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Studies of the Alkaline Earth Complexes in Various Solutions. III. Calcium(II) and Strontium(II) Complexes with Sulfate and Oxalate Ions in 1M Perchlorate Media

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The complex formation of calcium and strontium with sulfate and oxalate ions has been studied in 1 M perchlorate media at 25°C by a liquid-liquid distribution method. The radioisotopes, calcium-45 and strontium-85 at tracer concentrations were used in conjunction with thenoyltrifluoroacetone in methylisobutylketone or in carbon tetrachloride containing tributylphosphate. The complex formation was determined by a graphical method from the decrease in the extraction of the metal ions with the increases in the concentration of sulfate or oxalate ions in the aqueous phase. The results were explained by the formation of the first and the second complexes, and the stability constants, $\beta_n=[ML_n{}^{2-2n}]/[M^{2+}][L^{2-}]^n$, were determined as follows; Sulfate systems, Ca(II): $\log\beta_1=1.10$, $\log\beta_2=1.36$, Sr(II): $\log\beta_1=0.72$, $\log\beta_2=1.29$. Oxalate systems, Ca(II): $\log\beta_1=1.66$, $\log\beta_2=2.69$, Sr(II): $\log\beta_1=1.25$, $\log\beta_2=1.90$.

Although there has been much work on the solubilities of calcium and strontium sulfates or oxalates in water, relatively few attention seems to have been paid to the association of the metal ions with these anions in aqueous solutions. In the present paper, the authors have studied the complex formation of these metal ions with sulfate or oxalate ions in 1 M sodium perchlorate media at 25°C by a liquid-liquid distribution technique. The formation of the metal complexes was determined from the decrease in the extraction of the metal ions with thenoyltrifluoroacetone (TTA) in methylisobutylketone (MIBK) or in carbon tetrachloride containing tributylphosphate (TBP) when the perchlorate ions in the aqueous phase were replaced with the ligand anions. The stability constants of the complex species were determined by a graphical method.

Experimental

Tracers. Calcium-45 was obtained from the Nuclear Science and Engineering Co., U. S. A. as a hydrochloric acid solution. It was diluted with 1 M sodium perchlorate solution. The stock solution thus prepared contained 1.5×10^{-5} M calcium.

Strontium-85 was obtained from Union Carbide Co., U. S. A. as a nitrate solution. The stock solution containing 7.5×10^{-6} M strontium was prepared in the same manner as that of calcium.

Reagents. All the reagents were of analytical grade. Sodium perchlorate, TBP and MIBK were prepared and purified as described in Papers I and II.[1,2] Other reagents were used without further purification.

Procedures. All the procedures were carried out in a thermostatted room at 25±0.5°C. MIBK containing 0.1 M TTA was used as the organic phase for the calcium systems and carbon tetrachloride containing 0.1 M TTA and 0.1 M TBP for the strontium systems. The aqueous phase was buffered with a small amount of acetate or triethanol amine (initial concentration was 0.01 M). The aqueous phase was prepared always to contain 1.0 M sodium ions and various amounts of perchlorate and sulfate or oxalate ions, together with 3×10^{-7} M calcium ions containing calcium-45 or 1.5×10^{-7} M strontium ions containing strontium-85. A three milliliter portion of the organic phase and a 5 m*l* portion of the aqueous phase were placed in stoppered glass tubes (volume 20 m*l*). The two phases in the tubes were agitated mechanically for half an hour and centrifuged for 3 min at 2000 rpm. A small portion was taken from the aqueous phase, transferred to a small glass vessel and the hydrogen ion concentration was determined potentiometrically using a glass electrode and a standard solution of $-\log[H^+]=2.00$ containing 0.0100 M perchloric acid and 0.99 M sodium perchlorate. The radioactivity of the two phases was measured as follows: Calcium systems; A one milliliter aliquot was pipetted from the organic phase, placed on a stainless steel dish (diameter 25 mm) and dried up. The residue in the dish was then decomposed gradually on a hot plate under a controlled heating. A two milliliter portion was pipetted from the aqueous phase and transferred to another glass tube and then a 1.8 m*l* portion of 0.1 M sodium hydroxide and a 2 m*l* portion of MIBK containing 0.1 M TTA were added to this aqueous phase. These two phases were agitated mechanically for half an hour and centrifuged. The calcium in the aqueous phase was thus quantitatively extracted into the organic phase (*cf.* Ref. 3). A one milliliter portion of this organic phase was pipetted, placed on a stainless steel dish of the same size and treated in the same manner as described above. The β-radioactivity of the sample in the dishes was measured with an end-window type

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[1] T. Sekine, M. Sakairi and Y. Hasegawa, This Bulletin, **39**, 2142 (1966).

