1480 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1480—1485 (1971) [Vol. 44, No. 6

# Studies of the Alkaline Earth Complexes in Various Solutions. VI. The Extraction and Complex Formation of Beryllium(II) in Sodium Perchlorate Media Containing Some Univalent Inorganic Anions

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The distribution of beryllium(II) between methylisobutylketone containing TTA (thenoyltrifluoroacetone) and aqueous 4.0 M sodium perchlorate constant ionic media has been measured by using a carrier-free beryllium-7 tracer. The distribution behavior, determined as a function of the TTA and the hydrogen ion concentration, was explained in terms of the extraction of the $Be(TTA)_2$, the $Be(ClO_4)_2$ and the mixed species $Be(TTA)(ClO_4)$, and their extraction constants were determined. Then, the stability constants for the chloride, bromide, and nitrate complexes were determined from the decrease in the TTA extraction when some of the perchlorate ions in the aqueous phase were replaced by the ligand anions. Those of the thiocyanate complexes, on the other hand, were determined from the extraction of $Be(SCN)_2$ species with TBP (tributylphosphate) in hexane. It was concluded that the stabilities of these complexes are very low; the values $\beta_1$ and $\beta_2$ range between 1 and 0.1, but still these complexes should be taken into account in any discussion of the chemical behavior under some experimental conditions.

Although much has been reported on the complex formation of beryllium(II) with the fluoride ion in aqueous solutions, few seem to have studied those with other halide anions.[1]

In the present investigation, the authors have determined the distribution of beryllium(II) between aqueous sodium perchlorate media containing chloride, bromide, iodide, nitrate or thiocyanate ions and methylisobutylketone (MIBK) containing thenoyltrifluoroacetone (TTA) or hexane containing tributylphosphate (TBP). The distribution data were explained in terms of the complex formation, and the stability constants were determined by a graphic method. It was also found that the extraction of beryllium(II) mixed complexes with perchlorate and TTA anion or the beryllium(II) perchlorate should be taken into account in order to explain the distribution behavior of this metal ion under some experimental conditions.

## Experimental

*Tracer and Reagents.* All of the reagents were of a reagent grade. Carrier-free beryllium-7 was used as the tracer. Sodium perchlorate was prepared from sodium carbonate and perchloric acid, and was recrystallized three times from water. MIBK and TBP were washed with 0.1 M perchloric acid, water, and 0.1 M sodium hydroxide, and then several times with water. The other reagents were used without further purification. The concentration of the stock perchlorate or nitrate solution was determined by weighing the residues after a certain amount of the solution had been dried in an air-bath at 120°C. The concentration of the chloride, bromide, iodide or thiocyanate stock solution was determined by titration with standard solutions of silver nitrate.

*Procedures.* Most of the procedures carried out were similar to those described in the previous paper.[2] MIBK containing TTA or hexane containing TBP was used as the organic phase. The aqueous phase was kept at 4.0 M $Na(ClO_4)$ throughout the experiments, and when it was necessary, an acetate buffer (0.01 M initially) was added to the solution. The procedures were always carried out in a thermostatted room at 25°C. The hydrogen ion concentration in the aqueous phase was measured potentiometrically by using a standard solution containing 0.0100 M perchloric acid and 3.99 M sodium perchlorate as the standard of $-\log[H^+]=2.000$ in the 4.0 M ionic media.

## Statistical Treatment

In the present work, the net distribution ratio, $D$, was defined and measured as follows:

$$D = [Be(II)]_{org.total}/[Be(II)]_{total}$$

In this paper, the chemical species in the organic phase are denoted by the subscript "org", while those in the aqueous phase have no subscript.

$$D = \frac{\gamma\text{-count-rate per m}l\text{ of the org. phase}}{\gamma\text{-count-rate per m}l\text{ of the aq. phase}} \tag{1}$$

1. *Extraction of Be(II) in Perchlorate Solutions into MIBK Containing TTA.* The equilibria for the extraction of beryllium(II) in a perchlorate medium with an acidic HA are generally described as follows:

$$Be^{2+} + 2HA(org) \rightleftarrows BeA_2(org) + 2H^+ \tag{2}$$

$$Be^{2+} + HA(org) + ClO_4^- \rightleftarrows BeAClO_4(org) + H^+ \tag{3}$$

$$Be^{2+} + 2ClO_4^- \rightleftarrows Be(ClO_4)_2(org) \tag{4}$$

When the perchlorate concentration in the aqueous phase is kept constant, the equilibrium constants can be described as:

$$K_{ex_0} = [BeA_2]_{org}[H^+]^2/[Be^{2+}][HA]^2_{org} \tag{5}$$

$$K_{ex_1} = [BeAClO_4]_{org}[H^+]/[Be^{2+}][HA]_{org} \tag{6}$$

$$K_{ex_2} = [Be(ClO_4)_2]_{org}/[Be^{2+}] \tag{7}$$

When we assume that only the $Be^{2+}$ species is present in the aqueous perchlorate media, whereas the $BeA_2$, $BeAClO_4$ and $Be(ClO_4)_2$ species are all present in the organic phase, the net distribution ratio may be described as:

$$D = \frac{[BeA_2]_{org} + [BeAClO_4]_{org} + [Be(ClO_4)_2]_{org}}{[Be^{2+}]} \tag{8}$$

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," the Chemical Society, spec, pub. **17** (1964).

