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Kinetic Studies of the Solvent Extraction of Metal Complexes. I. The Extraction of the Beryllium(II)-TTA Chelate from Aqueous Perchlorate Media into Carbon Tetrachloride and Methyl Isobutyl Ketone

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The rate of extraction of beryllium ions from aqueous 4.0M or 0.1M sodium perchlorate-chloride or -nitrate ionic media into carbon tetrachloride or MIBK (methyl isobutyl keton) as a chelate complex with TTA (thenoyltrifluoroacetone) has been determined at 25°C. The rate of extraction in the carbon tetrachloride system is first-order with respect both to the beryllium ion and the dissociated TTA anion in the aqueous phase. The rate constant for this reaction is about $2\times10^4 \mathrm{M}^2\mathrm{min}^{-1}$. The rates in these systems are not influenced by the replacement of perchlorate ions by nitrate or chloride ions in the ionic media when the ionic concentration is kept constant. On the other hand, it was found that three extraction reactions take place in the MIBK systems. The rate of these extractions is in all cases first-order with respect both to the beryllium ion and the dissociated TTA anion, but is zeroth-, first, or second-order with respect to the perchlorate ions in the aqueous phase. Because of this, the extraction is much faster when the perchlorate concentration is larger; for example, when the concentration of the TTA anion is kept constant, the extraction from a 4.0M sodium perchlorate solution is about 200 times faster than that from the 4.0M sodium chloride solution. From these experimental results, the following conclusions were reached. In the carbon tetrachloride system, the beryllium ion first forms the TTA chelate in the aqueous phase, and then the complex is extracted into the organic phase. The rate-determining step is the 1:1 complex formation in the aqueous phase. In the MIBK system, on the other hand, the formation of the TTA complex in the aqueous phase, followed by its extraction into the organic phase (zeroth-order reaction with respect to the perchlorate ion), also occurs, but at the same time, the beryllium ion in the aqueous phase is first extracted into the organic phase as ion-pairs, such as $BeCl(ClO_4)$ or $BeNO_3(ClO_4)$ and $Be(ClO_4)_2$ (first- and second-order reactions with respect to the perchlorate ions respectively), and the ion-pairs then react with the TTA anions in the organic phase. The enhancement of the rate of extraction by the perchlorate ions in the MIBK system seems to be explained by the overall effect of these extraction mechanisms.

The solvent extraction of the beryllium(II)-TTA (thenoyltrifluoroacetone) chelate complex has been known as a slow reaction. It was reported that the rate of this extraction is dependent on the hydrogen-ion concentration and that a prolonged agitation is necessary until the distribution equilibrium is established, especially when the pH is not high;[1] an agitation for one week was carried out in order to obtain the distribution equilibrium of the beryllium(II)-TTA chelate between *o*-xylene and aqueous solutions,[2] for instance. A slow beryllium(II) extraction with TTA has been also observed in our laboratory; it took one week or more to obtain the distribution equilibrium when beryllium(II) in perchlorate media was extracted with 0.01 M to 0.1 M TTA in chloroform or in carbon tetrachloride by the mechanical agitation of the two phases in glass tubes placed on a rotating framework at 20 rpm.[3] At the same time, it was also observed that the extraction is much faster when MIBK (methylisobutyl ketone) is used as the organic solvent; the extraction equilibrium was achieved within 12 hr by the same mechanical agitation.[3,4]

In this paper, the present authors have carried out a kinetic study of the beryllium(II) extraction with TTA in order to ascertain further details on this remarkable difference in the rate of extraction when these two organic solvents are used. The aqueous phase employed was 4.0 M or 0.1 M constant ionic media containing sodium perchlorate and sodium chloride or sodium nitrate. From these experimental data, the rate of extraction was given as a function of the concentration of the components and the important role of the perchlorate ions in the extraction mechanism has been established. The results were further discussed by comparing them with these of a distribution equilibrium study carried out under the same conditions.[4]

Experimental

Reagents. A radioactive tracer, beryllium-7, has always been used in order to determine the distribution ratio. It was obtained as a hydrochloric acid solution and was diluted with 0.01 M perchloric acid in order to prepare the stock tracer solution. A reagent-grade beryllium hydroxide was dissolved in perchloric acid, and the concentration was determined by gravimetry after beryllium(II) 2-methyloxinate had been precipitated. The stock carrier solution was prepared by the dilution of this solution. It contained 5×10^{-3} M beryllium and 0.01 M perchloric acid. The TTA was obtained from the Dōjindō Co. The MIBK was obtained from the Tokyo Kasei Co.; it was washed with 0.1 M perchloric acid, water, and a 0.1 M aqueous sodium hydroxide solution successively, and then several times with water. The sodium perchlorate was prepared from sodium carbonate and perchloric acid. It was recrystallized three times from water. All of the other reagents were of a reagent grade and were used without further purification.

Procedures. All of the procedures were carried out in a thermostatted room at 25±0.3°C. Stoppered glass tubes (volume, 20 m*l*) were always used in order to equilibrate the two phases. The organic solution of TTA prepared was stored overnight before the experiments. The aqueous phase initially contained 1.0×10^{-4} M labeled beryllium, sodium perchlorate, and, in some cases, sodium chloride or sodium nitrate and a 0.01 M sulfanilate buffer. The total ionic concentration was 4.0 M or 0.1 M. A 5.0-m*l* portion of the organic solution and a 5.0-m*l* portion of the aqueous solution were placed in the glass tube, and the two phases were agitated vigorously by means of a mechanical shaker. In order to ascertain the effect of the material diffusion on the rate of extraction, a series of experiments were carried out as follows: a 5.0-m*l* portion of the aqueous solution and a 5.0-m*l* portion of the organic solution were taken, each from a certain batch, and placed in a glass tube. The tube was placed on the mechanical shaker and was shaken for 5 min at a certain shaking speed. The distribution ratio of beryllium(II) was then determined in a manner which will be described later. Several experiments were carried out by changing the shaking speed, and the distribution ratio thus obtained was plotted against the speed. It was found that the distribution ratio was dependent on the speed when it was low. However, beyond a certain speed (which was dependent on the nature and the volume of the two phases), the distribution ratio (which was much lower than the value at equilibrium) became no longer dependent on the speed. Such a "plateau region" of the shaking speed was determined before each series of experiments, and the shaking of that series of experiments was always carried out under those conditions.

