPO concentration was the same, the extraction of beryllium or calcium thiocyanate was better than that of the perchlorate, that of magnesium or strontium thiocyanate was nearly similar to that of the perchlorate, while barium perchlorate was extracted better than its thiocyanate. From these results it was concluded that these five perchlorates and strontium and barium thiocyanates were extracted as ion-pairs, $[M(topo)_4]^{2+}(X^-)_2$, ($X^- = ClO_4^-$ or SCN^-), while beryllium thiocyanate was extracted as solvates of noncharged complexes, $M(SCN)_2(topo)_n$, ($n=2$ and 3), and that magnesium and calcium thiocyanates in the organic phase ($n=3$ and 4) should have both ionic and coordinative properties. The poor extraction of magnesium salts was assumed to be due to their strong hydration.

In the previous study, the authors observed that the solvent extraction of alkali metal ions with trioctylphosphine oxide (TOPO) in hexane as perchlorate improved in the order lithium(I)>sodium(I)>potassium(I)>rubidium(I)>caesium(I). This was explained by suggesting that the extraction is mainly dependent on the stability of the TOPO solvates, which is higher when the ionic size is smaller.[1] In the present reseach we studied the solvent extraction of alkaline earth ions as perchlorate and thiocyanate with TOPO in hexane and have considered the effect of possible coordination of these metal ions with the anions on their solvent extraction with solvating type extractants.

Experimental

Materials. The materials were the same as reported previously.[1,2] The beryllium perchlorate stock solution was prepared by dissolving its hydroxide, obtained by precipitation from sulfate solutions. The other alkaline earth stock solutions were prepared by dissolving their chloride in sodium perchlorate or thiocyanate solutions.

The content of beryllium(II) was analyzed by gravimetry of its 2-methyl-8-quinolinolate;[3] that of the other alkaline earths was determined by titration with a standard EDTA or silver nitrate solution.

Procedures. Experiments were carried out in a thermostated room at 25 °C. The metal stock solution and 1 mol dm^{-3} sodium perchlorate or thiocyanate solution were placed in a stoppered glass tube. The initial metal concentration of barium was 5×10^{-3} mol dm^{-3} and that of the other metal ions was 1×10^{-3} mol dm^{-3}. For the experiments with beryllium, the hydrogen-ion concentration was adjusted at 1×10^{-3} mol dm^{-3} by perchloric acid or hydrochloric acid. The same volume of a hexane solution of TOPO was then added and the two solutions were agitated mechanically for half an hour and then centrifuged. A portion of the organic phase was transferred into another glass tube and the metal ions contained were back-extracted into diluted nitric or hydrochloric acid. The concentrations of strontium(II) and barium(II) in this solution and those in the aqueous phase were determined by flame spectrophotometry and those of the other metals by an atomic absorption method.

Statistical. Distribution ratio of the metal, M(II), is defined as

$$D = [M(II)]_{org}/[M(II)], \qquad (1)$$

where the subscript "org" denotes the species in the organic phase and the absence of a subscript denotes that in the aqueous phase. The extraction equilibrium of the metal with TOPO can be written as

$$M^{2+} + 2X^- + n\text{topo(org)} \rightleftharpoons MX_2(\text{topo})_n(\text{org})$$

$$K_{ex,n} = [MX_2(\text{topo})_n]_{org}[M^{2+}]^{-1}[X^-]^{-2}[\text{topo}]_{org}^{-n}, \qquad (2)$$

$$D = \sum K_{ex,n}[\text{topo}]_{org}^{n}, \qquad (3)$$

where X^- denotes a perchlorate or thiocyanate ion. The concentration of free TOPO in the organic phase is reduced by the solvation of the metal ions and sodium ions co-existing in the organic phase. (Both sodium perchlorate and thiocyanate are extracted as tri-solvates into hexane and the extraction constants $K_{ex.NaX}(=[NaX)\text{topo})_3]_{org}[Na^+]^{-1}[X^-]^{-1}[\text{topo}]_{org}^{-3})$ are $10^{1.01}$ and $10^{0.38}$, respectively.[2]) Since the concentration of both sodium ions and X^- in the aqueous phase are nearly equal to 1 mol dm^{-3}, the equilibrium concentration of TOPO can be related to its total concentration by the following equation;