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

Equation (8) can be also written from Eqs. (5), (6), and (7) as:

$$D = K_{ex_0}([\mathrm{HA}]_{org}/[\mathrm{H}^+])^2 + K_{ex_1}([\mathrm{HA}]_{org}/[\mathrm{H}^+]) + K_{ex_2} \tag{9}$$

or

$$D([\mathrm{H}^+]/[\mathrm{HA}]_{org})^2 = K_{ex_0} + K_{ex_1}([\mathrm{H}^+]/[\mathrm{HA}]_{org}) + K_{ex_2}([\mathrm{H}^+]/[\mathrm{HA}]_{org})^2 \tag{10}$$

Equation (9) shows that the value $K_{ex_2}$ can be determined from the distribution ratio when the organic phase contains no HA, and Eq. (10) shows that the value $D([\mathrm{H}^+]/[\mathrm{HA}]_{org})^2$ should be constant at any $[\mathrm{H}^+]/[\mathrm{HA}]_{org}$ when the organic phase contains, practically, only the $\mathrm{BeA_2}$ species, while it will increase with the increase in $[\mathrm{H}^+]/[\mathrm{HA}]_{org}$ when an extraction of metal species containing perchlorate ions into the organic phase occurs.

The above statistical treatments were made on the assumption that the ion-pairs, $\mathrm{Be(ClO_4)_2}$ and $\mathrm{BeAClO_4}$, undergo no dissociation in the organic phase. However, when there is a dissociation of perchlorate ions in the solvating polar solvent, MIBK, the organic concentration of beryllium(II) should be described as:

$$[\mathrm{Be(II)}]_{org.\ total} = [\mathrm{BeA_2}]_{org} + [\mathrm{BeAClO_4}]_{org} + [\mathrm{BeA^+}]_{org} + [\mathrm{Be(ClO_4)_2}]_{org} + [\mathrm{BeClO_4}^+]_{org} + [\mathrm{Be^{2+}}]_{org} \tag{11}$$

and the following dissociation constants for the organic species should also be determined:

$$K_{diss.1(org)} = \frac{[\mathrm{BeA^+}]_{org}[\mathrm{ClO_4}^-]_{org}}{[\mathrm{BeAClO_4}]_{org}} \tag{12}$$

$$K_{diss.2,1(org)} = \frac{[\mathrm{BeClO_4}^+]_{org}[\mathrm{ClO_4}^-]_{org}}{[\mathrm{Be(ClO_4)_2}]_{org}} \tag{13}$$

$$K_{diss.2,2(org)} = \frac{[\mathrm{Be^{2+}}]_{org}[\mathrm{ClO_4}^-]_{org}}{[\mathrm{BeClO_4}^+]_{org}} \tag{14}$$

The following equation are then obtained:

$$[\mathrm{BeAClO_4}]_{org} + [\mathrm{BeA^+}]_{org} = [\mathrm{BeA(ClO_4)}]_{org}(1 + K_{diss.1(org)}/[\mathrm{ClO_4}^-]_{org}) \tag{15}$$

$$[\mathrm{Be(ClO_4)_2}]_{org} + [\mathrm{BeClO_4}^+] + [\mathrm{Be^{2+}}]_{org} = [\mathrm{Be(ClO_4)_2}]_{org}(1 + K_{diss.2,1(org)}/[\mathrm{ClO_4}^-]_{org} + K_{diss.2,1(org)} \times K_{diss.2,2(org)}/[\mathrm{ClO_4}^-]^2{}_{org}) \tag{16}$$

The organic perchlorate ion concentration can be described as follows (disregarding the $\mathrm{A}^-$ ion and hydroxide ion):

$$[\mathrm{ClO_4}^-]_{org} = [\mathrm{Na^+}]_{org} + [\mathrm{H^+}]_{org} + [\mathrm{BeA^+}]_{org} + [\mathrm{BeClO_4}^+]_{org} + 2[\mathrm{Be^{2+}}]_{org} \tag{17}$$

Equation (17) shows that the perchlorate ion concentration in the organic phase is dependent not only on the sodium and hydrogen ion concentrations, but also on the concentrations of the cationic beryllium species in the organic phase. Consequently, if the total beryllium concentration is changed, or when the hydrogen ion or the extractant concentration is changed, the total organic perchlorate ion concentration in Eq. (17) which will be introduced into Eqs. (15) and (16) should be changed.