In order to determine the rate of extraction, a series of experiments were carried out at different shaking intervals, but otherwise under the same experimental conditions. When the agitation was stopped, the two phases in the tube were immediately centrifuged and a certain portion was pipetted from each phase and transferred into small test tubes. The γ-radioactivity of each phase was counted by means of well-type (NaI) scintillation counter. Another portion was also taken from the aqueous phase and transferred into a glass vessel. The hydrogen-ion concentration (the stoichiometric unit) was determined by potentiometry by using standard perchloric acid, in which the ionic concentration was 0.1 M or 4.0 M.

The beryllium content in the two phases was determined from the initial beryllium concentration and the γ-radioactivity of the two phases as:

$$[\mathrm{Be(II)}]_{org} = [\mathrm{Be(II)}]_{initial} \times (\gamma\text{-count-rate})_{org}/(\gamma\text{-count-rate})_{initial}$$

$$[\mathrm{Be(II)}] = [\mathrm{Be(II)}]_{initial} \times (\gamma\text{-count-rate})_{aq}/(\gamma\text{-count-rate})_{initial}$$

Statistical

The rate of extraction could be influenced by many factors. As has been described, the agitation of the two phases in this study was always done in the plateau region, where the rate was independent of the speed of the two-phase agitation. Thus, the diffusion or the transport of materials could be eliminated from consideration; the rate is dependent only on the concentrations of the materials in the system.

On the basis of these facts, the extraction rate may be generally described as follows:

$$-\frac{\mathrm{d}[\mathrm{Be}^{2+}]}{\mathrm{d}t} = k^*[\mathrm{Be}^{2+}]^a[\mathrm{HA}]^b_{org}[\mathrm{H}^+]^c[\mathrm{ClO_4}^-]^d \qquad (1)$$

Here, the term of water is omitted because it is not possible to change the water activity without influencing the other factors.

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

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

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

[4] T. Sekine, Y. Komatsu, and M. Sakairi, *ibid.*, **44**, 1480 (1971).

The dissociation and the distribution constants of the chelating acid are described as:

$$K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \tag{2}$$

$$K_D = \frac{[\mathrm{HA}]_{org}}{[\mathrm{HA}]} \tag{3}$$

$$\frac{K_D}{K_a} = \frac{[\mathrm{HA}]_{org}}{[\mathrm{H}^+][\mathrm{A}^-]} \tag{4}$$

When b is equal to c^{-1}, Eq. (1) can also be described as:

$$-\frac{\mathrm{d}[\mathrm{Be}^{2+}]}{\mathrm{d}t} = k[\mathrm{Be}^{2+}]^a[\mathrm{A}^-]^e[\mathrm{ClO}_4^-]^d \tag{5}$$

where $k = k^*K_DK_a^{-1}$.

As the perchlorate and the extractant (HA) are in a large excess in relation to beryllium, and as the aqueous phase is buffered, the rate can be described as follows:

$$-\frac{\mathrm{d}[\mathrm{Be}^{2+}]}{\mathrm{d}t} = q[\mathrm{Be}^{2+}]^a \tag{6}$$

Here q is the multiplication of the rate constant, k^*, and the other concentrations which are kept at certain values. When the reaction order with respect to beryllium is unity, as it is in the present study, the following simplified statistical treatments are possible.

Equation (6) can be rewritten as:

$$-\frac{\mathrm{d}[\mathrm{Be}^{2+}]}{\mathrm{d}t} = q[\mathrm{Be}^{2+}] \tag{7}$$

$$-\log[\mathrm{Be}^{2+}] = qt + c_0 \tag{8}$$

Equation (8) shows that the above assumption should stand if the $\log[\mathrm{Be}^{2+}]$ *vs.* t plot is a straight line with a slope of $-q$.

The reaction order with respect to the other species can be determined from the rate measurements when two of the concentrations out of these three are kept at certain values. For example, when the concentrations of the extractant and perchlorate ions are kept at B and D, then the quantity q_{H^+} can be defined as follows:

$$\log q_{\mathrm{H}^+} = \log k^*B^bD^d + c\log[\mathrm{H}^+] \tag{9a}$$

As can be seen from Eq. (9a), the $\log q_{\mathrm{H}^+}$ *vs.* $-\log[\mathrm{H}^+]$ plot should be a straight line with a slope of $-c$ under such conditions; thus, the reaction order with respect to the hydrogen ion, c, can be determined.

By similar procedures, the rest of the values of the b and d reaction orders can be determined from the slope of the plot given by the following equations:

$$\log q_{\mathrm{HA}} = \log k^*C^cD^d + b\log[\mathrm{HA}]_{org} \tag{9b}$$

$$\log q_{\mathrm{ClO}^-} = \log k^*B^bC^c + d\log[\mathrm{ClO}_4^-] \tag{9c}$$

However, as will be seen below, the reaction order with respect to the perchlorate ions, d, was not a constant in some systems, but changed as the perchlorate concentration was changed; this was, therefore, further treated.

The reaction order with respect to the perchlorate can, then, be generally described as:

$$-\frac{\mathrm{d}[\mathrm{Be}^{2+}]}{\mathrm{d}t} = k^*[\mathrm{Be}^{2+}][\mathrm{HA}]_{org}^b[\mathrm{H}^+]^c(1+k_1[\mathrm{ClO}_4^-] + \cdots + k_n[\mathrm{ClO}_4^-]^n) \tag{10}$$

or

$$= k[\mathrm{Be}^{2+}][\mathrm{A}^-]^e(1+k_1[\mathrm{ClO}_4^-] + \cdots + k_n[\mathrm{ClO}_4^-]^n) \tag{11}$$

In such cases, the following equation should be used instead of Eq. (9c):

$$\log q_{\mathrm{ClO}_4^-} = \log k^*B^bC^c + \log(1+k_1[\mathrm{ClO}_4^-] + \cdots + k_n[\mathrm{ClO}_4^-]^n) \tag{12}$$

Thus, the $\log q_{\mathrm{ClO}_4^-}$ *vs.* $\log[\mathrm{ClO}_4^-]$ plot is not a straight line but a curve with two asymptotes:

$$[\mathrm{ClO}_4^-] \to 0 \quad \log q_{\mathrm{ClO}_4^-} = \log k^*B^bC^c$$

$$[\mathrm{ClO}_4^-] \to \infty \quad \log q_{\mathrm{ClO}_4^-} = n\log[\mathrm{ClO}_4^-]$$

As the limiting slope was found to be +2 in the present study, the k_1 and k_2 constants were determined by a curve-fitting of the $\log q_{\mathrm{ClO}_4^-}$ *vs.* $\log[\mathrm{ClO}_4^-]$ with the following family of standard curves, as has been described in other papers:[5,6]

$$Y = \log(1+pv+v^2) \quad X = \log v \tag{13}$$

The above treatments are probably valid only when the effect of the reverse reaction or the back extraction is negligible.