[2] T. Sekine and M. Sakairi, This Bulletin, **40**, 261 (1967).

G. M. counter. Strontium systems; Two milliliter portions were pipetted from the two phases and transferred into small stoppered glass tubes. The γ-radioactivity of the samples was then measured with a well-type (NaI) scintillation counter.

The net distribution ratios of the metals were calculated as follows;

$$D = \frac{\text{radioactivity per m}l\text{ org. phase}}{\text{radioactivity per m}l\text{ aq. phase}} = \frac{[\mathrm{M(II)}]_{org,\ \mathrm{total}}}{[\mathrm{M(II)}]_{aq,\ \mathrm{total}}}$$

Results

The details of the statistical treatment have been described in previous papers.[1,2] The present results were also treated by the same way. The equations used are as follows;

$$D = [\mathrm{M(II)}]_{org,\ \mathrm{total}}/[\mathrm{M(II)}]_{aq,\ \mathrm{total}} \tag{1}$$

$$K_{ex_0} = ([\mathrm{MA_2}]_{org}/[\mathrm{M^{2+}}])[\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2} \tag{2}$$

$$\beta_n = [\mathrm{ML}_n{}^{2-2n}]/[\mathrm{M^{2+}}][\mathrm{L^{2-}}]^n \tag{3}$$

$$D[\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2}/K_{ex_0} = \left(1+\sum_{n=1}^{n}\beta_n[\mathrm{L^{2-}}]^n\right)^{-1} \tag{4}$$

The notations HA and $\mathrm{L^{2-}}$ in this paper denote TTA and sulfate or oxalate ion, respectively.

When the first and the second complexes, ML and $\mathrm{ML_2{}^{2-}}$ are formed, the $\log D[\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2}/K_{ex_0}$ *vs.* $\log[\mathrm{L^{2-}}]$ plot will be fitted one of the following family of standard curves;

$$X = \log a;\ Y = -\log(1 + Ra + a^2) \tag{5}$$

and the stability constants may be determined from the parameters of the "best-fit" standard curves.

Perchlorate System. Figure 1 gives the $\log D$ *vs.* $-\log[\mathrm{H^+}]$ plot when the TTA concentration was 0.1 M. In Fig. 1, the plot falls on a straight line with a slope +2 except in the highest $-\log[\mathrm{H^+}]$ region. In other experiments, the plot $\log D[\mathrm{H^+}]^2$ *vs.* $\log[\mathrm{HA}]_{org}$ also showed a straight line with a slope +2.

From these, it was concluded that the extraction equilibria can be described by the following equation;[*1]

$$\mathrm{M^{2+}} + 2\mathrm{HA}(org) \rightleftarrows \mathrm{MA_2}(org) + 2\mathrm{H^+}$$

The extraction constant in Eq. 2 was determined from the data excluding those deviate from the straight lines in Fig. 1. The extraction constants are listed in Table 1-a.

Sulfate Systems. The distribution ratios of the (II)metals are decreased by replacements of perchlorate ions in the aqueous phase by sulfate

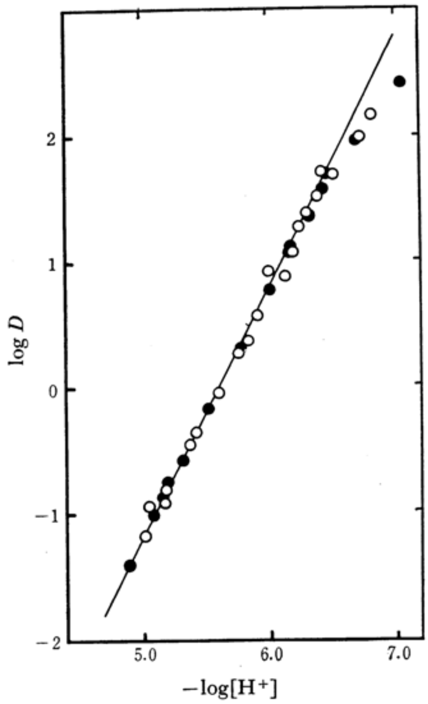

Fig. 1. Change in $\log D$ for calcium(II) and strontium(II) in 1M $\mathrm{NaClO_4}$ as a function of $-\log[\mathrm{H^+}]$. The organic phases are 0.1 M TTA-MIBK solution for Ca(II) and 0.1 M TTA +0.1 M TBP-$\mathrm{CCl_4}$ solution for Sr(II).
Open circles: Ca(II), the straight line gives $\log D = -2\log[\mathrm{H^+}] - 11.20$
Closed circles: Sr(II), the straight line gives $\log D = -2\log[\mathrm{H^+}] - 11.20$