Fortunately such a consideration seems to be unnecessary. According to the results previously obtained by our laboratory,[3] the distribution ratio of sodium perchlorate between MIBK and an aqueous solution is $1.4 \times 10^{-2}$, thus, an MIBK phase in an equilibrium with 4.0 M sodium perchlorate should contain about $5 \times 10^{-2}$ M sodium perchlorate. Furthermore, the extraction of perchloric acid from the aqueous phase will not be very large[4] and the perchlorate ion concentration in the organic phase should not be considerably changed even when the hydrogen ion concentration in the aqueous phase is changed within the range studied in this paper. For these reasons, even when the dissociation of the ion-pair species in the organic phase occurs, the expressions in Eqs. (6) to (10) can be used to describe the distribution behavior in the present system. However, when the aqueous sodium perchlorate concentration is much lower and/or the beryllium concentration is much higher, the possibility of the effect of the dissociation in the organic phase should be considered.

2. *TTA Extraction and Complex Formation of Be(II).* Under conditions where only the extraction of $\mathrm{BeA_2}$ species is assumed, the following equation can be used instead of Eq. (10):

$$K_{ex_0} = D_0[\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2} \tag{18}$$

where $D_0$ denotes the distribution ratio when the aqueous phase contains no complex forming ligands, that is, $D_0 = [\mathrm{BeA_2}]_{org}/[\mathrm{Be^{2+}}]$.

When the $\mathrm{Be^{2+}}$ species associates with a uninegative ligand, $\mathrm{L}^-$, the over-all stability constants for the *n*-th complex is defined as:

$$\beta_n = [\mathrm{BeL}_n^{2-n}]/[\mathrm{Be^{2+}}][\mathrm{L}^-]^n \tag{19}$$

and the total aqueous concentration of beryllium(II) can be described as:

$$[\mathrm{Be(II)}]_{total} = [\mathrm{Be^{2+}}](1 + \sum \beta_n[\mathrm{L}^-]^n) \tag{20}$$

The distribution ratio can then be described as:

$$D = [\mathrm{BeA_2}]_{org}/[\mathrm{Be^{2+}}](1 + \sum \beta_n[\mathrm{L}^-]^n) \tag{21}$$

From Eqs. (18) and (21), the following equation is obtained:

$$D[\mathrm{H^+}]^2[\mathrm{HA}]_{org}^{-2} Ke \times 0^{-1} = (1 + \sum \beta_n[\mathrm{L}^-]^n)^{-1} \tag{22}$$

3. *TBP Extraction of Neutral Complexes.* When the neutral complex of beryllium(II) with $\mathrm{L}^-$ is extracted with *e* molecules of an organophilic adduct-forming extractant, E, the extraction can be described as:

$$\mathrm{BeL_2} + e\mathrm{E}(org) \rightleftarrows \mathrm{BeL_2E}_e(org) \tag{23}$$

$$K'_{DM} = [\mathrm{BeL_2E}_e]_{org}/[\mathrm{BeL_2}][\mathrm{E}]_{org}^e \tag{24}$$

When the concentration of the extractant, E, is kept at a constant value, $c_1$, the following constant can be employed instead of that in Eq. (24):

$$K_{DM} = [\mathrm{BeL_2}]_{org}/[\mathrm{BeL_2}] \quad (\text{at } [\mathrm{E}]_{org} = C_M) \tag{25}$$

The net distribution ratio of beryllium(II) can then be described as:

$$D = \frac{[\mathrm{BeL_2}]_{org}}{[\mathrm{Be^{2+}}] + [\mathrm{BeL^+}] + [\mathrm{BeL_2}] + \cdots} \tag{26}$$

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[3] Y. Hasegawa, T. Ishii, and T. Sekine, This Bulletin, **44**, 275 (1971).

[4] T. Sekine, T. Fukushima, and Y. Hasegawa, *ibid.*, **43**, 2638 (1970).

or

$$D[\mathrm{L}^-]^{-2} = K_D\beta_2/(1 + \textstyle\sum \beta_n[\mathrm{L}^-]^n) \qquad (27)$$

*4. Graphic Determination of the Stability Constants.* The equilibrium constants in these equations can be determined graphically from the experimental results as follows. When the $D$ in Eq. (9) is denoted by $-y$, and the $[\mathrm{HA}]_{org}/[\mathrm{H}^+]$, by $v$, or when the $D[\mathrm{H}^+]^2\cdot[\mathrm{HA}]_{org}^{-2}K_{ex_0}^{-1}$ or $D[\mathrm{L}^-]^{-2}$ term in Eq. (22) or Eq. (27) is denoted by $y$, and the $[\mathrm{L}^-]$ in these equations, by $v$, the equations can generally be described as:

$$\log y = \log c - \log(a_0 + a_1v + a_2v^2 + \cdots) \qquad (28)$$

By plotting $\log y$ *vs.* $\log v$, the constants, $a_0$, $a_1$, $a_2$, $\cdots$, are determined by the "curve-fitting" method presented in previous papers.[5,6]

