A Kinetic Study of the Isotopic Exchange of Indium between the Indium Ion and its N-2-Hydroxyethylethylenediamine-N, N′, N′-triacetate Complex in an Acid Solution

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Since tervalent gallium, indium and thallium give co-ordination compounds of a typical d^{10} structure, a kinetic study of the isotopic exchange of these elements, which has been left unchallenged, will provide useful information on the nature of the so-called outer co-ordination compounds. With the aid of a tracer study with indium-114 m, the present authors previously found[1] that exchange of indium proceeds with a measurably slow rate between the indium ion and its *N*-2-hydroxyethylethylenediamine-*N*, *N′*, *N′*-triacetate (written as EDTA-OH henceforth) complex in an acid solution and that the rate depends on the hydrogen ion concentration. The rate is immeasurably small in a neutral solution. It appears to increase in a basic solution of a pH more than 10, where indium remains in the aqueous phase only in the presence of a large amount of a masking agent such as citrate and tartrate. This paper deals with the kinetics of this exchange reaction, especially in a pH range from 2 to 3.5, where the exchange rate is proportional to the hydrogen ion concentration.

Results

According to McKay[2], the exchange constant is expressed by

$$R=-2.303\cdot\frac{ab}{(a+b)}\cdot\frac{\log(1\text{-}F)}{t}$$

where *a* and *b* stand for the molar concentration of the indium ion and its EDTA-OH complex respectively, *t* is the lapse of time, and *F* the fraction of the reaction. First, the relationship between *R*, and *a* and *b* was examined, the results being shown in Figs. 1 and 2 respectively. It is clearly seen that *R* is proportional to the concentration of the complex (*b*), regardless of the presence of a buffer, whereas it is independent of the concentration of the indium ion (*a*). Hence, the reaction constant *k* is given by *R*/*b* and has a dimension T^{-1}. The pH dependence was tabulated in Table I in Ref. 1 and is also shown in Fig. 3, in which a linear relationship is seen in a pH range from 2.5 to 3.2. In a more acid solution, the exchange proceeds too fast to permit a precise kinetic study, but there appears to be an appreciable deviation from the linear relationship.

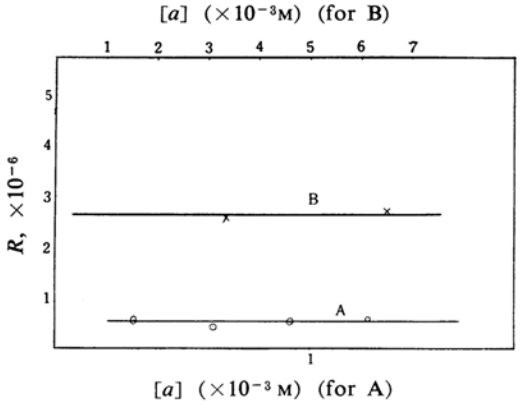

Fig. 1. Relationship between the concn. of In^{3+} and the exchange const. *R*.
A : ⊙ ; μ, 0.2 (KNO_3) ; *T*, 25°C ; pH, 2.93 ; acetate buffer, 0.043 M ; [*b*], 0.24 $\times10^{-3}$ M
B : × ; μ, 0.2 (KNO_3) ; *T*, 25°C ; pH, 3.15 ; citrate buffer, 0.033 M ; [*b*], 0.71 $\times10^{-3}$ M

TABLE I. INFLUENCE OF THE IONIC STRENGTH

μ	pH	$k/[H^+]$ l./mol./sec.
0.042	2.35	1.6×10^{-2}
0.092	2.45	1.7×10^{-2}
0.300	2.63	2.4×10^{-2}

at 25°C ; acetate buffer 0.042 M

It is rather noticeable that the exchange constant *R* increased by the use of a buffering agent such as citrate and acetate. Especially in the presence of citrate, *R* increased linearly with an increase in the concentration of the dihydrogen citrate ion, as is shown in Fig. 4. On the other hand, acetate affected the *R* value to a much less extent.

The temperature dependence of *R* is shown in Fig. 5, in which $\log k/[H^+]$ is plotted against $1/T$ (*T*, absolute temperature). The Arrhenius

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[1] K. Saito and M. Tamura, *J. Inorg. Nucl. Chem.*, **13**, 334 (1960).

[2] H. A. C. McKay, *Nature*, **142**, 997 (1938).