TABLE 1

a) Extraction constants of the metal ions from 1M $\mathrm{Na(ClO_4)}$ at 25°C

$$K_{ex_0} = ([\mathrm{M(II)}]_{org}/[\mathrm{M(II)}]) \times [\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2}$$

	$\log K_{ex_0}$	Organic phase
Be(II)*	−2.45	0.03M TTA in MIBK
Ca(II)	−9.20	0.1M TTA in MIBK
Sr(II)	−9.20	0.1M TTA and 0.1M TBP in $\mathrm{CCl_4}$
Ba(II)**	−10.01	0.1M TTA and 0.2M TBP in $\mathrm{CCl_4}$

b) Stability constants of alkaline earth complexes in 1M $\mathrm{Na(ClO_4)}$ at 25°C

$$\beta_n = [\mathrm{ML}_n{}^{2-2n}]/[\mathrm{M^{2+}}][\mathrm{L^{2-}}]^n$$

Ligand		Be(II)*	Ca(II)	Sr(II)	Ba(II)**
$\mathrm{SO_4{}^{2-}}$	$\log\beta_1$	—	1.10	0.72	0.66
	$\log\beta_2$	1.78	1.36	1.29	1.42
	$\log\beta_3$	2.08	—	—	—
$\mathrm{C_2O_4{}^{2-}}$	$\log\beta_1$	3.55	1.64	1.25	0.58
	$\log\beta_2$	5.40	2.68	1.90	2.20

* From Ref. 2. ** From Ref. 1.

[*1] The metal-TTA complex in the organic phase combines with some molecules of MIBK or TBP to form adduct chelate complexes. The details of this adduct formation have been given in Ref. 3.

3) T. Sekine and D. Dyressen, *Anal. Chim. Acta*, **37**, 217 (1967).

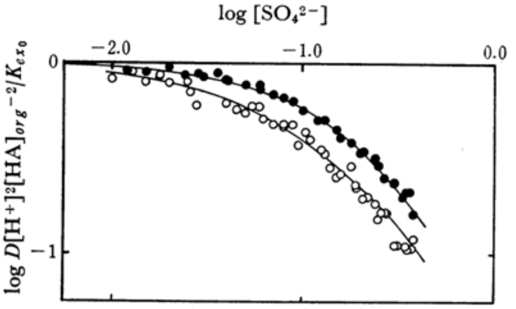

Fig. 2. Decrease in the extraction of calcium(II) (open circles) or strontium(II) (closed circles) as a function of the sulfate ion concentration. The solid curves were calculated by the following equations:
for the calcium systems; $X=\log[SO_4^{2-}]$,
$Y=-\log(1+12.6[SO_4^{2-}]+22.9[SO_4^{2-}]^2)$,
for the strontium systems; $X=\log [SO_4^{2-}]$,
$Y=-\log(1+5.3[SO_4^{2-}]+19.5[SO_4^{2-}]^2)$.

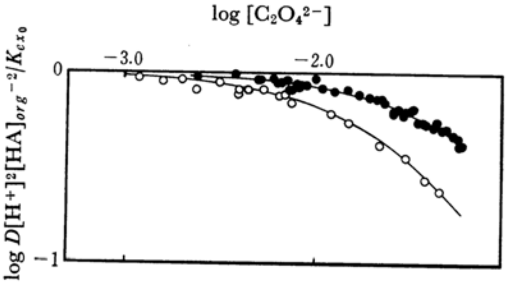

Fig. 3. Decrease in the extraction of calcium(II) (open circles) or strontium(II) (closed circles) as a function of the oxalate ion concentration. The solid curves were calculated by the following equations:
for the calcium systems; $X=\log[C_2O_4^{2-}]$,
$Y=-\log(1+46[C_2O_4^{2-}]+493[C_2O_4^{2-}]^2)$,
for the strontium systems; $X=\log[C_2O_4^{2-}]$,
$Y=-\log(1+17.8[C_2O_4^{2-}]+79.4[C_2O_4^{2-}]^2)$.