## Results

Figure 1 shows the extraction of beryllium(II) in sodium perchlorate solutions at $-\log[\mathrm{H}^+]$ 2.00 into MIBK. As no anionic species other than perchlorate ions is present in the aqueous phase, the extracted species should be the ion-pair $\mathrm{Be}^{2+}(\mathrm{ClO_4}^-)_2$ and the extraction can be given by Eq. (4). Although no control of the activity was made in these experiments, the slope of the plot is +2 between 1 M to 3 M sodium perchlorate, as can be expected from Eq. (4). The deviation of the data at the higher salt concentrations may be due to the change in the activities.

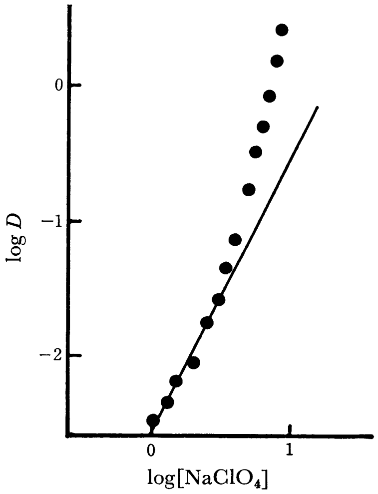

Fig. 1. Distribution of beryllium(II) between MIBK and aqueous sodium perchlorate at $[\mathrm{H}^+] = 10^{-2}$ M. The straight line shows the slope +2.

Figure 2 gives the $\log D$ *vs.* $\log[\mathrm{HA}]_{org}/[\mathrm{H}^+]$ plot for the distribution of beryllium(II) between MIBK containing TTA at various concentrations and 4 M sodium perchlorate solutions at various hydrogen ion concentrations. The distribution ratio of beryllium(II) in 4 M perchlorate media at $-\log[\mathrm{H}^+]$ 2.00 into MIBK containing no TTA was found to be $6.9\times10^{-2}$, as may be seen from Fig. 1. This value gives the $K_{ex_2}$ in Eq. (9). The distribution ratio increases with the increase in $[\mathrm{HA}]_{org}/[\mathrm{H}^+]$, and the slope of the plot increases from zero to two. This can be explained as follows. In the lowest $[\mathrm{HA}]_{org}/[\mathrm{H}^+]$ region, where the slope is zero, beryllium(II) is extracted as the $\mathrm{Be(ClO_4)_2}$ species, and in the highest region, where the slope is two, it is extracted as the $\mathrm{BeA_2}$ species, while in the region where the slope is between zero to two, extracted beryllium species in the organic phase should be mixtures of $\mathrm{Be(ClO_4)_2}$, $\mathrm{BeAClO_4}$, and $\mathrm{BeA_2}$. The plot in Fig. 2 was analyzed by the curve-fitting method; the equilibrium constants thus obtained are given in Table 1. The solid curve in Fig. 1 is the extraction curve calculated from these constants.

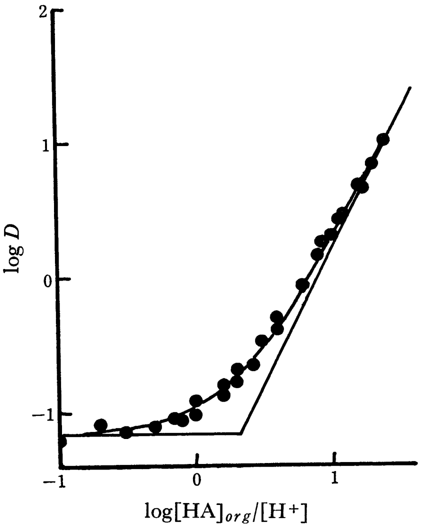

Fig. 2. Distribution ratio of beryllium(II) between MIBK containing TTA and 4 M $(\mathrm{H,Na})\mathrm{ClO_4}$ as a function of $[\mathrm{HA}]_{org}/[\mathrm{H}^+]$. The two straight lines are $Y = -1.16$ and $Y = 2X - 1.80$. The solid curve gives $Y = \log(1.6\times10^{-2}X^2 + 2.3\times10^{-2}X + 6.9\times10^{-2})$. Here $Y = \log D$ and $X = \log[\mathrm{HA}]_{org}/[\mathrm{H}^+]$.