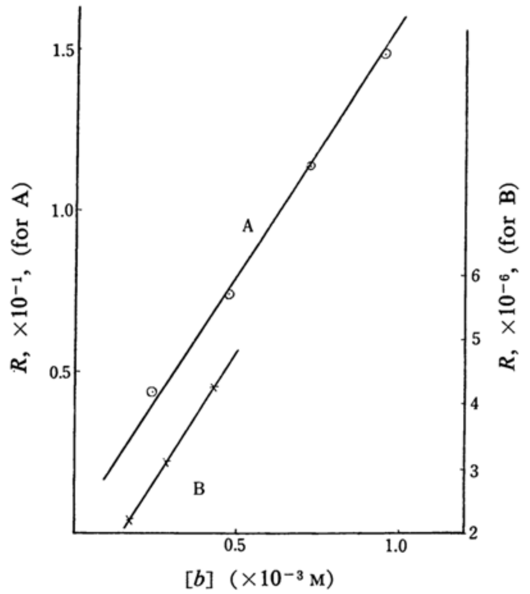

Fig. 2. Relationship between the concn. of In-EDTA-OH and the exchange const. R.
A: ⊙; μ, 0.2 (KNO_3); T, 25°C; pH, 3.05; acetate buffer, 0.05 M; [a], 0.97 $\times 10^{-3}$ M
B: ×; μ, 0.2(KNO_3); T, 25°C; pH, 2.91; without buffer; [a], 0.32×10^{-3} M

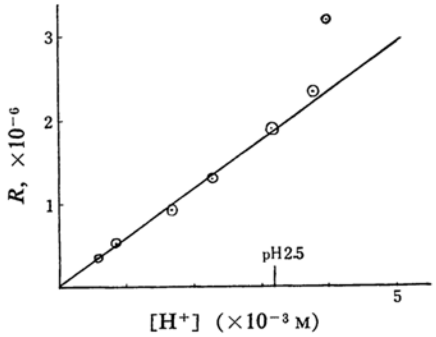

Fig. 3. pH Dependence of the exchange constant.
μ, 0.2 (KNO_3); T, 25°C; without buffer; [a], 1.51×10^{-3} M; [b], $0.55\times{}^{-3}$ M

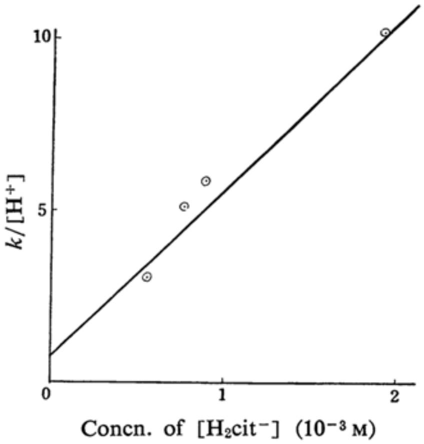

Fig 4. Effect of the concentration of the citrate ion upon the exchange constant.

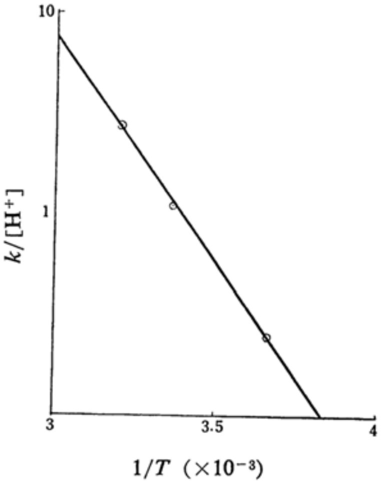

Fig. 5. Temperature dependence of the exchange constant.
μ, 0.2 (KNO_3); pH, 3.01; without buffer; [a], 1.51×10^{-3} M; [b], 0.55×10^{-3} M

TABLE II. INFLUENCE OF THE CHLORIDE ION

Concn. of KNO_3 M	Concn. of KCl M	pH	$k/[H^+]$ 1./mol./sec.
0.222	0	2.57	0.96×10^{-2}
0.218	0.0037	2.68	0.92×10^{-2}
0.204	0.0185	2.65	1.24×10^{-2}
0	0.222	2.59	$6.6\ \times 10^{-2}$

[μ, 0.222; 25°C; without buffer]

activation energy was calculated to be 11 kcal. per mole. The influence of the ionic strength is tabulated in Table I, the μ being changed with potassium nitrate. The influence appears to be very small. When potassium chloride was used in place of nitrate, the exchange rate significantly increased, as is seen in Table II.

