BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2681—2684 (1966)

Studies of Scandium in Various Solutions. III. The Solvent Extraction and Complex Formation of Scandium(III) with Acetylacetone and Thenoyltrifluoroacetone

By Tatsuya SEKINE, Akira KOIZUMI and Mitsuo SAKAIRI

Department of Chemistry, Tokyo College of Science, Kagurazaka, Shinjuku-ku, Tokyo

(Received April 13, 1966)

The distribution of scandium(III) at a tracer concentration was determined between chloroform with acetylacetone or thenoyltrifluoroacetone and 0.1 M aqueous perchlorate solutions at 25°C. The change in the distribution ratio of the metal ion with the change in the chelating acid concentration or with the change in the hydrogen-ion concentration was explained in terms of the extraction of the tris chelate complexes into the organic phase and the formation of the primary complexes in the aqueous phases. The equilibrium constants in these systems were determined graphically, by a curve-fitting method to be as follows:

$$K_{ex}=[ScA_3]_{org}[H^+]^3/[Sc^{3+}][HA]^3_{org}$$
$$K_1=[ScA^{2+}]/[Sc^{3+}][A^-]$$

HA	Acetylacetone	Thenoyltrifluoroacetone
$\log K_{ex}$	−6.35	−1.30
$\log K_1$	8.3	7.1

Acetylacetone (AA) and thenoyltrifluoroacetone (TTA) in various organic solvents have been used for the extraction of scandium(III) in aqueous solutions.[1-5]

For the present paper, the authors studied the distribution of trace amounts of scandium(III) between chloroform solutions of AA or TTA and aqueous solutions of 0.1 M (Na, H)ClO$_4$ at 25°C; they also determined the extraction constants and the stability constants of scandium(III) aqueous complexes with these β-diketones.

Statistical Treatment

The distribution equilibrium of scandium(III) in an aqueous phase into an immiscible organic phase with an organophilic chelating acid, HA, may be described as follows:

$$Sc^{3+} + 3HA(org) \rightleftarrows ScA_3(org) + 3H^+ \qquad (1)$$

$$K_{ex} = [ScA_3]_{org}[H^+]^3/[Sc^{3+}][HA]^3_{org} \qquad (2)$$

In the equations, the subscript *"org"* denotes a species in the organic phase, while the absence of a subscript denotes a species in the aqueous phase.

The concentration of scandium in the two phases may be determined radiometrically, and the net distribution ratio may be defined as:

$$D = [Sc(III)]_{org,total}/[Sc(III)]_{total} \qquad (3)$$

When it is assumed that (i) scandium(III) exists in the aqueous phase only as Sc^{3+} or as the chelate complexes, ScA^{2+}, ScA$_2$$^+$,···, and that (ii) scandium(III) exists in the organic phase only as the neutral tris chelate complex, ScA$_3$, the net distribution ratio in Eq. 3 may be described as:

$$D = [ScA_3]_{org}/([Sc^{3+}]+[ScA^{2+}] + [ScA_2{}^+]+\cdots) \qquad (4)$$

The statistical treatment of the distribution ratios may then be carried out by applying the law of mass action.[6]

The complex formation equilibria in the aqueous phase may be described as:

$$Sc^{3+} + nA^- \rightleftarrows ScA_n{}^{3-n} \qquad (5)$$

$$\beta_n = [ScA_n{}^{3-n}]/[Sc^{3+}][A^-]^n \qquad (6)$$

By introducing Eqs. 2 and 6 into Eq. 4, the following equation is obtained:

$$D[H^+]^3[HA]^{-3}_{org} = K_{ex}/(1+\beta_1[A^-] + \beta_2[A^-]^2+\cdots) \qquad (7)$$

The chelating acid is distributed between the two phases as:

$$HA \rightleftarrows HA(org) \qquad (8)$$

$$K_D = [HA]_{org}/[HA] \qquad (9)$$

---

[1] J. Starý and E. Hladký, *Anal. Chim. Acta,* **28,** 227 (1963).

[2] A. M. Poskanzer and B. M. Foreman, *J. Inorg. Nucl. Chem.,* **16,** 323 (1961).

[3] E. Sheperd and W. W. Meinke, *U. S. Atomic Energy Comm. Report, AECU*-3879.

[4] T. C. Rains, H. P. House and O. Menis, *Anal. Chim. Acta,* **22,** 315 (1960).

[5] T. Sekine, *Proceedings 7th International Conference on Coordination Chemistry,* **7J4**, Stockholm (1962).

[6] J. Rydberg, *Acta Chem. Scand.,* **4,** 1503 (1950).