Results

In the present study, beryllium was always added to the aqueous phase, and the data used for the analysis were obtained only from the early stage of the extraction; therefore, the statistical treatments given above can be adopted without any corrections for the back extraction.

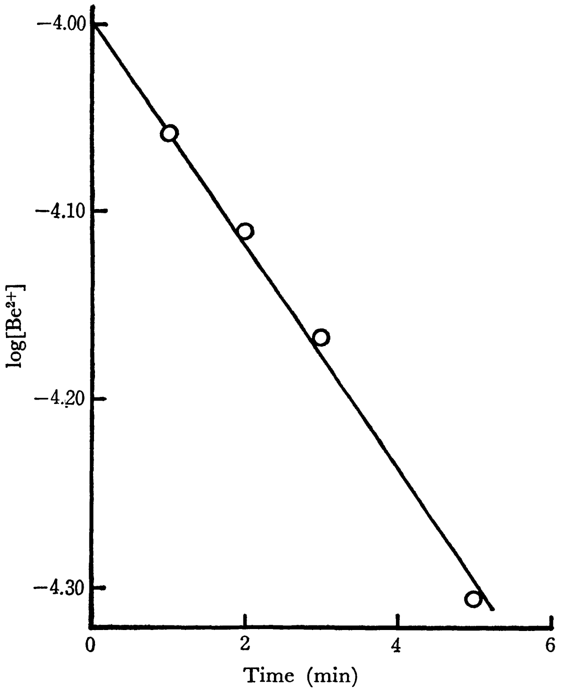

Fig. 1. Dependence of the rate of Be(II) extraction as TTA chelate on the Be^{2+} concentration.
Org. phase. MIBK containing 0.1 M TTA.
Aq. phase. 4.0 M $\mathrm{NaClO_4}$ at $-\log[\mathrm{H}^+]=3.00$.

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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).

In all of the experiments, the TTA concentration in the initial organic phase was 0.1M and the perchlorate concentration was 0.1M or 4.0M, except when the dependence of the rate on these concentrations was determined. The hydrogen-ion concentration was, in general, 1.0×10^{-3}M. However, when the rate was too small or too large for accurate measurement, the experiments were carried out at a somewhat higher or lower hydrogen-ion concentration and the q_{HA} and $q_{\mathrm{ClO_4^-}}$ values in Eqs. (9b) and (9c) were normalized to those at $-\log[\mathrm{H^+}]$ 3 by assuming that they are inversely proportional to the hydrogen-ion concentration.

Extraction of Beryllium Perchlorate. Beryllium(II) in sodium perchlorate solutions is extracted even into MIBK in the absence of any chelating ligand, as has been pointed out (Ref. 4 Fig. 1). This extraction proceeds very rapidly, and the distribution equilibrium is reached within 30 sec under the present experimental conditions. The distribution ratio of beryllium(II) between MIBK and 4.0M sodium perchlorate is $10^{-1.16}$.

Reaction Order with Respect to Be^{2+}. In most experiments, the $-\log[\mathrm{Be^{2+}}]$ *vs.* t plot under certain conditions was a straight line. Figure 1 gives an example of this. As can be seen from Eq. (8), this shows that the reaction order with respect to the beryllium ion is unity. However, when the two-phase agitation was carried out for a very long time, a deviation of the plot from a straight line was observed. The deviation is probably caused by the back extraction.

(A) Extraction into Carbon Tetrachloride. Reaction Order with Respect to the Hydrogen Ions: The rate of extraction was determined when the TTA concentration in carbon tetrachloride was 0.1M, the aqueous sodium perchlorate concentration was 0.1M or 4.0M and the hydrogen-ion concentration was between $10^{-2.5}$ and $10^{-3.5}$M. The value of q in Eq. (8) at a certain hydrogen-ion concentration was determined from the slope of the $-\log[\mathrm{Be^{2+}}]$ *vs.* t plot; the series of log q values thus obtained at different hydrogen-ion concentrations, log $q_{\mathrm{H^+}}$, are plotted against $-\log[\mathrm{H^+}]$ in Fig. 2a. In the 4.0M ionic media, the plot is a straight line with a slope of $+1$, although the results are somewhat erroneous; it would be possible to conclude that the rate of extraction is inversely proportional to the hydrogen-ion concentration in this system. In the 0.1M ionic media, the plot is also almost a straight line with a slope of $+1$ in the higher $-\log[\mathrm{H^+}]$ region. However, it deviates from the line as $-\log[\mathrm{H^+}]$ decreases. The present authors cannot yet explain this deviation in the lower $-\log[\mathrm{H^+}]$ region, but still it could be concluded that the reaction order with respect to the

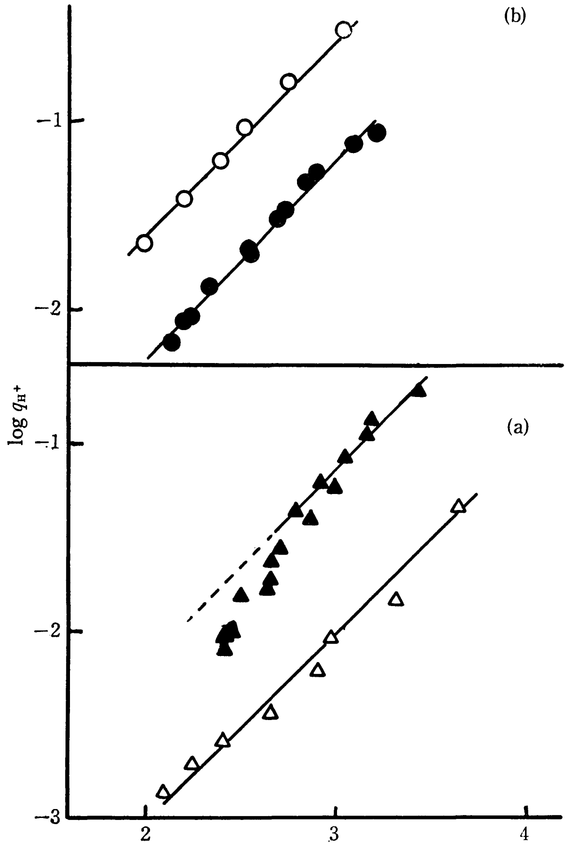

Fig. 2. Dependence of the Be(II) extraction as TTA chelate on the hydrogen ion concentration. The notation $q_{\mathrm{H^+}}$ on the ordinate is given in Eq. (9a).

