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Studies of the Alkaline Earth Metal Complexes in Various Solutions. II. Beryllium(II) Complexes with Sulfate and Oxalate in 1 M Na(ClO_4)

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The complex formation of beryllium(II) with sulfate and oxalate ions in 1 M Na(ClO_4) at 25°C has been studied by a liquid-liquid distribution method. The radioactive tracer beryllium-7 at very low concentration was used in conjunction with thenoyltrifluoroacetone in methylisobutylketone. The stability constants of the beryllium complexes were determined graphically from the distribution data by a curve-fitting method. The data seemed to be explained by the formation of the following complex species;

$$\beta_n = [BeL_n^{2-2n}] / [Be^{2+}][L^{2-}]^n,$$

where $\log \beta_2 = 1.78$ and $\log \beta_3 = 2.08$ for sulfate and $\log \beta_1 = 3.55$ and $\log \beta_2 = 5.40$ for oxalate. The formation of the primary sulfate complex, $BeSO_4$, or the tertiary oxalate complex, $Be(C_2O_4^{2-})_3^{4-}$, was not concluded within the ligand concentration region studied.

The chemical properties of beryllium(II) are sometimes quite different from the other members of alkaline earth metal ions; usually, beryllium(II) forms more stable complex species than the other members of ions in aqueous solutions.

In the present paper, the authors studied the complex formation of beryllium(II) with sulfate and oxalate ions in 1 M Na(ClO_4) at 25°C by a liquid-liquid distribution method using radioactive tracer at very low concentration.

Experimental

Tracer. Carrier-free beryllium-7 was obtained from the New England Nuclear Co., U. S. A. It was diluted with a mixed solution of 0.1 M perchloric acid and 0.9 M sodium perchlorate.

Reagents. Methylisobutylketone (MIBK) was obtained from the Tokyo Kasei Co. It was washed with 0.1 M perchloric acid, water, 0.1 M sodium hydroxide and several times with water and finally equilibrated with 1.0 M sodium perchlorate. Other reagents were the same as described in Paper I.

Procedures. MIBK solution of thenoyltrifluoroacetone (TTA) at 0.03 M was prepared, let stand overnight and used as the organic phase. The aqueous phase was buffered with sulfanilate (initially 0.01 M). The experimental procedures were the same as described in Paper I of this series work except that the agitation of the two phases was continued more than 12 hr and that the γ-radioactivity was measured usually just after the separation of the two phases.

Results

The details of the statistical treatment have been described in the previous paper. The present results were also treated by the same way. The equations used are as follows;

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

$$K_{ex_0} = ([BeA_2]_{org}/[Be^{2+}])[H^+]^2[HA]_{org}^{-2} \tag{2}$$

$$\beta_n = [BeL_n^{2-2n}]/[Be^{2+}][L^{2-}]^n \tag{3}$$

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

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

The plot $\log D[H^+]^2[HA]_{org}^{-2}/K_{ex_0}$ *vs.* $\log[L^{2-}]$ was found to fit one of the following family of standard curves;

$$X = \log v; \quad Y = -\log(1+\sum_{n=1}^{n} p_n v^n) \tag{5}$$

and the stability constants were determined from the parameters of the "best-fit" standard curve.

Rate of the Extraction. It has been known that the extraction of beryllium(II) in aqueous solutions with TTA in non-polar solvent is a slow reaction.[1,2] The present authors also observed that it took one week or more to achieve the distribution equilibrium when beryllium(II) in perchlorate media was extracted with 0.01 M to 0.1 M TTA in chloroform or in carbontetrachloride by mechanical rotation at 20 rpm. However, when MIBK is used as the organic solvent, an agitation for much shorter interval seems to be enough to achieve the distribution equilibrium; it was observed that agitations of the two phases by the same mechanical rotator for 12 hr showed

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[1] R. A. Bolomey and L. Wish, *J. Am. Chem. Soc.*, **72**, 4483 (1950).

[2] H. J. Debruin and R. B. Temple, *Austral. J. Chem.*, **15**, 153 (1962).

the same distribution ratio of beryllium(II) between MIBK with 0.03 M TTA and 1 M $NaClO_4$ of $-\log[H^+]$ between 2.0 to 4.0 as that obtained by agitations over 24 hr under the same experimental conditions. Thus the agitations were always continued overnight (12 to 16 hr) through the experiments.