TABLE 1. EQUILIBRIUM CONSTANTS FOR THE EXTRACTION OF THE BERYLLIUM COMPLEXES

(a) TTA extraction from 4 M $\mathrm{NaClO_4}$ into MIBK phase.

| $\log K_{ex_0}$ | $\log K_{ex_1}$ | $\log K_{ex_2}$ |
|---|---|---|
| −1.80 | −1.64 | −1.16 |

$$\mathrm{Be}^{2+} + n\mathrm{ClO_4^-} + (2-n)\mathrm{HA}(org) \rightleftarrows \mathrm{BeA}_{2-n}(\mathrm{ClO_4})_n(org) + (2-n)\mathrm{H}^+$$

$$K_{ex_n} = \frac{[\mathrm{BeA}_{2-n}(\mathrm{ClO_4})_n]_{org}[\mathrm{H}^+]^{2-n}}{[\mathrm{Be}^{2+}][\mathrm{HA}]_{org}^{2-n}}$$

(from 4 M $\mathrm{NaClO_4}$)

(b) TBP extraction of $\mathrm{Be(SCN)_2}$ complex in 4 M $\mathrm{Na(SCN,\ ClO_4)}$

| $\log K_{\mathrm{DM}}$ | $\log K_{\mathrm{DM}'}$ |
|---|---|
| 1.71 | 3.81 |

$$\mathrm{Be(SCN)_2} + 3\mathrm{TBP}(org) \rightleftarrows \mathrm{Be(SCN)_2(TBP)}(org)$$

$$K_{\mathrm{DM}} = \frac{[\mathrm{Be(SCN)_2}]_{or}}{[\mathrm{Be(SCN)_2}]} \qquad ([\mathrm{TBP}]_{org} = 0.2\ \mathrm{M})$$

$$K_{\mathrm{DM}'} = \frac{[\mathrm{Be(SCN)_2(TBP)_3}]_{org}}{[\mathrm{Be(SCN)_2}][\mathrm{TBP})]_{org}}$$

Figure 3 gives the $\log D[\mathrm{H}^+]^2[\mathrm{HA}]_{org}^{-2}K_{ex_0}^{-1}$ *vs.*

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[5] T. Sekine and M. Ono, This Bulletin, **38** 2087 (1965).

[6] T. Sekine, M. Sakairi, and Y. Hasegawa, *ibid.*, **39** 2141 (1966).

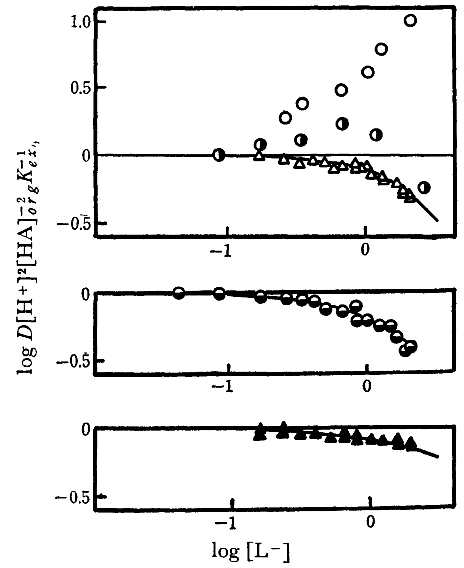

Fig. 3. Change in the extraction of beryllium(II) in 4 M $Na(L, ClO_4)$ as a function of the ligand concentration. In the figure, $L^-$ is $Cl^-$(◒), $Br^-$(△), $I^-$(◑), $NO_3^-$(▲), or $SCN^-$(○). The organic phase was MIBK containing 0.01 M TTA for the thiocyanate system and 0.2 M TTA for the others. The hydrogen ion concentration in the aqueous phase is $10^{-3.2}$ M for the thiocyanate system and $10^{-2.0}$ M for the others. The solid curves are $Y=-\log(1+a[L^-]+b[L^-]^2)$ where $a=0.44$ and $b=0.19$ for $Cl^-$, $a=0.13$ and $b=0.18$ for $Br^-$ and $a=0.22$ and $b=0$ for $NO_3^-$. The constants for the iodide and thiocyanate systems were not determined by the reasons given in the text.

log [L⁻] plot when the ligand anion in 4.0 M $Na(ClO_4)$ was chloride, bromide, or nitrate ions. In these experiments, the TTA concentration in MIBK was 0.2 M, and the $-\log[H^+]$ in the aqueous phase was 2.00 or 2.53.