(a) Org. phase. CCl_4 containing 0.1M TTA.
Aq. phase. 4.0M $NaClO_4$ (open triangles).
0.1M $NaClO_4$ (closed triangles).
(b) Org. phase. MIBK containing 0.1M TTA.
Aq. phase. 4.0M $NaClO_4$ (open circles).
0.1M $NaClO_4$ (closed circles).

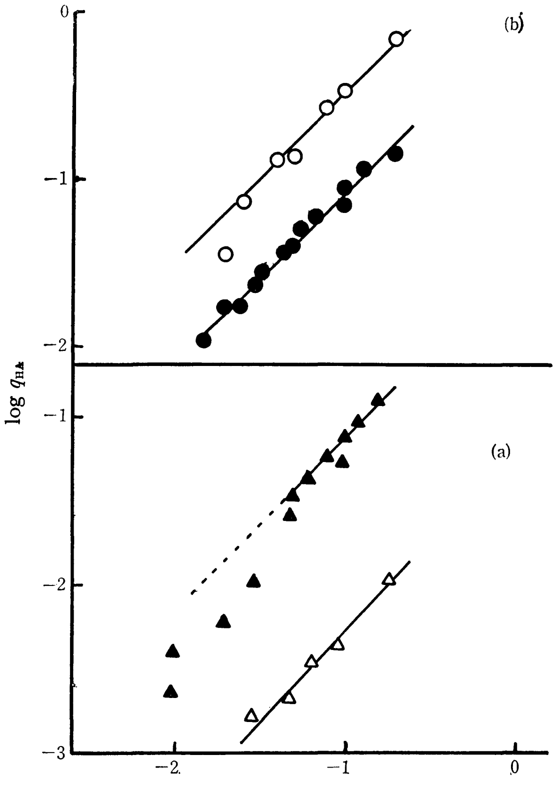

Fig. 3. Dependence of the rate of Be(II) extraction as TTA chelate on the TTA concentration in the organic phase. The notation q_{HA} on the ordinate is given in Eq. (9b).

(a) Org. phase. CCl_4 containing TTA.
Aq. phase. 4.0M $NaClO_4$ (open triangles).
0.1M $NaClO_4$ (closed triangles).
(b) Org. phase. MIBK containing TTA.
4.0M $NaClO_4$ (open circles).
0.1M $NaClO_4$ (closed circles).

hydrogen-ion concentration is −1 when the hydrogen-ion concentration is around 1×10^{-3}M or less.

Reaction Order with Respect to TTA: The rate of extraction was determined when the hydrogen-ion concentration was $10^{-2.9}$M in the 0.1M ionic media and $10^{-3.1}$M in the 4.0M ionic media. The results are given in Fig. 3a. In the 4.0M ionic media, the plot is a straight line with a slope of +1, it was concluded that the extraction is proportional to the TTA concentration. In the 0.1M media, the plot is also almost a straight line with a slope of +1 in the higher TTA concentration region. However, it deviates from the line as the concentration decreases. The authors also cannot explain this deviation now, but they believe that it could be concluded that the reaction order with respect to TTA is +1 when the TTA concentration is about 5×10^{-2}M or more.

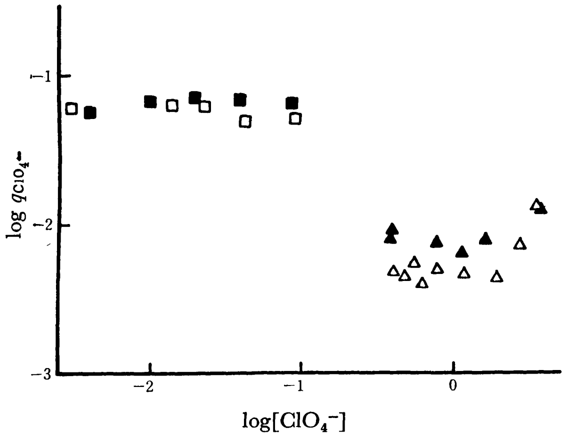

Fig. 4. Dependence of the rate of Be(II) extraction as TTA chelate on the aqueous perchlorate concentration when it is replaced by sodium nitrate (closed symbols) or by sodium chloride (open symbols). The notation $q_{ClO_4^-}$ on the ordinate is given in Eq. (9c).

Org. phase. CCl_4 containing 0.1M TTA.
Aq. phase. 4.0M Na(Cl, ClO_4) (open triangles)
4.0M Na(NO_3, ClO_4) (closed triangles)
0.1M Na(Cl, ClO_4) (open squares)
0.1M Na(NO_3, ClO_4) (closed squares)

Reaction Order with Respect to Perchlorate Ions. The rate of extraction was determined when the TTA concentration was 0.1M and the perchlorate ion concentration was changed. The hydrogen-ion concentration in these experiments was $10^{-3.5}$M in the 4.0M or 0.1M Na(NO_3, ClO_4) media, $10^{-3.6}$M in the 4.0M Na(Cl, ClO_4) media, and $10^{-2.8}$M in the 0.1M Na(Cl, ClO_4) media. Figure 4 gives the results (*cf.* Eq. (9c)). From Fig. 4, it can be seen that the rate of extraction is almost constant in the 0.1M media, that it decreases somewhat in the 4.0M media when the perchlorate ions are replaced by chloride or nitrate ions, but that it becomes almost constant when the concentration of these ions is above 2.0M. Thus, it can be concluded that the rate of extraction is practically independent of the composition of the salt in the aqueous phase.