Discussion

Only a little information is available concerning the mechanism of the isotopic exchange of the co-ordination compounds of EDTA and its analogues, especially of those with tervalent metal ions. Jones and Long[3] reported that the isotopic exchange of iron between the ferric ion and its EDTA complex was dependent on the pH value in a complexed manner in the range from 1 to 2.5 and that at least three separate kinetic terms participated in the exchange. In the case of indium, the kinetic

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[3] S. S. Jones and F. A. Long, *J. Phys. Chem.*, 56, 251 (1952).

term appears to be much simpler under the given conditions. The dissociation of the indium EDTA-OH complex must play an important role in determining the exchange rate, because the concentration of the uncomplexed indium does not affect the rate in either the presence or the absence of a buffering agent which is capable of forming complex ions with indium. The pH dependence of the k value suggests that the indium EDTA-OH complex is in a protonated form in the given pH range, and its dissociation appears to be the rate-determining step. (Z, EDTA-OH radical)

$$[{}^*\mathrm{InZ}\cdot\mathrm{OH_2}] + \mathrm{H^+} \rightleftharpoons [{}^*\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ \quad \text{(Equil.)}$$

$$[{}^*\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ + \mathrm{In^{3+}}\cdot\mathrm{OH_2} \rightleftharpoons [\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ + {}^*\mathrm{In^{3+}}\cdot\mathrm{OH_2}$$

$$[\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ \rightleftharpoons [\mathrm{InZ}\cdot\mathrm{OH_2}] + \mathrm{H^+} \quad \text{(Equil.)}$$

The second step can also be written as follows:

$$[{}^*\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ \xrightarrow{\text{slow}} {}^*\mathrm{In^{3+}}\cdot\mathrm{OH_2} + \mathrm{HZ^{2-}}$$

$$\mathrm{HZ^{2-}} + \mathrm{In^{3+}}\cdot\mathrm{OH_2} \xrightarrow{\text{fast}} [\mathrm{InHZ}\cdot\mathrm{OH_2}]^+$$

The dissociation of the complex $[\mathrm{InHZ}\cdot\mathrm{OH_2}]^+$ may presumably involve the rupture of one or two of the In-O linkage as the first step, which eventually results in the release of the radioactive indium ion. The free protonated EDTA-OH radical HZ^{2-} could combine with the hydrated indium ion at a greater rate than that of the dissociation. Since neither the equilibrium constant of the protonation nor the rate constant of the rate-determining step is known, further quantitative elucidation must be abundoned. Nevertheless, it is a rather marked fact that the rate is independent of the concentration of one of the components to be exchanged.

When the hydrogen ion concentration is higher, protonation could occur on two acetate radicals of the complex side by side,

$$[{}^*\mathrm{InHZ}\cdot\mathrm{OH_2}]^+ + \mathrm{H^+} \rightleftharpoons [{}^*\mathrm{InH_2Z}\cdot\mathrm{OH_2}]^{2+} \quad \text{(Equil.)}$$

the diprotonated complex undergoing a similar dissociation at a comparable or a greater rate. Deviation from the linear relationship seen in Fig. 3 could be thus accounted for by taking the participation of the diprotonated complex into consideration. If such a dissociation were regarded as the rate-determining step, it would be rather reasonable to assume that the Arrhenius activation energy is as low as 11 kcal. per mole and that the change in ionic strength affects the rate to a less extent.

Nothing decisive can be stated concerning the role of an acidic radical such as citrate and acetate. It has already been established that the co-ordinated water in an indium EDTA complex can be replaced by an acidic component such as chloride and bromide[4]. It would not be unusual if a similar replacement occurred in an aqueous solution of an indium EDTA-OH complex.

$$[\mathrm{InZ}\cdot\mathrm{OH_2}] + \mathrm{H_2cit^-} \rightleftharpoons [\mathrm{InZ}\cdot\mathrm{H_2cit}]^- + \mathrm{H_2O}$$

When it is assumed that the dissociation of the protonated acido complex proceeds faster than that of the aquo complex, the relationship shown in Fig. 4 will be accounted for. Such an explanation expresses, with a little different shade of meaning, the idea that the dissociation of the protonated complex is accelerated in the presence of an organic oxy-acid, which can pull the indium ion to form a complex. The extent to which the dissociation is facilitated depends on the nature and the concentration of the organic compound, citrate exerting a greater influence than acetate. Such an effect must be reflected in the change in Arrhenius activation energy and in the influence of the ionic strength. The accuracy of an isotopic tracer study, however, is not high enough to make such a change clear. The influence of the chloride ion indicated in Table II can be similarly understood. Although the chloride ion forms chloro complexes with indium ions in an acid solution, the formation constant is so small that its effect is appreciable only in the presence of a large amount of the chloride ion.

A gallium complex of EDTA-OH also undergoes isotopic exchange of gallium with the gallium ion in a more acid region[5]. The rate depends on the hydrogen ion concentration to a more marked extent and will be compared with the present result elsewhere.