As may be seen from Fig. 2, the slope of the plot is practically +2 when $\log[HA]_{org}/[H^+]$ is 1.3 or 1.8. It has been observed that the extraction was practically proportional to $([HA]_{org}/[H^+])^2$ even when the concentration of chloride, bromide, or nitrate ions in the aqueous phase was 2.0 M. Thus, it may be concluded that the extraction of metal species containing the ligand, MAL or $ML_2$, is negligible and that only the $BeA_2$ species is extracted into the organic phase when the ligand concentration is less than 2.0 M. From these facts, we may see that Eq. (22) is valid for the calculation of the stability constants from these data. The constants thus determined are given in Table 2. The solid curves in Fig. 3 are the extraction curves calculated from the stability constants in Table 1 and the value $K_{ex_2}=10.^{-1.80}$

Table 2. Stability constants of beryllium(II) complexes in 4 M $Na(ClO_4)$ at 25°C

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

| ligand | $\log\beta_1$ | $\log\beta_2$ |
|---|---|---|
| $Cl^-$ | −0.85 | −0.70 |
| $Br^-$ | −0.70 | −0.80 |
| $NO_3^-$ | −0.63 | — |
| $SCN^-$ | −0.16 | −0.60 |

Beryllium(II) in 4.0 M perchlorate media containing iodide or thiocyanate ions was also extracted with TTA in MIBK. However, the results were complicated, as can also be seen in Fig. 3; the addition of the ligand even increases the extraction in some ligand concentration regions. This was assumed to be due to the extraction of the complex formed, $BeL_2$, or of the mixed complexes with TTA, BeAL, into MIBK. Thus, it was not possible to obtain the stability constants of the beryllium(II) iodide or thiocyanate complexes by the TTA-extraction method.

Beryllium(II) in 4.0 M sodium perchlorate containing one of these five ligands was also extracted into hexane containing TBP. It was observed that the distribution ratio is always very low (about $10^{-2}$ or less) when the aqueous phase contains chloride, bromide, iodide, or nitrate ions at various concentrations and when the organic phase contained 0.2 M TBP in hexane. However, when the aqueous phase contained thiocyanate ions, a remarkable extraction of beryllium(II) was observed.

Figure 4 gives the log *D* *vs.* log[SCN⁻] plot when the organic phase is hexane containing 0.2 M TBP and when the aqueous phase is 4.0 M $Na(SCN, ClO_4)$ at $-\log[H^+]$ values between 3.5 and 4.0. It may be seen from Fig. 4 that the distribution increases with the increase in the thiocyanate concentration and that the slope $d\log D/d\log[SCN^-]$ decreases from 2 to about 1 or less. Assuming that only the $Be(SCN)_2$ species is extracted with TBP, the results were analyzed using Eq. (27). Figure 5 gives the $\log D/[SCN^-]^2$ *vs.* log [SCN⁻] plot. The constants were determined from Fig. 5 by the curve-fitting method; they are given in Tables 1 and 2. The solid curve in Fig. 5 is the curve calculated from these constants. When the thiocyanate concentration is lower than 0.1 M, the data deviate from the statistically expected curve based on Eq. (27).

In order to see the effect of the hydrogen ion concentration on the TBP extraction of beryllium thio-

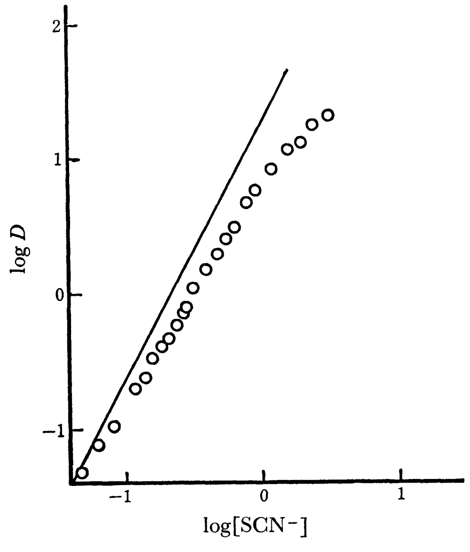

Fig. 4. Extraction of beryllium(II) from 4 M $Na(SCN, ClO_4)$ at $[H^+]=10^{-4}$ M into hexane containing 0.2 M TBP as a function of the thiocyanate concentration. The straight line shows the slope of +2.

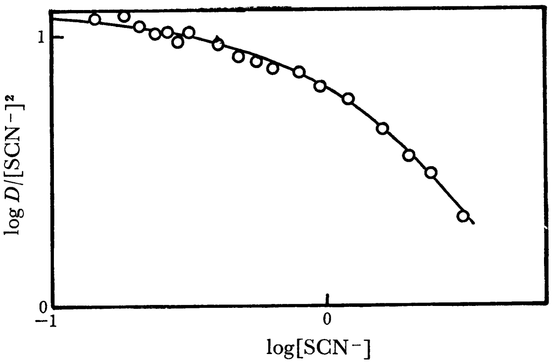

Fig. 5. Determination of the stability constants of the thiocyanate complexes by the curve fitting. The data in Fig. 4 were plotted as $\log D[\mathrm{SCN}^-]^2$ *vs.* $\log[\mathrm{SCN}^-]$ and were fitted with the curve $Y = \log c - \log(1 + a[\mathrm{SCN}^-] + b[\mathrm{SCN}^-]^2)$ were $a$ is $\beta_1(=0.69)$, $b$ is $\beta_2(=0.25)$ and $c$ is $K_D\beta_2(=12.6)$.