The chelating acid may dissociate in the aqueous phase as:

$$HA \rightleftarrows H^+ + A^- \tag{10}$$

$$K_a = [H^+][A^-]/[HA] \tag{11}$$

When a certain volume of an organic phase with the chelating acid at an initial concentration, $[HA]_{org,\,initial}$ is equilibrated with an aqueous phase of the same volume, the following equation holds:

$$[HA]_{org,\,initial} = [HA]_{org} + [HA] + [A^-] \tag{12}$$

From Eqs. 9, 11 and 12, the following equations can be introduced:

$$[A^-] = [HA]_{org,\,initial}/(1 + K_a{}^{-1}[H^+] + K_D K_a{}^{-1}[H^+]) \tag{13}$$

$$[HA]_{org} = [HA]_{org,\,initial}/(1 + K_D{}^{-1} + K_D{}^{-1}K_a[H^+]^{-1}) \tag{14}$$

Thus, the values $[A^-]$ and $[HA]_{org}$ at the equilibrium can be calculated from the initial concentration of the chelating acid in the organic phase, the hydrogen ion concentration, and the two equilibrium constants, K_D and K_a. The extraction constant and the stability constants of the scandium complexes may then be determined by introducing these values into Eq. 7.

Experimental

Reagents.—Scandium-46 was obtained from the New England Nuclear Co., U. S. A., as a hydrochloric acid solution. This was diluted with 0.1 M perchloric acid and used as the stock solution. All of the reagents were of a reagent grade. Acetylacetone and thenoyltrifluoroacetone were obtained from Dojindo & Co., Ltd. The sodium perchlorate was recrystallized two times from water. The chloroform was washed three times with water. The other reagents were used without further purification.

Procedures.—All of the procedures were carried out in a thermostatted room at 25±0.5°C. Stoppered glass tubes (volume: 20 ml.) were employed to equilibrate the two phases. The tracer solution, a buffer solution, a 0.1 M sodium perchlorate solution, and finally a chloroform solution of acetylacetone or thenoyltrifluoroacetone were placed in the tubes. Sulfanilate or pyridine (the initial concentration was 0.01 M) was used as the buffer. In some experiments, the scandium tracer in the aqueous phase was first extracted with the chelating acid into the organic phase and the scandium in the organic phase was back-extracted into fresh aqueous solutions. The initial volume of the two phases was always 5.0 ml., and the initial concentration of scandium in either the aqueous or the organic phase was 6×10^{-5} M.

The two phases in the tubes were agitated by a mechanical rotator for more than one hour and centrifuged at 2000 r. p. m. for three minutes. A 2-ml. portion was then pipetted from both the phases and transferred into small test tubes. The γ-radioactivity of the solutions was measured with a well-type (NaI) scintillation counter. A small portion was also taken from the aqueous phase, and the hydrogen ion concentration was measured potentiometrically, using 0.010 M perchloric acid +0.09 M sodium perchlorate as the standard of $-\log [H^+]=2.000$.

Results

Figures 1 and 2 give the distribution ratio of scandium(III) in the acetylacetone (AA) systems or the thenoyltrifluoroacetone (TTA) systems at various hydrogen ion concentrations. Figure 1 shows the $\log D$ vs. $-\log [H^+]$ plot when the initial concentration of the chelating acids in the organic phase is 0.100 M while Fig. 2 gives the $\log D[H^+]^3$ vs. $\log [HA]_{org}$ plot when the initial concentration of the chelating acid is different. In Fig. 1, the open circles give the data obtained when the tracer was initially added to the organic phase. The straight line of slope three in the figures are the calculated distribution curves obtained from the extraction constants, K_{ex}, in Table II.

The K_D and K_a values for AA and TTA which appear in the literature were introduced into Eqs. 13 and 14. The equations thus obtained are given in Table I.

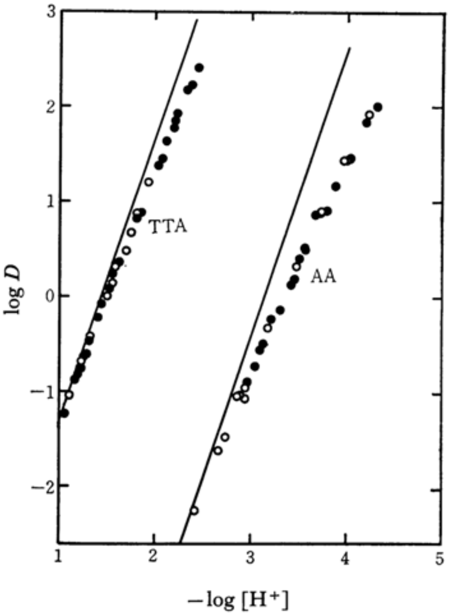

Fig. 1. Distribution of Sc(III) between chloroform with 0.1 M (initial concentration) chelating acid and 0.1 M (Na, H)ClO$_4$ at 25°C as a function of $-\log [H^+]$.

Open circles; extraction of Sc(III) in the aqueous phase into the organic phase.

Closed circles; back-extraction of Sc(III) in the organic phase into the aqueous phase.

The straight line for the TTA plot is $\log D = -3\log [H^+] - 4.32$ and that for the AA plot is $\log D = -3\log [H^+] - 9.44$.