Experimental

Preparation and Properties of the Complex.— Since this complex is a new compound, its preparation and properties will be described briefly. Indium was dissolved in dilute nitric acid, the hydroxide precipitated with aqueous ammonia solution, centrifuged, washed and boiled with EDTA-OH, slightly less in amount to the equivalent. When the mixture became almost transparent, the solution was filtered to remove the excessive indium hydroxide, evaporated, and treated with ethanol to give prismatic crystals of aquo *N*-2-hydroxyethylethylenediamine-*N*, *N′*, *N′*-triacetato indium monohydrate which lost 8.78% of water at 110°C, corresponding to two moles per mole of the complex (calcd., 8.46%).

Found: N, 6.43; In, 26.78. Calcd. for $C_{10}H_{15}O_7N_2In\cdot 2H_2O$: N, 6.62; In, 26.94%.

When titrated with a sodium hydroxide solution, an aqueous solution of this complex gave a titration curve as shown in Fig. 6, from which the apparent

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[4] K. Saito and H. Terrey, *J. Chem. Soc.*, **1956**, 4701.

[5] K. Saito and M. Tsuchimoto, *J. Inorg. Nucl. Chem.* in press (appear in early issue, 1962).

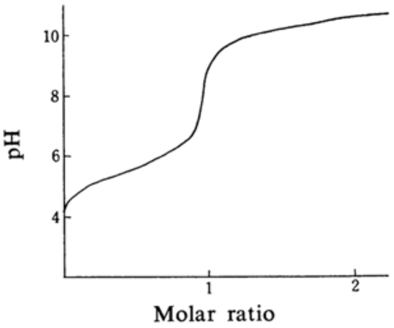

Fig. 6. Titration of [In·EDTA-OH·H_2O]·H_2O with sodium hydroxyde. [InZ·OH_2]H_2O, 0.2×10^{-4} M; $\mu = 0.05$ (KNO_3); 25°C

dissociation constant was calculated to be approximately 1.5×10^{-6} at 25°C in an ionic strength $\mu=0.05$. This value is significantly greater than that of the indium EDTA complex (1.6×10^{-9})[4], indicating that the co-ordinated water is bound to indium more firmly than in the latter complex. In an acid solution as used in the present study, the dissociation of the co-ordinated water can be ignored. By the use of an irradiated unit In-114 m, a radioactive indium EDTA-OH comlex of a due specific activity was obtained crystalline.

Procedure for Kinetic Runs.—An aqueous solution (200 ml.) of indium nitrate of a known pH value, containing potassium nitrate and the buffer, was mixed in a thermostat with a radioactive indium EDTA-OH solution (100 ml.) of the same pH value. A 25 ml. portion was taken out at certain intervals and treated with 8-quinolinol in ethanol (0.5%, 1 ml., less than the equivalent amount of indium nitrate), and the pH was adjusted to about 3.2 with brom phenol blue as indicator. The precipitate was filtered off through a sintered glass filter plate No. 4, washed with water, dried at 110°C, weighed and submitted to radioactivity measurement. The molar ratio of 8-quinolinol to indium remained unchanged when the precipitate was formed in the presence of an excess of indium. The separation was satisfactorily effected within 2 min., and no appreciable heterogeneous isotopic exchange was observed between the precipitate and the solute under the given conditions. The zero time exchange was negligible.

Measurement of Radioactivity.—A scintillation spectrometer with a sodium iodide crystal (diameter, 4.8 cm.; thickness, 4.8 cm.) was used with due accessories. The weighed filter plate was covered with cellotape and fixed on a methylmethacryllate plate (thickness, 1 cm.) which absorbed 1.98 MeV. β-rays of ^{114}In. The plate was placed upon the scintillator crystal, and the photo- and the Compton electrons coming from γ-rays of In-114 m were counted, the less distinctive back-scattering peak being biased by a pulse-height analyzer. The overall counting efficiency was about 20%. The integrated counting rate increased linearly with the increase in the amount of radioactive indium, and the specific counting rate of the precipitate was calculated from the weighed amount of the indium 8-oxyquinolinol complex.

All the chemicals were of reagent grade. Indium nitrate was prepared from metallic indum of a purity more than 99.99%. The pH value was measured with a glass electrode, the error being less than 0.02 pH.

Summary

1) The isotopic exchange of indium between the indium ion and its EDTA-OH complex was kinetically studied in an acid solution, indium-114 m being used as tracer.

2) Separation of the indium ion from its EDTA-OH complex was satisfactorily carried out with 8-quinolinol (oxin) at a pH about 3, and no appreciable heterogeneous exchange was observed between the precipitate and the solute.

3) The exchange constant R was proportional to the concentration of the complex, the hydrogen ion and the ions such as dihydrogen citrate, but was independent of the concentration of the indium ion. It was affected by the ionic strength to a less extent, and the Arrhenius activation energy was 11 kcal. per mole.

4) A plausible reaction mechanism was postulated on the basis of the kinetic data. The dissociation of the protonated indium EDTA-OH complex appears to be the rate-determining step.

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