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Studies of the Alkaline Earth Complexes in Various Solutions. I. Barium(II) Complexes with Sulfate and Oxalate Ions in 1M Sodium Perchlorate Media

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The distribution of barium(II) at a very low concentration was determined between a carbon tetrachloride solution of 0.1 M thenoyltrifluoroacetone and 0.2 M tributylphosphate and aqueous solutions of 1 M $Na(ClO_4)$ at 25°C. The net distribution ratio is decreased when a part of the perchlorate ions are replaced by sulfate or oxalate ions. This decrease was explained in terms of the complex formation of Ba^{2+} with these ligands. The stability constants were determined graphically from the experimental data as follows:

Ligand	log β_1	log β_2
SO_4^{2-}	0.66	1.42
$C_2O_4^{2-}$	0.58	2.20

(1 M $Na(ClO_4)$, 25°C)

The solubility of barium sulfate and oxalate has been reported by many authors, but the complex formation of barium ion with these anions in an aqueous solution has not been studied very much.[1] This may be due to the fact that the concentration of barium ions in sulfate or oxalate solutions is too low to be studied by such methods as the e.m.f. measurement, conductometry and spectropothometry.

In the present work, the authors studied the complex formation of barium with sulfate and oxalate ions in sodium perchlorate media at 25°C. A carrier-free radioactive barium-140 tracer was used to keep the barium concentration very low in order to prevent the formation of precipitates. The decrease in the free barium ion concentration in the aqueous phase caused by the complex formation was determined by a solvent extraction technique recently developed in our laboratory.[2] The stability constants were determined by a graphical method from the distribution data.

Experimental

Tracer.—Barium-140 was obtained from the Radiochemical Center, Amersham, England. It was diluted with a mixture of 0.1 M perchloric acid and 0.9 M sodium perchlorate.

Reagents.—All of the reagents used were of analytical grade. Thenoyltrifluoroacetone (TTA) was obtained from the Dojin Yakukagaku Co. Tributylphosphate (TBP) was obtained from the Tokyo Kasei Co. The TBP was washed with 0.1 M perchloric acid, water, 0.1 M sodium hydroxide, and several times with water respectively, and was finally equilibrated with a 1.0 M sodium perchlorate solution. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and was recrystallized two times from water. The concentration of the stock sodium sulfate solution was determined from the weight of the residue left after a portion of the solution had been dried up in an air bath at 120°C. The stock sodium oxalate solution in 1 M $Na(ClO_4)$ was prepared by dissolving a weighed portion of sodium oxalate crystals in a sodium perchlorate solution.

Procedures.—All of the procedures were carried out in a thermostatted room at 25°C. Stoppered glass tubes (volume: 20 ml.) were used to equilibrate the organic and the aqueous phases. The tracer solution, various amounts of a sodium sulfate or sodium oxalate solution, a buffer solution, a sodium perchlorate solution and the organic solution were placed in the tubes. The aqueous phase was maintained at 1.0 M $Na(ClO_4)$; the aqueous phase always contained 1.0 M sodium ions and various amounts of sulfate or oxalate ions, together with perchlorate ions. A small amount of triethanolamine or sodium acetate (the initial concentration was 0.01 M) was added to the aqueous phase to buffer the hydrogen ion concentration. The organic phase was a mixture of 0.1 M TTA and 0.2 M TBP in carbon tetrachloride. The initial volume of the two phases was always 5.0 ml.

The two phases in the tubes were vigorously agitated by a mechanical shaker for fifteen minutes and then centrifuged for three minutes at 2000 r. p. m. A 2.0-ml. portion was pipetted from the two phases and transferred into small, stoppered glass test tubes for the measurement of the γ-radioactivity. Another portion of the aqueous phase was transferred into small glass vessels, and the hydrogen ion concentration was determined

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," Spec. Pub. 17, The Chemical Society, London (1964).