Extraction from Perchlorate Media. Figure 1 shows the plot log *D* *vs.* $-\log[H^+]$ when the organic phase is MIBK with 0.03 M TTA and the aqueous phase is 1 M $NaClO_4$ with no complex forming ligand. From Eq. (2) it is expected that the plot falls on a straight line of slope 2 if the distribution ratio in Eq. (1) can be expressed as $D=[BeA_2]_{org}/[Be^{2+}]$.

The plot in Fig. 1 does not fall exactly on a straight line of slope 2.0 but is fitted better with a straight line of slope 1.8 to 1.9 and the extraction constant calculated from the distribution data using Eq. (2) slightly decreases with the increase in the $-\log[H^+]$. This slight deviation of the plot from the straight line of slope 2.0 seems to be explained by the extraction of some amounts of the TTA mixed complex with perchlorate ion in the lower $-\log[H^+][HA]_{org}^{-1}$ region. The details of this will be given in another paper of this series work.

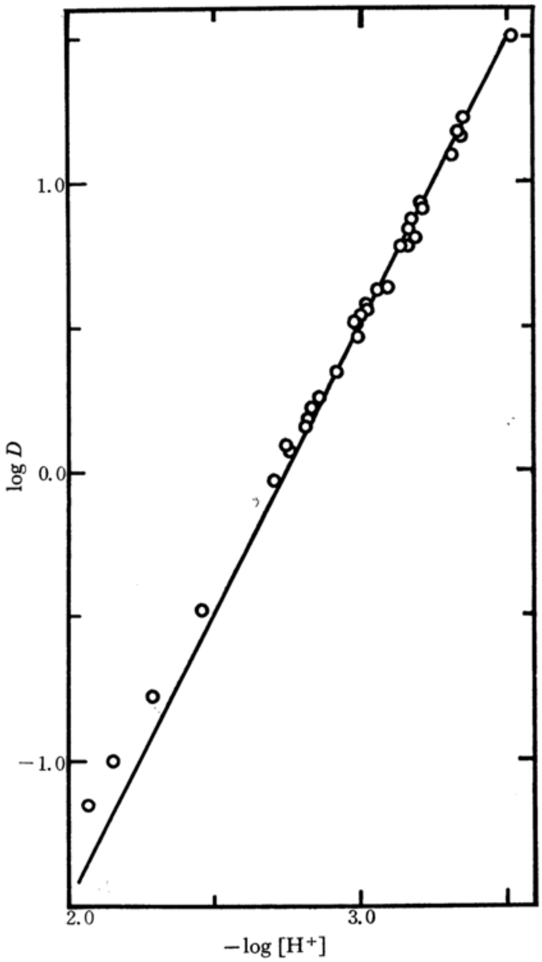

Fig. 1. Distribution ratio of beryllium(II) as a function of the hydrogen ion concentration at 25°C.
Organic phase: MIBK with 0.03 M TTA
Aqueous phase: 1.0 M $NaClO_4$
The straight line with a slope +2 is $\log D = 2\log[H^+]^{-1} - 5.51$

However, as the change in the extraction constant

TABLE 1. DECREASE IN THE EXTRACTION OF BERYLLIUM(II) AS A FUNCTION OF THE CONCENTRATION OF SULFATE ION IN THE AQUEOUS PHASE

Organic phase: 0.03 M TTA in MIBK
Aqueous phase: 1.0 M $Na(ClO_4)$
Temp.: 25°C

$-\log[SO_4^{2-}]$	$-\log D[H^+]^2[HA]_{org}^{-2}/K_{ex_0}$
1.602	0.00
1.523	0.02
1.456	0.00
1.398	0.03
1.347	0.07
1.301	0.09
1.222	0.07
1.222	0.07
1.187	0.18
1.187	0.15
1.155	0.15
1.097	0.15
1.097	0.15
1.071	0.21
1.046	0.19
1.022	0.23
1.000	0.24
0.959	0.27
0.959	0.25
0.921	0.35
0.886	0.39
0.854	0.32
0.854	0.46
0.824	0.43
0.796	0.44
0.796	0.40
0.770	0.50
0.745	0.49
0.745	0.56
0.721	0.56
0.699	0.55
0.699	0.59
0.658	0.72
0.638	0.68
0.620	0.71
0.602	0.78
0.585	0.82
0.569	0.93
0.553	0.95
0.553	0.92
0.523	0.95

is not very large, especially in the higher $-\log[H^+]$ range, the average value was calculated by the data from the $-\log[H^+]$ region between 3.0 to 3.5 as; $\log K_{ex_0} = \log D[H^+]^2[HA]_{org}^{-2} = -2.45$ and this value was used for the calculation of the stability constants.