From these findings, it was concluded that the rate of beryllium extraction into carbon tetrachloride with TTA is expressed by the following equation (*cf.* Eq. (1)):

$$-\frac{d[Be^{2+}]}{dt} = k^*[Be^{2+}][HA]_{org}[H^+]^{-1}[ClO_4^-]^0 \tag{14}$$

As may be seen from Eqs. (2) to (5), Eq. (14) can also be rewritten as:

$$-\frac{d[Be^{2+}]}{dt} = k[Be^{2+}][A^-] \tag{15}$$

The rate constants calculated from these results are given in Table 1.

TABLE 1. A SUMMARY OF THE RATE CONSTANTS FOR THE EXTRACTION OF BERYLLIUM(II)-TTA CHELATE COMPLEXES AT 25°C

(A) Extraction into carbon tetrachloride

$$-\frac{d[Be^{2+}]}{dt}=k[Be^{2+}][A^-][ClO_4^-]^0$$

	0.1M $NaClO_4$	4.0M $NaClO_4$
log k	4.5	4.3

(B) Extraction into MIBK

$$-\frac{d[Be^{2+}]}{dt}=k[Be^{2+}][A^-](1+k_1[ClO_4^-]+k_2[ClO_4^-]^2)$$

	0.1M ionic media		4.0M ionic media	
	Na (NO_3, ClO_4)	Na (Cl, ClO_4)	Na (NO_3, ClO_4)	Na (Cl, ClO_4)
log k	4.8	4.7	4.9	4.4
log kk_1	6.5	6.3	5.8	5.7
log kk_2	5.9	5.7	4.9	5.2

The dissociation and distribution constants at 25°C used for the calculation of [A^-] from $[HA]_{org}$ and [H^+] are as follows. (taken from unpublished data by T. Sekine *et al.*)

		0.1M $NaClO_4$	4.0M $NaClO_4$
log[H^+][A^-]/[HA]		−6.46	−6.57
log $\frac{[HA]_{org}}{[HA]}$	CCl_4	1.30	1.93
	MIBK	2.25	2.62

(B) Extraction into MIBK. The distribution ratio of beryllium(II) between MIBK and 0.1M sodium perchlorate media is estimated to be $10^{-4.5}$ from the extrapolation of the data in Fig. 1, Ref. 4. Thus, the perchlorate extraction is negligible in the 0.1M ionic media. However, in the 4.0M ionic media, the distribution ratio into MIBK is already $10^{-1.16}$ in the absence of TTA. As has been described, the rate of extraction of the perchlorate ion-pairs is very large; thus, the beryllium(II) extraction with TTA from 4.0M perchlorate media is proceeded by the much faster perchlorate extraction.

On the basis of these findings, the rate of beryllium(II) extraction with TTA in MIBK was calculated after a correction for this beryllium(II) perchlorate extraction made as follows. In a preliminary experment, an aqueous phase initially containing the same amounts of beryllium, hydrogen, and perchlorate ions as in the systems to be studied had been equilibrated with an MIBK phase containing no TTA, and the beryllium concentrations in the two phases were measured. The extraction into MIBK containing TTA was assumed to be started from these phases; that is, the aqueous beryllium(II) concentration measured above was used as the initial aqueous beryllium(II) concentration, and the organic beryllium(II) concentration preliminarily determined (which should correspond to the organic beryllium perchlorate fraction) was substracted from the organic concentration obtained in the presence of TTA.

Reaction Order with Respect to Hydrogen Ions: The rate of extraction was determined when the hydrogen-ion concentration was between $10^{-2.0}$ and $10^{-3.5}$M. The results are given in Fig. 2b. Both in the 0.1M and in the 4.0M media, the plot is a straight line with a slope of +1, as can be seen from Fig. 2b. Thus, it was concluded that the extraction is inversely proportional to the hydrogen-ion concentration in the aqueous phase.

Reaction Order with Respect to TTA: The rate of extraction was determined when the hydrogen-ion concentration was $10^{-2.5}$M in the 0.1M ionic media and $10^{-2.4}$M in the 4.0M media. In both these ionic media, the log q_{HA} *vs.* log$[\mathrm{HA}]_{org}$ plot is a straight line with a slope of +1, as is shown in Fig. 3b. Thus, it was concluded that the extraction rate is proportional to the TTA concentration in the organic phase.

Reaction Order with Respect to Perchlorate Ions: The rate of extraction was determined when the TTA concentration was 0.1M and the hydrogen-ion concentrations were $10^{-3.0}$M (0.1M Na($\mathrm{NO_3}$, $\mathrm{ClO_4}$)), $10^{-3.4}$M (0.1M Na(Cl, $\mathrm{ClO_4}$)), $10^{-2.7}$M (4.0M Na($\mathrm{NO_3}$, $\mathrm{ClO_4}$)), and $10^{-3.3}$M (4.0M Na(Cl, $\mathrm{ClO_4}$)). In all of the experiments, the log $q_{\mathrm{ClO_4^-}}$ *vs.* log$[\mathrm{ClO_4^-}]$ plot was not a straight line. The slope always increased as the perchlorate concentration increased. Figures 5 and 6 show the results.

The data in these figures were analyzed by the curve-fitting, and it was concluded that the limiting slope for each plot was always +2; the plot can be represented by the following equation (*cf.* Eq. (12)):

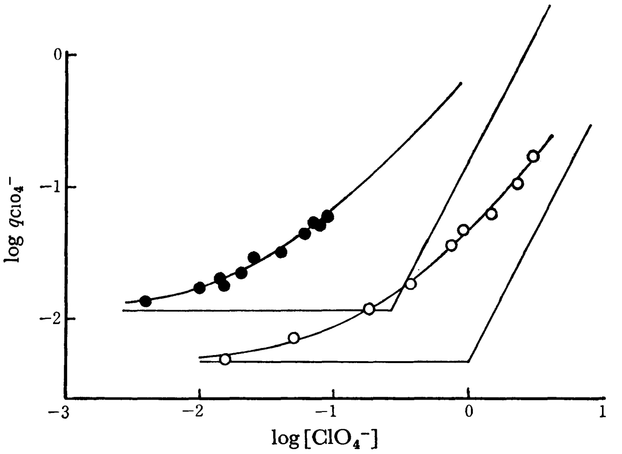

Fig. 5. Dependence of the rate of Be(II) extraction as TTA chelate on the perchlorate concentration in the sodium perchlorate-nitrate systems.
Org. phase. MIBK containing 0.1M TTA.
Aq. phase. 4.0M Na($\mathrm{ClO_4}$, $\mathrm{NO_3}$) (open circles).
0.1M Na($\mathrm{ClO_4}$, $\mathrm{NO_3}$) (closed circles).
The solid curve for the open circles gives
$Y=4.9\times10^{-3}(1.0X^2+8.0X+1)$
and for the closed circles gives
$Y=1.2\times10^{-2}(15X^2+48X+1)$.