[2] T. Sekine, S. Obuchi and M. Sakairi, This Bulletin, to be published.

potentiometrically using 0.0100 M $HClO_4$ + 0.99 M $NaClO_4$, as the standard of $-\log[H^+] = 2.00$. The solutions in the small glass test tubes were let stand for more than seventeen days, until the decay equilibrium was reached between barium-140 (the half life is 12.80 days) and lanthanum-140 (the half life is 40.22 hr.); the γ-radioactivity was then measured with a well-type (NaI) scintillation counter.

Statistical Treatment

The *n*th step of the complex formation of a dipositive metal ion, M^{2+}, with a dinegative ligand ion, L^{2-}, may be described as:

$$M^{2+} + nL^{2-} \rightleftarrows ML_n^{2-2n} \tag{1}$$

$$\beta_n = [ML_n^{2-2n}]/[M^{2+}][L^{2-}]^n \tag{2}$$

The distribution of this metal ion between an organic phase with an organophilic chelating acid, HA, and an aqueous phase with no complex-forming ligands may be described as:

$$M^{2+} + 2HA(org) \rightleftarrows MA_2(org) + 2H^+ \tag{3}$$

$$K = [MA_2]_{org}[H^+]^2/[M^{2+}][HA]_{org}^2 \tag{4}$$

Here the subscript "*org*" denotes a chemical species in the organic phase.

The net distribution ratio of the metal ion between the organic and the aqueous phase may be defined as:

$$D = [M(II)]_{org,\ total}/[M(II)]_{total} \tag{5}$$

The extraction constant may be defined as:

$$K_{ex} = D[H^+]^2[HA]_{org}^{-2}$$

When there is no complex-forming ligand in the aqeuous phase, the distribution ratio of the metal ion may be described as:

$$D_0 = [MA_2]_{org}/[M^{2+}] \tag{7}$$

The extraction constant is then:

$$K_{ex_0} = ([MA_2]_{org}/[M^{2+}])[H^+]^2[HA]_{org}^{-2} \tag{8}$$

Here the subscript "0" denotes a system where the ligands, L^{2-}, are absent in the aqueous phase. We see that the K_{ex_0} in Eq. 8 equals the K in Eq. 4; therefore, K_{ex_0} should give a constant value at a certain temperature.

When there is the complex-forming ligand in the aqueous phase at a certain concentration $[L^{2-}]$, the distribution ratio may be described from Eqs. 2 and 5 as:

$$\begin{aligned} D &= [MA_2]_{org}/([M^{2+}]+[ML]+[ML_2^{2-}]+\cdots) \\ &= ([MA_2]_{org}/[M^{2+}])(1+\sum_1^n\beta_n[L^{2-}]^n)^{-1} \end{aligned} \tag{9}$$

The extraction constant is then:

$$\begin{aligned} K_{ex} &= ([MA_2]_{org}/[M^{2+}])[H^+]^2[HA]_{org}^{-2} \\ &\quad \times (1 + \sum_1^n\beta_n[L^{2-}]^n)^{-1} \end{aligned} \tag{10}$$

By dividing Eq. 10 by Eq. 8, we obtain the following equation:

$$\frac{K_{ex}}{K_{ex_0}} = (1 + \sum_1^n\beta_n[L^{2-}]^n)^{-1} \tag{11}$$

Thus we may determine the stability constants, β_n, from Eq. 11.

When an organophilic neutral ligand, N, is added to the organic phase and the metal chelate forms adducts with N, the equilibrium may be described as:

$$MA_2(org) + lN(org) \rightleftarrows MA_2N_l(org) \tag{12}$$

$$\beta_{a,l} = [MA_2N_l]_{org}/[MA_2]_{org}[N]_{org}^l \tag{13}$$

When there is no complex-forming ligand, L^{2-}, in the aqueous phase and when there is an adduct-forming ligand in the organic phase at a constant concentration, $[N]_{c,\ org}$, the distribution ratio and the extraction constant are:

$$\begin{aligned} D &= ([MA_2]_{org} + [MA_2N]_{org} + [MA_2N_2]_{org} \\ &\quad + \cdots)/[M^{2+}] \\ &= ([MA_2]_{org}/[M^{2+}]) \\ &\quad \times (1 + \sum_1^l \beta_{a,l}[N]_{c,org}^l) \end{aligned} \tag{14}$$

$$\begin{aligned} K_{ex_0} &= ([MA_2]_{org}/[M^{2+}])[H^+]^2[HA]_{org}^{-2} \\ &\quad \times (1 + \sum_1^l \beta_{a,l}[N]_{c,org}^l) \end{aligned} \tag{15}$$

The extraction constant in Eq. 15 is $1+\sum_1^l\beta_{a,l}[N]_{c,org}^l$ times the constant in Eq. 8, but the former should also give a constant value at a certain temperature as long as the concentration of N is kept constant.

When there is a complex-forming ligand in the aqeuous phase at a concentration, $[L^{2-}]$, we may introduce the following equation by the same procedure;

$$\begin{aligned} K_{ex} &= ([MA_2]_{org}/[M^{2+}])[H^+]^2[HA]_{org}^{-2} \\ &\quad \times (1 + \sum_1^l\beta_{a,l}[N]_{c,org}^l) \\ &\quad \times (1 + \sum_1^n\beta_n[L^{2-}]^n)^{-1} \end{aligned} \tag{16}$$

From Eqs. 15 and 16 we may also see that Eq. 11 is valid even in a solvent extraction system where the distribution ratio is enhanced by the adduct formation (synergism).

The stability constants can be determined from the distribution data by a curve-fitting method[3-5] using Eq. 11.

It may be possible to discuss the problem more

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[3] L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).

[4] F. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York (1961).

[5] T. Sekine and Y. Hasegawa, This Bulletin **39**, 240 (1966).

generally, but here we assume that only the first and the second complexes, ML and ML_2^{2-}, are formed in the aqueous solution.

When we replace K_{ex}/K_{ex_0}, $\beta_2^{1/2}[L^-]$ and $\beta_1\beta_2^{-1/2}$ with y, a and R respectively, we obtain the following equation instead of Eq. 11:

$$y = (1 + Ra + a^2)^{-1} \tag{17}$$

By introducing various values into R in Eq. 17, a family of standard curves represented by the following equations are obtained:

$$\begin{aligned} Y &= \log y = -\log(1 + Ra + a^2) \\ X &= \log a \end{aligned} \tag{18}$$

One of these curves will be found to fit the plot of the experimental data, $\log(K_{ex}/K_{ex_0})$ vs. $\log[L^{2-}]$. Since $\log a$ equals $^1/_2\log\beta_2+\log[L^{2-}]$, the value of $\log\beta_2$ can be obtained from the position of the experimental plot, $\log(K_{ex}/K_{ex_0})$ vs. $\log[L^{2-}]$, on the $\log a$ axis, and R equals $\beta_1\beta_2^{-1/2}$; that is, $\log\beta_1$ equals $\log R+{}^1/_2\log\beta_2$, then the β_1 value can be calculated from the values R and β_2.

Results

Perchlorate System.—It was concluded from another study⁶⁾ that the main barium complex species in a carbon tetrachloride solution of 0.1 M TTA (HA) and various amounts of TBP (L) is BaA_2L_2 in the higher TBP-concentration region. Therefore, the distribution equilibrium can be written as:

$$Ba^{2+} + 2HA(org) + 2L(org) \rightleftarrows BaA_2L_2(org) + 2H^+$$

Figure 1 gives the dependence of the distribution ratio of barium ions on the hydrogen ion concentration when the organic phase is a carbon tetrachloride solution of 0.1 M TTA and 0.2M TBP and when the aqueous phase is 1.0 M sodium perchlorate.