Sulfate Complexes. Table 1 gives the decreases in the distribution ratio of Be(II) as a function of the concentration of sulfate ion. In all of these experiments, the $-\log[H^+]$ of the aqueous phase was kept above 3.0 and no correction was made for the association of sulfate ion with hydrogen ions because the dissociation constant for acid sulfate ion was reported as $10^{-1.02} = [SO_4^{2-}][H^+]/[HSO_4^-]$ in 1 M $NaClO_4$.3) The stability constants for the complexes were determined graphically by a curve-fitting for the plot $\log D[H^+]^2[HA]_{org}^{-2}/K_{ex_0}$ *vs.* $\log[SO_4^{2-}]$ which is given in Fig. 2. As it is seen in Fig. 2, the distribution ratio decreases drastically with the increase in the sulfate ion concentration in the aqueous phase. After some trials, it was found that the plot in Fig. 2 was best fitted with the standard curve $Y = -\log(1+2.5\,v^2+v^3)$, $X = \log v$ and the stability constants for the complex species $Be(SO_4)_2^{2-}$ and $Be(SO_4)_3^{4-}$ were determined from the fitted standard curve as are given in Table 3.

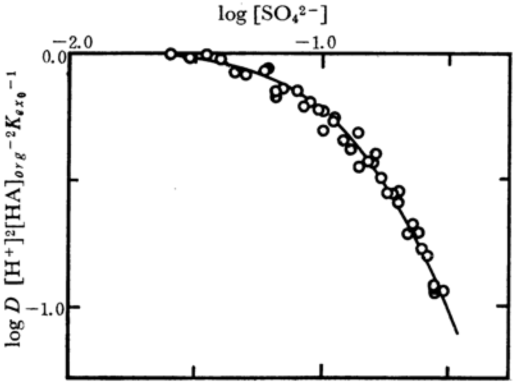

Fig. 2. Decrease in the distribution of beryllium(II) as a function of sulfate ion concentration at 25°C.
Organic phase: MIBK with 0.03 M TTA
Aqueous phase: 1.0 M $Na((1/2)SO_4, ClO_4)$
The solid curve shows
$\log D[H^+]^2[HA]_{org}^{-2}K_{ex_0}^{-1} = -\log(1+60[SO_4^{2-}]^2+120[SO_4^{2-}]^3)$

Oxalate Complexes. Table 2 gives the decrease in the distribution ratio of Be(II) as a function of the concentration of oxalate ion. These experiments were carried out in solutions at $-\log[H^+]$ 3.0 to 3.4. The concentration of the dissociated oxalate ion in the solutions at different $-\log[H^+]$ was calculated from the total oxalate

TABLE 2. DECREASE IN THE EXTRACTION OF BERYLLIUM(II) AS A FUNCTION OF THE CONCENTRATION OF OXALATE ION IN THE AQUEOUS PHASE

Organic phase: 0.03 M TTA in MIBK
Aqueous phase: 1.0 M $Na(ClO_4)$
Temp.: 25°C

$-\log[C_2O_4^{2-}]$	$-\log D[H^+]^2[HA]_{org}^{-2}/K_{ex_0}$
4.854	0.03
4.745	0.01
4.678	0.04
4.420	0.07
4.301	0.10
4.276	0.08
4.215	0.07
4.161	0.10
4.111	0.14
4.000	0.11
3.996	0.15
3.943	0.16
3.921	0.17
3.836	0.19
3.796	0.22
3.770	0.21
3.712	0.23
3.665	0.26
3.569	0.30
3.542	0.34
3.523	0.28
3.409	0.35
3.377	0.41
3.364	0.38
3.353	0.38
3.337	0.34
3.274	0.47
3.216	0.48
3.210	0.51
3.165	0.54
3.143	0.58
3.113	0.54
3.091	0.60
3.091	0.57
3.073	0.63
3.018	0.63
2.971	0.69
2.959	0.70
2.896	0.75
2.889	0.80
2.886	0.78
2.824	0.85
2.790	0.88
2.770	0.89
2.726	0.95
2.721	0.95
2.684	0.98
2.629	1.05
2.602	1.12
2.561	1.16