$$\begin{aligned}[\text{topo}]_{org,total} &= [\text{topo}]_{org} + \sum n[MX_2(\text{topo})_n]_{org} \\ &\quad + 3[NaX(\text{topo})_3]_{org} \\ &= [\text{topo}]_{org} + \sum nK_{ex,n}[M^{2+}][\text{topo}]_{org}^{n} \\ &\quad + 3K_{ex,NaX}[\text{topo}]_{org}^{3}. \qquad (4)\end{aligned}$$

The constants which fit best with the experimental data, and the equilibrium TOPO concentration, were calculated using a least squares program.

Results

Figures 1a—c give the extraction curves from 1 mol dm^{-3} $NaClO_4$ and Figs. 2a—c from 1 mol dm^{-3} NaSCN, both as a function of the TOPO concentration in the organic phase at equilibrium. These results may be summarized as follows: (i) The perchlorate extractions of magnesium(II), strontium(II), and barium(II) are nearly the same, that of calcium(II) is about one and half orders better than the extraction of these metal

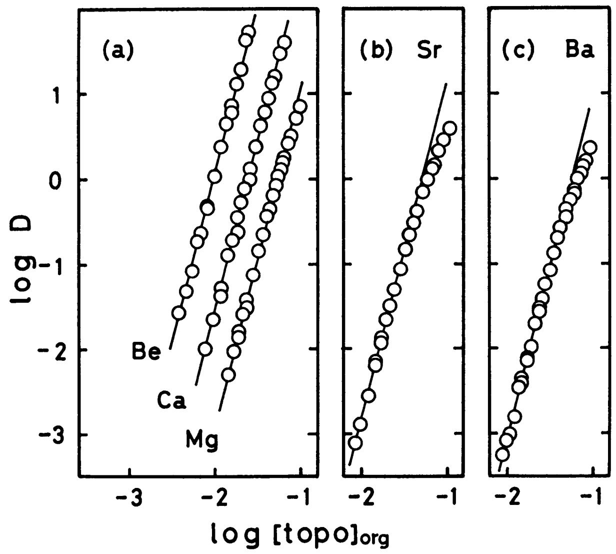

Fig. 1. Extraction of alkaline earth metal ions from 1 mol dm^{-3} $NaClO_4$ with TOPO in hexane. The TOPO concentrations are the values at equilibrium. Some data at higher TOPO concentrations in Figs. b and c were not used for the calculation of the constants (see text). The solid lines were calculated by introducing the constants in Table 1 into Eq. 3.

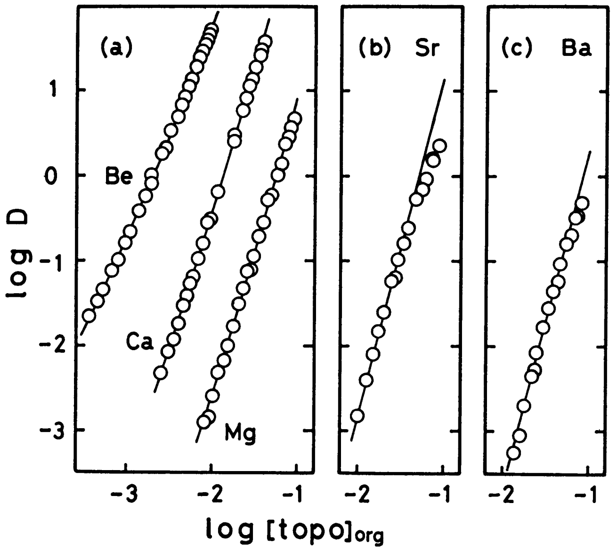

Fig. 2. Extraction of alkaline earth metal ions from 1 mol dm^{-3} NaSCN with TOPO in hexane. The TOPO concentrations are the values at equilibrium . Some data at higher TOPO concentrations in Figs. b and c were not used for the calculation of the constants (see text). The solid lines were calculated by introducing the constants in Table 1 into Eq. 3.