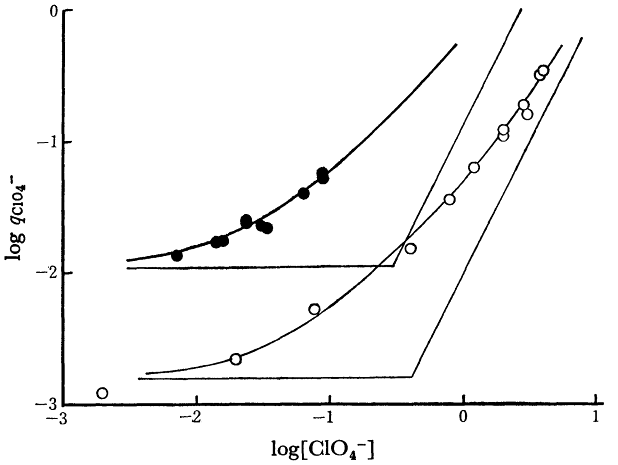

Fig. 6. Dependence of the rate of Be(II) extraction as TTA chelate on the perchlorate concentration in the sodium perchlorate-chloride systems.
Org. phase. MIBK containing 0.1M TTA.
Aq. phase. 4.0M Na($\mathrm{ClO_4}$, Cl) (open circles).
0.1M Na($\mathrm{ClO_4}$, Cl) (closed circles).
The solid curve for the open circles gives
$Y=1.6\times10^{-3}(5.9X^2+19X+1)$
and for the closed circles gives
$Y=1.1\times10^{-2}(11X^2+44X+1)$.

$$\log q_{\mathrm{ClO_4^-}} = \log k[\mathrm{A^-}] + \log(1+k_1[\mathrm{ClO_4^-}] + k_2[\mathrm{ClO_4^-}]^2) \tag{16}$$

The constants, k^*, k_1, and k_2, in Eq. (10) (and, at the same time, k_1 and k_2 in Eq. (16)) were determined from the parameters of the best-fit standard curve, and the values of k in Eq. (16) were calculated from these values of k^* and the dissociation and distribution constants of TTA in Eqs. (2) and (3) by using Eqs. (4) and (5). The constants are listed in Table 1.

(C) *Effect of the Rate of TTA Distribution.* As has been pointed out, the rate of the distribution of TTA in the organic phase into aqueous solutions is rather slow. For example, the distribution equilibrium is established after 18 hr of two-phase agitation when carbon tetrachloride containing 0.1M TTA is placed in contact with 0.1M sodium perchlorate at pH 2[7] (by a rotating framework at 20 rpm on which stoppered glass tubes containing the two phases were placed. The two-phase agitation in the present study is much more vigorous than this). In order to see the effect of this slow distribution of TTA into the aqueous phase on the rate of beryllium extraction, carbon tetrachloride containing TTA was agitated with aqueous solutions containing no beryllium, but otherwise the same as in the experiments shown in Fig. 1. After the two phases had been agitated vigorously for 5 min, the tracer and carrier were added to the aqueous phase, the agitation was started again, and the extraction was determined as a function of the interval of the agitation after this addition of beryllium to the aqueous phase. However, it was found that the results were practically identical with those in Fig. 1: that is, no difference was observed in the rate of beryllium(II) extraction when the TTA

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7) T. Sekine and Y. Hasegawa, "Solvent Extraction Research," ed. by A. S. Kertes and Y. Marcus, Wiley-Interscience, New York (1969), p. 289.

has been distributed between the two phases beforehand and when the TTA was initially added to the organic phase and the beryllium(II) was initially added to the aqueous phase: thus, the distribution of the TTA started at the same time as the metal extraction.

Discussion

Freiser and his co-workers have presented a series of papers on the kinetics of the solvent extraction of divalent metal ions with dithizone and its derivatives.[8–11] They have established that the rate-determining step of the solvent extraction in these system is the formation of the first metal chelate in the aqueous phase (with the exception of zinc extraction with di-α-naphthyldithiocarbazone)[9] if the two phases are vigorously shaken; thus, the effect of the diffusion of materials is eliminated.

In these papers, it was suggested that the rate of metal dithionate formation increases in an approximately linear fashion with the rate of dissociation of water from various metal ions, and that a loss of coordinated water is involved in the rate-determing step.[8–9] However, it was also suggested that, as a relatively minor variation in large ligand anions changes the rate constant for the complex formation considerably in some cases, the initial complex involves a metal-ligand bonding of some sort; in other words, the first complex which is formed rapidly can not be a simple ion-pair.[10]

There have been also some studies of the rate of solvent extraction.[12] It was pointed out that the rates of extraction of chelating systems containing TTA, *N*-benzyl-*N*-phenyl-hydroxylamine, or pyridylazonaphthol seem to be controlled by the chelate formation.[13]

Enhancements of the rate of extraction by the addition of other ligands to the aqueous phase have been pointed out. Finston and his co-workers[14–16] have reported that the rate of extraction of iron(III) and zirconium with TTA in benzene enhanced by the addition of ammonium thiocyanate to the aqueous perchlorate media and that the enhancement is larger when MIBK is added to the organic phase. They suggested in these papers that the enhancements of the extraction caused by the thiocyanate is due to a change in the mechanism of the extraction; the thiocyanate formed in the aqueous phase is first extracted into the organic phase, and then the thiocyanate ions are replaced by TTA in the organic phase. The enhancement of the rate caused by the addition of the thiocyanate is probably due to the fact that above two processes are faster than the TTA chelate formation in the aqueous phase, which is the rate-determining step when the thiocyanate is absent in the system. They also suggested that the synergic enhancement of metal chelate extraction can, at least in some cases, be explained in terms of this kind of kinetic effect.