ions. Figure 2 gives the decrease in the $D[H^+]^2[HA]_{org}^{-2}$ as a function of the sulfate concentration. In these experiments the total concentration of sodium sulfate was regarded as the sulfate ion concentration in the aqueous phase, because the $-\log[H^+]$ was kept between 4.8 and 6.2 and the pK_{a_2} of sulfuric acid in 1 M Na(ClO$_4$) at 25°C is 1.02.[4]

Each plot was found to fit the standard curves, for the calcium system, $X=\log a$, $Y=-\log(1+2.8a+a^2)$ and for the strontium system, $X=\log a$, $Y=-\log(1+1.2a+a^2)$. The stability constants determined are listed in Table 1-b).

Oxalate Systems. The distribution ratios of the metals are also decreased by replacements o perchlorate ions in the aqueous phase by oxalate ions. In these experiments the total concentration of sodium oxalate in the aqueous phase was also regarded as the oxalate concentration because the $-\log[H^+]$ was kept between 5.3 and 6.1 and the pK_{a_2} of oxalic acid in 1 M Na(ClO$_4$) at 25°C is 3.54.[5] It was not possible to obtain a higher oxalate concentration because the solubility of sodium oxalate in 1 M sodium perchlorate is not large. The plots were found to fit the following standard curves; for the calcium systems, $X=\log a$, $Y=-\log(1+2.0a+a^2)$, for the strontium systems, $X=\log a$, $Y=-\log(1+2.0a+a^2)$. This is explained by the formation of the MC_2O_4 and the $M(C_2O_4)_2^{2-}$ species. The stability constants obtained are listed in Table 1-b).

Table 1-b) shows that the stability constants of the complexes with either sulfate or oxalate ligand decrease in the order Be(II) > Ca(II) > Sr(II) > Ba(II).

Discussion

The solubility of calcium or strontium oxalate is very small. The previous data of the solubility products of these oxalates are around 10^{-9} in dilute electrolyte media.[6] In the present work, the highest value of $[Ca(II)]_{total}\times[C_2O_4^{2-}]$ is about 1×10^{-8} and this value is larger than the solubility product. However, the recovery of calcium from the phases is quantitative within the experimental accuracy, the distribution data change reasonably even in the highest oxalate concentration range and no indication of the formation of precipitates of calcium oxalate was observed. Probably, the value of the solubility in such solutions at a high electrolyte concentration may be different and moreover the total solubility of calcium oxalate is increased by the complex formation.

Money and Davies[7] calculated the stability constant of the calcium sulfate complex, CaSO$_4$, as $10^{2.28}$ at infinite dilution at 18°C while Bell and George[8] reported a value $10^{2.31}$ as the constant at zero ionic strength at 25°C. Money and Davies[7] also calculated the first stability constants of calcium and strontium oxalate complexes at infinite dilution at 18°C as $\sim10^{3.0}$ and $10^{2.54}$ respectively. Gelles and Hay[9] gave the constant for the calcium oxalate complex as $10^{3.0}$ in 0.1 M ionic media at 25°C.

As the concentration of the co-existing electrolyte is different, the previous data may not be compared directly with the present results. It is

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[4] E. Eichler and S. Rabidean, *J. Am. Chem. Soc.*, **77**, 5501 (1955).

[5] T. Sekine, *Acta Chem. Scand.*, **19**, 1476 (1965).

[6] W. M. Latimer, "Oxidation Potentials," 2nd ed., Pretice-Hall, Englewood Cleffs (1964).

[7] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[8] R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

[9] E. Gelles and R. M. Hay, *J. Chem. Soc.*, **1958**, 3673, 3684, 3689.

common, however, that a stability constant determined in solutions at lower electrolyte concentration is larger than that determined at higher electrolyte concentrations and so, it seems to be reasonable that the β_1 values previously reported for the complexes are much larger than the present values. No report seems to have pointed out the formation of the second complexes of calcium and strontium with these ligands.

The stability constants of alkaline earth(II) complexes with sulfate or oxalate ions in 1 M $Na(ClO_4)$ seem to decrease, with the increase of the ionic radius.

The solubilities of the alkaline earth sulfates decrease in the order Ca(II) > Sr(II) > Ba(II), but those of oxalates decrease slightly in the inverse order,6) and the first stability constant of the alkaline earth complexes with sulfate or oxalate ions in 1 M $Na(ClO_4)$ always decrease with the increase of the ionic radius.

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