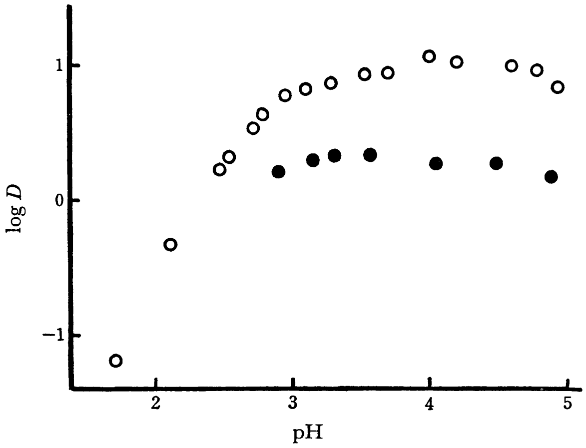

Fig. 6. Hydrogen ion concentration dependence of the extraction of beryllium thiocyanate complex.
Organic phase: Hexane containing 0.2 M TBP.
Aqueous phase: 2 M NaSCN + 2 M $\mathrm{NaClO_4}$ (open circles), 0.4 M NaSCN + 3.6 M NaClO (closed circles).

cyanate, the distribution ratio was determined as a function of $-\log[\mathrm{H}^+]$ when the TBP concentration was 0.2 M and when the thiocyanate concentration was 2.0 M or 0.4 M. The results are given in Fig. 6. As may be seen from Fig. 6, the distribution ratio is practically independent of the hydrogen ion concentration when it is between $10^{-3.5}$ and $10^{-4.5}$.

Figure 7 shows the distribution of beryllium(II) in the aqueous phase containing 3.0 M sodium perchlorate and 1.0 M sodium thiocyanate at a $-\log[\mathrm{H}^+]$ value of about 4.0 into hexane as a function of the organic TBP concentrations. In Fig. 7, it may be seen that the slope of the plot is +3; thus, the extraction equilibrium can be described by the following equation:

$$\mathrm{Be(SCN)_2} + 3\mathrm{TBP}(org) \rightleftarrows \mathrm{Be(SCN)_2(TBP)_3}(org)$$

As has been described, two different solvent extraction methods were used for the determination of the beryllium complexes in the present study. The metal TTA chelate extraction method is applicable only to the chloride, bromide, and nitrate complexes, whereas the TBP adduct neutral complex extraction method was applicable to the thiocyanate complexes. Neither of them was suitable for the iodide complexes.

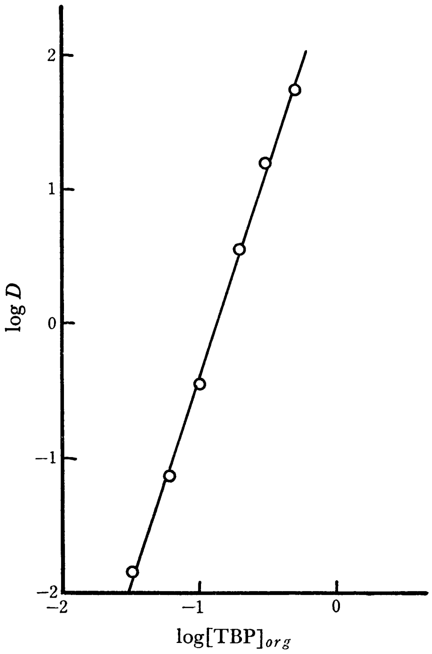

Fig. 7. TBP dependence of the beryllium thiocyanate extraction. Organic phase: hexane containing TBP. Aqueous phase: 3 M $\mathrm{NaClO_4}$ + 1 M NaSCN and $[\mathrm{H}^+]$ is about $10^{-4}$ M.

## Discussion

In a previous paper,[2] a deviation of the $\log D$ of beryllium(II) *vs.* $-\log[\mathrm{H}^+]$ plot from the slope +2 was observed when the organic phase was MIBK containing 0.03 M TTA and when the aqueous phase was 1.0 M sodium perchlorate (Fig. 1 in Ref. 2). In that study, however, the deviation was too small to allow a reasonable analysis of the coextraction of the perchlorate or mixed TTA-perchlorate complex into MIBK (it may be seen from Fig. 1 in the present paper that the $K_{ex_2}$ from 1.0 M perchlorate media is $3 \times 10^{-3}$). As may also be seen from Fig. 1, the beryllium perchlorate extraction increases with an increase in the aqueous sodium perchlorate concentration and in the extraction of beryllium(II) in 4.0 M sodium perchlorate into MIBK in Fig. 2, even in the absence of TTA; this can be explained in terms of the beryllium perchlorate extraction. The change in the slope of the extraction curve, $\log D$ *vs.* $\log[\mathrm{HA}]_{org}/[\mathrm{H}^+]$, can also be understood in terms of perchlorate extraction, as can be seen from the calculated curve in Fig. 2 based on the constants already given.