ions and that of beryllium(II) is better still: one and half orders better than calcium(II). (ii) The differences of the extraction curves of the thiocyanates are greater than those of the perchlorates. (iii) The extraction of magnesium(II) and strontium(II) as perchlorate and the thiocyanate is nearly the same. The extraction of barium thiocyanate is somewhat inferior to that of its perchlorate, while the opposite is found with calcium(II). The extraction of beryllium thiocyanate is much better than its perchlorate.

The data were analyzed by using a least squares computer program. As is seen from the figures, the slope of the extraction curve of strontium(II) and barium(II) decreased in the higher TOPO concentration region both in the perchlorate and thiocyanate extraction systems. Since this trend could not be explained stoichiometrically, those data were eliminated from the least squares calculation. Beryllium(II) was reported to form thiocyanate complexes in aqueous solutions[4] and corrections for them are necessary in order to obtain accurate extraction constants from the data in the figures. It is assumed from the stability constants ($\beta_1=10^{-0.16}$ and $\beta_2=10^{-0.60}$ in 4 mol dm^{-3} $NaClO_4$) that the total concentration of the complexes is approximately equivalent to Be^{2+} in the 1 mol dm^{-3} thiocyanate solution. Thus the constants $K_{ex,n}$ obtained in the present study, assuming no complexes in the aqueous phase should be a little lower than the values defined by Eq. 2. The formation of thiocyanate complexes in the aqueous phase of the other alkaline earths should be slight[5] and no correction for that may be necessary.

Solvation of the alkaline earth salts and of the coextracted sodium perchlorate or thiocyanate should decrease the free TOPO concentration. In the higher concentration region, this was not negligible. For example, in the extraction of barium perchlorate from the 1 mol dm^{-3} $NaClO_4$ medium with 0.14 mol dm^{-3} of initial TOPO in hexane, it is calculated by Eq. 4 by introducing the values in Table 1 that about 20% of this TOPO combines with sodium perchlorate and 10% combines with barium perchlorate. Correction for this decrease in the free TOPO concentration by successive approximation was included in the computer program.

All of the extraction data of the perchlorates were found to be well explained in terms of solvation with four TOPO molecules in the organic phase. The $K_{ex,4}$ values obtained by the least squares calculation are listed in Table 1. In the extraction of thiocyanates, a solvation number of four well explained the data of strontium(II) and barium(II), but two types of solvates

Table 1. Extraction constants[a)] of alkaline earth metal perchlorates and thiocyanates with TOPO in hexane at 25°C[b)]

Metal	Perchlorate $\log K_{ex,4}$	Thiocyanate		
		$\log K_{ex,2}$	$\log K_{ex,3}$	$\log K_{ex,4}$
Be(II)	8.01±0.20	5.18±0.16	7.73±0.19	
Mg(II)	4.99±0.21		3.32±0.39	4.86±0.41
Ca(II)	6.39±0.17		5.45±0.14	7.12±0.32
Sr(II)[c)]	5.13±0.10			5.17±0.18
Ba(II)[c)]	4.92±0.13			4.29±0.21

a) The limit of error is 3σ. b) Aq phase: 1 mol dm^{-3} $NaClO_4$ or NaSCN. Org. phase: hexane containing TOPO. c) Some of the data for these ions in the higher TOPO concentration region in Figs. 1b, 1c, 2b, and 2c were eliminated in the calculation of these constants. See text.

were necessary in order to explaine the extraction of the other metal ions; solvation numbers of two and three for beryllium(II) and of three and four for magnesium(II) and calcium(II) were found to give a better fit of the calculated values with the experimental data than only one solvation number. The extraction constants thus computed are listed in Table 1.