The addition of acetate ions was found to enhance the rate of zinc dithizonate extraction; $ZnOAc^+$ reacts 25 times as fast as Zn^{2+}, whereas the formation of $NiOAc^+$ does not accelerate the nickel dithizonate extraction.[12] It was also reported that the extraction of chromium(III) with TTA is accelerated by the addition of fluoride ions;[17] this was explained in terms of the intermediate fluoride complexes, which destroy the hydrate shell of Cr^{3+} but do not prevent the formation of extractable chromium(III)-TTA complexes.

The extraction and complex formation equilibria in the systems studied in the present paper have already been reported in another paper.[4] It was observed that nitrate and chloride form relatively weak complexes with beryllium(II); the stability constants are log $\beta_1=-0.63$ for the $BeNO_3^+$ and log $\beta_1=-0.35$ and log $\beta_2=-0.70$ for the $BeCl^+$ and $BeCl_2$ species. At the same time, it was found that beryllium(II) in the aqueous phase containing 4.0M sodium perchlorate is extracted into MIBK containing TTA in three forms, $Be(ClO_4)_2$, $BeAClO_4$, and BeA_2. The extraction of beryllium(II) into MIBK containing no TTA is very small; the distribution ratio is almost proportional to the square of the aqueous sodium perchlorate concentration, which is lower than 4.0M (*cf.* Fig. 1 in Ref. 4).

As has been described, the two phases in this study were agitated so vigorously that the diffusion of materials had no effect on the rate of extraction; the rate-determining step in the system is probably a chemical reaction in one of the phases. This rate-determining reaction could be concluded from the results to be shown below.

The data in Figs. 2 and 3 indicate that the rate of extraction in the carbon tetrachloride systems can be described by $-d[Be^{2+}]/dt=k[Be^{2+}][A^-]$ except for the following data. It can be seen from Figs. 2a and 3a that the plot of the extraction from 0.1M ionic media into carbon tetrachloride deviates from the straight line with a slope of +1 in the lower $-\log[H^+]$ or $[HA]_{org}$ region. From the distribution and dissociation constants of TTA given in Table 1, it can be concluded that the rate of extraction is practically proportional to $[A^-]$ when it is higher than $10^{-6.0}$M, but that the apparent reaction order with respect to the TTA anions becomes larger than +1 for some unknown reasons when $[A^-]$ is lower than this.

The complex formation with nitrate or chloride ions seems to have no remarkable influence on the rate of extraction, for, as can be seen from Fig. 4, the rate in the carbon tetrachloride systems somewhat decreases when 4.0M sodium perchlorate is replaced by chloride

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[8] C. B. Honaker and H. Freiser, *J. Phys. Chem.*, **66**, 127 (1962).

[9] B. E. McClellan and H. Freiser, *Anal. Chem.*, **36**, 2262 (1964).

[10] J. S. Oh and H. Freiser, *ibid.*, **39**, 295 (1967).

[11] H. Freiser, "Solvent Extraction Chemistry," ed. by D. Dyrssen, J.-O. Liljenzin, and J. Rydberg, North-Holland Pub. Co., Amsterdam (1967), p. 85.

[12] H. Freiser, *Anal. Chem.*, **40**, 522R (1968).

[13] Yu. A. Zolotov, Khim. Osuovy Ekstraksion, Metoda Razdeleniya Elementov, *Akad. Nauk SSSR*, *Inst. Geokhim. i Analit. Khim* 1666, 44. cited in Ref. 12.

[14] H. L. Finston and Y. Inoue, *J. Inorg. Nucl. Chem.*, **29**, 199 (1967).

[15] H. L. Finston and Y. Inoue, *ibid.*, **29**, 2431 (1967).

[16] H. L. Finston and E. Gnizi, "Solvent Extraction Research," ed. by A. S. Kertes and Y. Marcus, Wiley-Interscience (1969), p. 333.

[17] O. M. Petrukhin, L. A. Izosenkova, I. N. Marov, Tu. N. Dubrov, and Yu. A. Zolotov, *Zh. Neorg. Khim.*, **12**, 1407 (1967), *Chem. Abstr.*, **67**, 57668 (1967).

or nitrate. At the same time, it can also be seen that the rate is practically independent of the ligand concentration when it is higher than 2.0M, in which region the concentration of the complexes and, consequently, that of free beryllium decreases. The authors have not yet found any reasonable explanation of this.

Although there are such exceptions, we may still conclude that the rate of extraction is generally represented by Eq. (15); this indicates that the rate-determining step is the first 1: 1 complex formation in the aqueous phase, as Freiser *et al.* have pointed out with regard to the divalent metal dithizonate extractions. The unit reactions for the extraction can be described as:

$$\mathrm{HA}(org) \rightleftharpoons \mathrm{HA} \quad (17a)$$

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^- \quad (17b)$$

$$\mathrm{Be}^{2+} + \mathrm{A}^- \longrightarrow \mathrm{BeA}^+ \quad (17c)$$

$$\mathrm{BeA}^+ + \mathrm{A}^- \rightleftharpoons \mathrm{BeA}_2 \quad (17d)$$

$$\mathrm{BeA}_2 \rightleftharpoons \mathrm{BeA}_2(org) \quad (17e)$$

Probably only the unit reaction in Eq. (17c) is responsible for the rate given by Eq. (15). As carbon tetrachloride is a nonpolar solvent, the extraction of beryllium species other than the bis-TTA complex is probably very poor. At the same time, the dissociation of TTA in this nonpolar solvent into A^- should be very small (the presence of the TTA anion is necessary in order to explain the rate of extraction in the MIBK systems, as will be shown below). Thus, only the above mechanism is dominant in the carbon tetrachloride system where $[A^-]$ is larger than $10^{-6.0}$M in the 0.1M media and in all the regions studied in the 4.0M ionic media.

In Fig. 4, a difference is observed in the apparent rate of extraction from 0.1M and 4.0M ionic media; the apparent rate constant in Eq. (9c) is ten times larger in the 0.1M media than that in the 4.0M media. However, this is due to the differences in the acid dissociation and two-phase distribution constants, K_a and K_D, in Eqs. (2) and (3). The rate constants for the unit reaction in Eq. (17c), given in Table 1, are not very different in these two ionic media.