As has been pointed out,[7] the extraction constant of the mixed complex can be calculated from the extraction constants of the two other species:

$$K_{ex_1}(stat.) = 2(K_{ex_2} \times K_{ex_0})^{1/2} = 10^{-1.18}$$

This statistical value is about three times the experimentally observed value ($10^{-1.64}$); thus, the mixed complex is somewhat less stable than the statistical

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[7] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2013 (1964).

value. The slope of the extraction curve is almost $+2$ when $\log[HA]_{org}/[H^+]$ is kept above 1.1; that is, the distribution ratio generally given by Eq. (8) in that range can be described as $D_0=[BeA_2]_{org}/[Be^{2+}]$. As all the determination of the stability constants by the TTA extraction is carried out in this $[HA]_{org}/[H^+]$ range, the analysis of the data based on Eq. (22) should be reasonable.

The use of Eq. (22) for the analysis of the data in Fig. 3 seems also to be reasonable because it was observed that the distribution ratio is proportional to the square of $[HA]_{org}/[H^+]$, even in the systems where some of the perchlorate ions were replaced by chloride, bromide, or nitrate ions.

As may be seen from Fig. 5, the experimental data well fit the solid line calculated from the constants based on Eq. (27). This seems to show that the distribution behavior of beryllium is represented by Eq. (27). It is remarkable that the stability of the extractable complex, $Be(SCN)_2$, is relatively low, but its extraction is high in the higher ligand concentration region. For example, when the thiocyanate concentration is 1.0 M, 13 percent of the aqueous beryllium(II) is in the form of $Be(SCN)_2$, but still about 86 percent of the initial aqueous beryllium is extracted into the organic phase. This is due to the high distribution constant of this complex. The extraction should be much higher at the higher TBP concentration.

Although the stabilities of the beryllium complexes given in Table 2 are not large, these very weak complexes are still important in order to understand the chemical behavior of this metal ion under certain experimental conditions, as we have seen in the TBP extraction of its thiocyanate.

The stability constants of beryllium(II) chloride and nitrate complexes were determined in 0.5 M perchlorate media at 18°C by Kolosova and Belyavskaya[8]; they were reported to be $\log\beta_1=1.11$, $\log\beta_2=0.30$, and $\log\beta_3=1.40$ for chloride complexes, and $\log\beta_1=-0.60$ and $\log\beta_2=1.62$ for nitrate complexes. These previous stability constants are much higher than the present data shown in Table 2, even if the lower ionic concentration is taken into account. No report seems to have been published on the stability constants for the beryllium(II) complexes with bromide or thiocyanate ions. Biermann and McCorkell[9] have studied the extraction of beryllium thiocyanate into MIBK, 1-hexanol, 2-octanol, and isoamylacetate when the initial aqueous beryllium concentration is rather high (above 0.1 M in the initial aqueous phase). They reported a remarkable pH dependence of the extraction; the percent extraction increases from pH 0.5 to 2.0, it is almost constant between pH 2.0 and 3.0, and then it decreases above pH 3.0. They explained it in terms that an increase of pH in the lower pH region causes the back extraction of the undissociated thiocyanic acid into the aqueous phase and increases the thiocyanate ion concentration. At the same time, the decrease in the thiocyanic acid in the organic phase increases the activity of the solvent. They also explained the decrease in the extraction in the higher pH region in terms of the hydrolysis of beryllium, which forms $BeOH^+$. They also assumed that the only beryllium species in the aqueous phase besides the above $BeOH^+$ is the $Be^{2+}$ (no complex formation in the aqueous phase) and concluded that the extraction is given by the equation $D_{Be}=0.3[SCN^-]^2$ where $D_{Be}=[Be(SCN)_2]_{org}/[Be^{2+}]$.

As can be seen from Fig. 6, in the present study we have not observed such a drastic decrease in $D$ above pH 4.0 as they reported. Thus, from the results in Fig. 6 and from the hydrolysis constants in the literature,[1] we have concluded that the hydrolysis around pH 4.0 is very small. Moreover, we can not accept the assumptions that the formation of the thiocyanate complex in the aqueous phase is negligible and that the slope of the $\log D$ *vs.* $\log[SCN^-]$ plot is two, as can be seen from the results in Fig. 4. The complex formation of alkaline earth metal ions with these ligand anions has not been studied very much because of the instability of the complexes, but, as is seen in this study, beryllium(II) shows some tendency to form complexes; this is probably due to the small ionic size of the $Be^{2+}$.

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[8] I. F. Kolosova and T. A. Belyavskaya, *Vestik Moskov Univ. Khim.*, **18**, No. 152 (1963).

[9] W. J. Biermann and R. McCorkell, *Can. J. Chem.*, **40** 1368 (1962); **41** 112 (1963); **45** 2846 (1967).