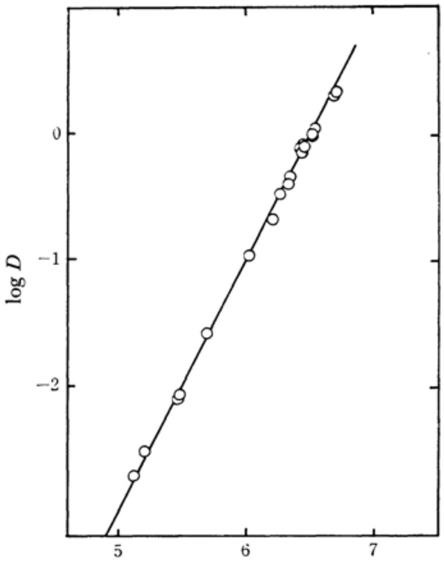

Fig. 1. Distribution ratio of barium(II) between 0.1 M TTA + 0.2 M TBP-carbon tetrachloride and 1.0 M $NaClO_4$, at 25°C. The straight line gives $\log D=-2\log[H^+]-12.01$. The extraction constant;

$$\log K_{ex_0}=D[H^+]^2[HA]_{org}^{-2}=-10.01$$

The plot falls on a straight line with a +2 slope, and the extraction constant calculated from the nineteen points in Fig. 1 is:

$$\log D_0[H^+]^2[HA]_{org}^{-2} = -10.01$$

These results seem to show that: (i) there is no complex formation of barium with TTA in the aqueous phase, and (ii) there is no extraction of barium complexes with perchlorate ions into the organic phase.

Thus we may conclude that the K_{ex_0} value obtained from these results can be used for the calculation of the stability constants by means of Eq. 11 (cf. Ref. 7).

Sulfate System.—The distribution ratio of barium(II) is decreased by the addition of sodium sulfate to the aqueous phase. Figure 2 gives the decrease in the extraction constant as a function of $\log[SO_4^{2-}]$. In these experiments the analytical concentration of sodium sulfate in the aqueous phase can be regarded as the concentration of sulfate ions, $[SO_4^{2-}]$, because the $-\log[H^+]$ was kept between 6.4 and 6.6 and the pK_a value of sulfuric acid in 1 M $Na(ClO_4)$ at 25°C is 1.02.⁸⁾

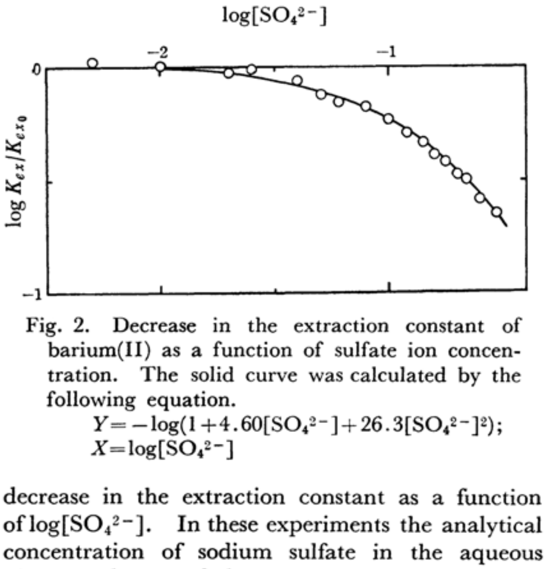

Fig. 2. Decrease in the extraction constant of barium(II) as a function of sulfate ion concentration. The solid curve was calculated by the following equation.

$Y=-\log(1+4.60[SO_4^{2-}]+26.3[SO_4^{2-}]^2)$;
$X=\log[SO_4^{2-}]$

The plot was found to fit a standard curve, $Y=-\log(1+0.9a+a^2)$, $X=\log a$. This indicates that

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6) T. Sekine and M. Sakairi, in press.

7) T. Sekine, M. Sakairi, F. Shimada and Y. Hasegawa, This Bulletin **38**, 847 (1965).

8) E. Eichler and S. Rabideau, *J. Am. Chem. Soc.*, **77**, 5501 (1955).

both the $BaSO_4$ and $Ba(SO_4)_2{}^{2-}$ complexes are formed. The stability constants finally determined are given in Table I.