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

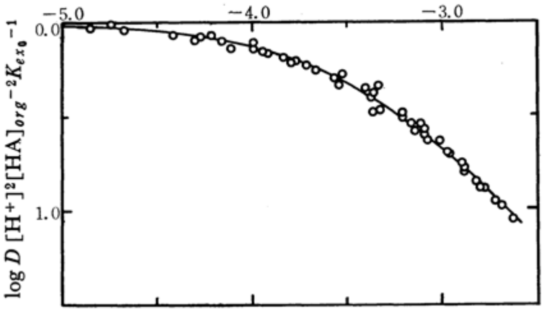

Fig. 3. Decrease in the distribution of beryllium(II) as a function of oxalate ion concentration at 25°C.
Organic phase: MIBK with 0.03 M TTA
Aqueous phase: 1.0 M $Na((1/2)C_2O_4, ClO_4)$
The solid curve shows
$\log D[H^+]^2[HA]_{org}^{-2}K_{ex_0}^{-1} = -\log(1+3.55\times10^3[C_2O_4^{2-}]+2.5\times10^5[C_2O_4^{2-}]^2)$

TABLE 3. STABILITY CONSTANTS FOR BERYLLIUM(II) COMPLEXES WITH SULFATE AND OXALATE IONS IN 1 M $Na(ClO_4)$ AT 25°C
$\beta_n=[BeL_n^{2-2n}]/[Be^{2+}][L^{2-}]^n$

L^{2-}	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
SO_4^{2-}	—	1.78	2.08
$C_2O_4^{2-}$	3.55	5.40	—

concentration using the acid dissociation constant $10^{-3.54}=[C_2O_4^{2-}][H^+]/[HC_2O_4^-]$ in 1 M $Na(ClO_4)$.[4]

The stability constants for the complexs were determined also by a curve-fitting method. It was found that the plot $\log D[H^+]^2[HA]_{org}^{-2}/K_{ex_0}$ *vs.* $\log[C_2O_4^{2-}]$ in Fig. 3 was best-fitted with the standard curve, $Y=-\log(1+7.1\ v+v^2)$, $X=\log v$, and the stability constants for the complex species BeC_2O_4 and $Be(C_2O_4)_2^{2-}$ were determined from the fitted standard curve as are given in Table 3.

Discussion

Belyavskaya and Kolosova[5,6] studied the sulfate complexes of beryllium(II) in 0.5 M $(NaClO_4)$ at 18°C by a cation-exchange method and gave a stability constant $\log\beta_1=0.72$. The experimental conditions of their work are not very much different from the present work. However, as we see in Fig. 2, the present results seem to indicate the formation of no primary complex $BeSO_4$ but the formation of the secondary and the tertiary complexes.

The stability constant for the primary beryllium oxalate complex, BeC_2O_4, has been described[5,7] as $\log\beta_1=4.87$ or as $\log\beta_1=4.93$. As the experimental conditions for these values were not described, the present values may not be compared directly with them.

Some data have been reported[5] for the magnesium(II) or calcium(II) sulfate complexes. The stability constants for the primary sulfate complex of these metal ions, MSO_4, at zero ionic strength are in the range $10^{2.1}$—$10^{2.3}$. Sekine, Sakairi and Hasegawa[8] reported the stability constants for barium(II) sulfate complexes in 1 M $Na(ClO_4)$ at 25°C as $\log\beta_1=0.66$ and $\log\beta_2=1.42$.

Some data have been also reported[5] for the magnesium(II), calcium(II) or strontium(II) oxalate complexes. The stability constants for the primary oxalate complexes of these metal ions at zero ionic strength range between 10^2—10^3. The stability constants for barium(II) oxalate complexes in 1 M $Na(ClO_4)$ at 25°C were reported[8] as $\log\beta_1=0.58$ and $\log\beta_2=2.20$.

These values seem to indicate that beryllium(II) forms more stable sulfate or oxalate complexes than the other members of alkaline earth metal ions.

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

[5] L. G. Sillén and A. E. Martell, "Stability Constants," Chem. Soc. Spec. Publ. 17 (1964).

[6] T. A. Belyavskaya and I. F. Kolosova, *Vestnik moskov Univ., Ser.* 2, No. 5, 55 (1962), cited in Ref. 5.

[7] A. K. Bhattacharya, personal communication to A. E. Martell, 1960, cited in Ref. 5.

[8] T. Sekine, M. Sakairi and Y. Hasegawa, This Bulletin, **39**, 2141 (1966).