In the MIBK systems, the rate of extraction is very much enhanced by the perchlorate ions in the aqueous phase. It seems that this can be explained in terms of the extraction of beryllium ion-pairs with perchlorate ions.

When the ionic concentrations in the aqueous phase is 0.1M and no perchlorate is present, the rate constants in the MIBK systems given by Eq. (15) are practically the same as that in the carbon tetrachloride systems. Thus, the rate-determining step should be the formation of the first complex in the aqueous phase, both in the MIBK systems containing no perchlorate in the aqueous phase and in all the cases in the carbon tetrachloride systems. When sodium perchlorate is added to the aqueous phase instead of the nitrate or chloride, ion-pairs such as $\mathrm{Be(NO_3)(ClO_4)}$ or $\mathrm{BeCl(ClO_4)}$ and $\mathrm{Be(ClO_4)_2}$ are extracted. If these extracted ion-pairs react with the dissociated TTA anion in the organic phase, and if this reaction in the organic phase is faster (although the authors cannot give any reasonable explanation for the faster reaction in the organic phase) than the reaction in the aqueous phase, the enhancements of the rate which are proportional to $[\mathrm{ClO_4^-}]$ and $[\mathrm{ClO_4^-}]^2$ can be explained; the over-all extraction rate should be given by the sum of these rates, as is described by Eq. (12).

In the MIBK systems, the rate of extraction in the absence of perchlorate ions, that is, k, is already larger than the rate in the carbon tetrachloride systems containing the same aqueous solutions. As was pointed out in a previous paper,[4] the extraction of beryllium in these nitrate or chloride solutions could not be measured within the limits of experimental accuracy ($D_{\mathrm{Be}}<10^{-2}$). However, still it is possible to assume that an extraction of the ion-pairs, $\mathrm{BeCl_2}$ or $\mathrm{Be(NO_3)_2}$, occurs from such salt solutions into MIBK. This extracted beryllium nitrate or chloride in MIBK (this extraction should be negligible into carbon tetrachloride or from a 0.1M ionic solution into MIBK) could react with TTA anions in the organic phase; the overall effect of that reaction in the aqueous phase which should occur simultaneously may explain why the rate is larger in this solvent than in carbon tetrachloride.

As has been pointed out,[4] the extraction of beryllium perchlorate in the aqueous phase increases with the increase in the aqueous perchlorate concentration. The first-order dependence of the rate on the perchlorate concentration is probably due to the extraction of the mixed species, $\mathrm{Be(NO_3, ClO_4)}$ or $\mathrm{Be(Cl, ClO_4)}$, while the second-order dependence is probably due to the extraction of the perchlorate, $\mathrm{Be(ClO_4)_2}$. These ion-pairs may react in the organic phase and form TTA complexes by exchanging the inorganic anion with the TTA anion.

It is remarkable that the extraction reaction in the MIBK systems is always dependent on the first order of $[A^-]$ and not on $[\mathrm{HA}]_{org}$. Until now, no information has been available about the dissociation constant of TTA and the hydrogen-ion concentration in the MIBK phase in an equilibrium with the aqueous phase, and the authors have no knowledge whether or not a portion of the TTA in the MIBK phase is in the dissociated anion, or whether or not the concentration of this TTA fraction, $[A^-]_{org}$, is proportional to that in the aqueous phase, $[A^-]$. However, it may be reasonable to assume that a part of weak acid, TTA, the concentration of which is more than two orders higher than that in the aqueous phase, is also in the dissociated anionic form or is in other forms such as NaA, than the HA form, and that this fraction of TTA reacts with the extracted beryllium ion-pairs in the MIBK phase. When this assumption is accepted, the enhancement of the rate of extraction can be explained as occurring when the rate of this 1: 1 complex formation in the organic phase is larger than that in the aqueous phase. It is also reasonable that the complex formation in the organic phase is not assumed in the carbon tetrachloride system, for in this nonpolar solvent, not only does the extraction of the ion-pairs occur, but also the concentration of the TTA anion, which is indispensable for the complex formation in the organic phase, is probably very low.

Eigen,[18] has pointed out that Be^{2+}, Al^{3+}, and other

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[18] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

strongly-hydrolysing trivalent metal ions show quite a slow substitution rate of water with a ligand and that the splitting of a water molecule (hydrolysis) is faster than the substitution. Thus, a ligand specificity (basicity) on the rate may be observed in these metal ions. The characteristic rate constants for water substitution in the inner coordination sphere of Be^{2+} given by Eigen is $10^{1.5}$—$10^{2.5}$ (sec^{-1}) or $10^{3.3}$—$10^{4.3}$ (min^{-1}) (Fig. 5 in Ref. 19). The reaction constants for the 1 : 1 beryllium-TTA complex in the carbon tetrachloride systems in the present study (which is independent of the concentration of the perchlorate ion and can thus be assumed to take place in the aqueous phase) are $10^{4.3}$ and $10^{4.5}$ (min^{-1}). As the pH in the present study is 2.0—3.5 and the metal concentration is very low, the hydrolysis of this metal ion may not be important.[19]

As has been pointed out, the distribution of the TTA in the organic phase into the aqueous phase has been recognized as a slow reaction. In the present study, TTA was initially added to the organic phase and beryllium(II) was initially added to the aqueous phase, and the agitation was started just after the two phases had come in contact in the vessels. When the distribution of this TTA into the aqueous phase in which the reaction between Be^{2+} and A^- occurs is very slow, the concentration, $[A^-]$, at a certain pH should be lower than the value at the equilibrium if the agitation has been carried out for such a short interval as 10 min or less, as in the present experiments. When this occurs, the apparent value of the rate constant, k, calculated by using the value of K_D at the equilibrium should be smaller than the true value, which could be calculated if the K_D value after such a short interval (this value of K_D should be larger than that at the equilibrium) were available. However, as has been described, the present authors have observed that the rate of the extraction of beryllium(II) obtained when the TTA has been distributed between the two phases before the addition of the metal ions is identical with the values obtained when the distribution of TTA is started at the same time as the metal extraction. The authors cannot yet explain why the results of these two series of experiments agree with each other. Further information seems to be necessary before a full explanation of this situation can be given.

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[19] L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society spec. pub. No. 17 (1964); H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, **10** 985 (1956); G. Schwarzenbach, *Pure Appl. Chem.*, **5**, 377 (1962).