TABLE I. STABILITY CONSTANTS OF BARIUM(II) COMPLEXES IN 1 M $Na(ClO_4)$ AT 25°C

$\beta_n=[BaL_n{}^{2-2n}]/[Ba^{2+}][L^{2-}]^n$

Ligand	$\log \beta_1$	$\log \beta_2$
$SO_4{}^{2-}$	0.66	1.42
$C_2O_4{}^{2-}$	0.58	2.20

Oxalate System.—The distribution ratio of barium(II) is also decreased by the addition of sodium oxalate to the aqueous phase. Figure 3 gives the decrease in the extraction constant as a function of $\log[C_2O_4{}^{2-}]$. In these experiments, the analytical concentration of sodium oxalate in the aqueous phase can be regarded as the concentration of oxalate ions, $[C_2O_4{}^{2-}]$, because the $-\log[H^+]$ value was kept between 6.4 and 6.6 and because the pK_{a_2} value of oxalic acid in 1 M $Na(ClO_4)$ at 25°C is 3.54.[9] It was not possible to obtain a higher oxalate concentration, because the solubility of sodium oxalate in 1 M sodium perchlorate is not large.

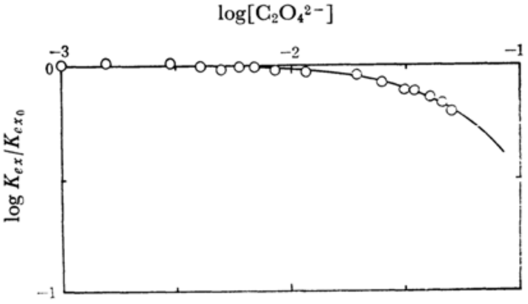

Fig. 3. Decrease in the extraction constant of barium(II) as a function of oxalate ion concentration. The solid curve was calculated by the following equation.
$Y=-\log(1+3.80[C_2O_4{}^{2-}]+159[C_2O_4{}^{2-}]^2)$;
$X=\log[C_2O_4{}^{2-}]$

The plot was found to fit a standard curve, $Y=-\log(1+0.3a+a^2)$, $X=\log a$. This indicates that both BaC_2O_4 and $Ba(C_2O_4)_2{}^{2-}$ complexes are formed. The stability constants finally determined are given in Table I.

Discussion

The solubility of barium sulfate and oxalate is very small. The previous data on the solubility products in dilute ionic media were around 10^{-10} for barium sulfate and around 10^{-8} for barium oxalate.[1,10]

Money and Davies[11] gave a stability constant for the barium oxalate complex at an infinite dilution at 18°C as $[BaC_2O_4]/[Ba^{2+}][C_2O_4{}^{2-}]=$ca. $10^{2.31}$, but this data canhot be compared directly with the present results because the concentrations of the electrolytes in the solutions are different. No data seem to have been presented on the stability of barium sulfate complexes.

In the present study, carrier-free barium-140 was always employed as the tracer, and the concentration of barium(II) was calculated to be less than 10^{-12} M if the barium impurity in the solution was neglected. It is difficult to estimate the amount of non-radioactive barium impurities in the system. However, we may conclude that the coprecipitation of the radioactive barium with the non-radioactive barium impurities in the system is negligible, because the recovery of the radioactivity from the two phases was always quantitative and the results in Figs. 2 and 3 are reproducible and reasonable.

The results in the table indicate that the stabilities of the barium complexes with these anions are much smaller than those of lanthanide and actinide complexes.[9,12] This seems to agree with the fact that the solubilities of barium sulfate and oxalate are not very much increased by an excess of these anions in aqueous solutions.

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

[10] W. M. Latimer, "Oxidation Potentials," 2nd ed. Prentice-Hall, Englewood Cliffs (1964).

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

[12] T. Sekine, *Acta Chem. Scand.*, **19**, 1469 (1965).