Discussion

As is seen from Fig. 1 and Table 1, the solvent extraction of alkaline earth perchlorates with TOPO is much better than that of alkali perchlorates[1] under identical conditions. The solvation number is four in the former extraction, but three in the latter one. The extraction of alkaline earth thiocyanates with TOPO is also much better than that of alkali metals.

The smaller the ionic size, the better the TOPO extraction which was found among the alkali perchlorates.[1] This tendency is also found among the alkaline earth perchlorates, except magnesium(II): the extraction of magnesium(II) is nearly similar to that of barium(II). The extraction order of the alkaline earth thiocyanates is also similar to that of their perchlorates, again except magnesium(II).

If we omit magnesium(II), this extraction order may be explained in terms of the higher ability of solvation with TOPO of smaller ions and of the difference in the nature of the chemical bonds between the anion and the metal ion. The solvation reduces hydrating water and also increases the molar volume of the cation; these effects are favorable for its extraction. A smaller ion tends to form more stable solvates than a larger one, although the former tends to be hydrated more strongly. On the other hand, since the metal ions combine with four molecules of TOPO in their extraction as perchlorates, the molar volumes of the resulting solvates should be rather similar even when the size of the central metal ion is different. For this reason, smaller metal ions are extracted better than larger ones. It is generally true that when the bond between the anion and the metal is coordinative the extraction is better than when it is ionic. The better extraction of beryllium thiocyanate than of its perchlorate indicates that the thiocyanate ions in the extracts coordinate with the central metal ion. The smaller solvation numbers of beryllium thiocyanate with TOPO than of its perchlorate also indicate that the thiocyanate ions occupy the coordination sphere of the metal ion in the extracts. As is seen from the stability of the alkaline earth thiocyanates in the aqueous phase, the coordination with thiocyanate ions should be weaker when the ionic size is larger. The extraction of thiocyanates of strontium(II) and barium(II) is rather similar to their perchlorates. The somewhat poorer extraction of barium thiocyanate than of its perchlorate may indicate that this thiocyanate is essentially an ion-pair; the same tendency was observed in the TOPO extraction of sodium(I)[2] and this was explained in this previous paper in terms of the larger molar size and the less polar nature of the perchlorate ion than of the thiocyanate ion, these factors make the extraction of the ion-pairs containing the former more favorable.

The poorer extraction of magnesium(II), both as perchlorate and thiocyanate, than of calcium(II) seems to suggest a stronger hydration for the magnesium(II) ion than for the calcium(II) ion. The same tendency has been pointed out before: the extraction of magnesium(II) with tributyl phosphate (TBP) as nitrate[6] and as halides[7] was also poorer than calcium(II). This was explained by a higher tendency of hydration of magnesium(II). Similar reasoning was also proposed for the poor extraction of nickel perchlorate and thiocyanate than of cobalt(II).[8] However, in order to continue discussion about this problem, much comparative work on the extractability of magnesium(II) and calcium(II) in several liquid-liquid systems seems to be necessary.

The extraction of ion-pairs into polar solvents is very often better when the metal ion is larger.[9] However, although the extracted perchlorates are ion-pairs in the present study, the magnitude of the extraction is mainly dependent on the ability to form the solvate with TOPO. The tendency of extraction is similar to that of coordination complexes: the smaller the metal ion, the better the extraction.

The differences among the extraction of the alkaline earth thiocyanates are larger than those of their perchlorates. This is especially marked with beryllium(II); the thiocyanate in the organic phase should be coordinative. As is described above, barium thiocyanate in the organic phase may be essentially ion-paired and the other thiocyanates may have both of these characters.

The extraction of alkaline earths as perchlorates[10,11] and thiocyanates[12–15] with TBP has been reported. The observations such as the order of extraction and the solvation numbers of extracts are similar with our results for the extraction with TOPO.

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