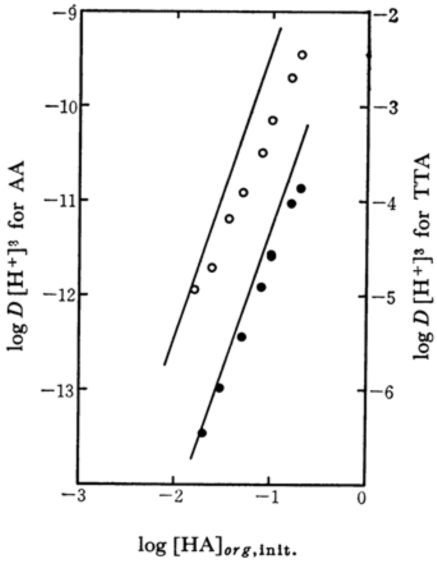

Fig. 2. Distribution of Sc(III) between chloroform with chelating acid and 0.1 M (Na, H)ClO_4 as a function of the initial chelating acid concentration in the organic phase.
Open circles; acetylacetone (AA)
Closed circles; thenoyltrifluoroacetone (TTA)

TABLE I. CONCENTRATION OF CHELATING ACIDS IN THE TWO PHASES AT 25°C
Organic phase; chloroform
Aqueous phase; 0.1 M (H, Na)ClO_4

(A) HA=Acetylacetone

$\log K_D = 1.37$(6) $\log K_a = -8.82$(6)

$[A^-] = [HA]_{org,initial}/(1+1.56\times10^{10}[H^+])$

$[HA]_{org} = [HA]_{org,initial}/(1.04+6.79\times10^{-11}[H^+]^{-1})$

(B) HA=Thenoyltrifluoroacetone

$\log K_D = 1.84$(5) $\log K_a = -6.23$(7)

$[A^-] = [HA]_{org,initial}/(1+1.18\times10^{8}[H^+])$

$[HA]_{org} = [HA]_{org,initial}/(1.01+8.51\times10^{-9}[H^+]^{-1})$

TABLE II. EQUILIBRIUM CONSTANTS FOR THE EXTRACTION AND THE COMPLEX FORMATION OF SCANDIUM(III) AT 25°C
Organic phase; chloroform
Aqueous phase; 0.1 M (H, Na)ClO_4
$K_{ex} = [ScA_3]_{org}[H^+]^3/[Sc^{3+}][HA]^3_{org}$
$K_1 = [ScA^{2+}]/[Sc^{3+}][A^-]$

HA	Acetylacetone	Thenoyltrifluoroacetone
$\log K_{ex}$	-6.35	-1.30
$\log K_1$	8.3_2	7.1_4

Figures 3 and 4 give $\log D\,[H^+]^3[HA]^{-3}_{org}$ vs. $\log[A^-]$ plot calculated from the data in Figs. 1 and 2 and Table I.

From Eq. 7, the following equation is obtained:

$$\log D[H^+]^3[HA]^{-3}_{org} = \log K_{ex} - \log(1+\beta_1[A^-] + \beta_2[A^-]^2+\cdots) \qquad (15)$$

Equation 15 shows that the $\log D\,[H^+]^3[HA]^{-3}_{org}$ vs. $\log[A^-]$ plot will be found to fit one of the family of standard curves[8-10]:

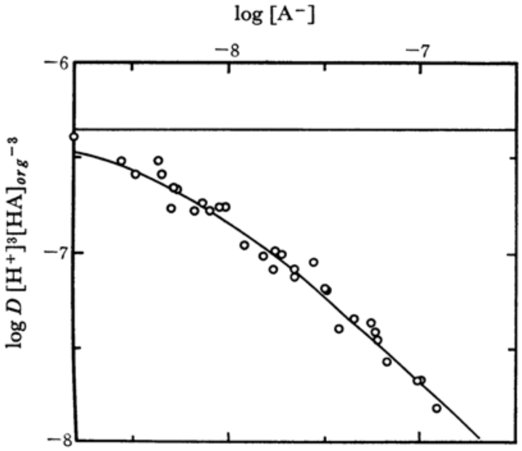

Fig. 3. Change in the extraction constant of Sc(III) with AA as a function of the concentration of the dissociated chelating acid in the aqueous phase.
The solid curve shows $\log D\,[H^+]^3[HA]^{-3}_{org}$ vs. $-\log(1+2.0\times10^8[A^-])$.

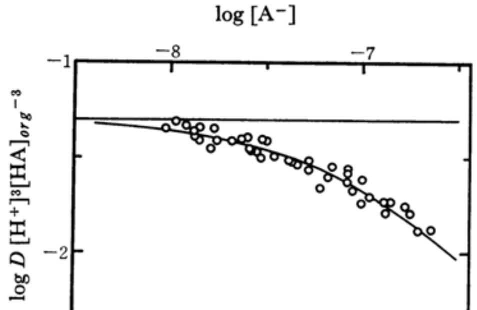

Fig. 4. Change in the extraction constant of Sc(III) with TTA as a function of the concentration of the dissociated chelating acid in the aqueous phase.
The solid curve shows $\log D\,[H^+]^3[HA]^{-3}_{org}$ vs. $-\log(1+1.3\times10^7[A^-])$.

---

7) J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).

8) L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).

9) F. J. G. Rossotti and H. Rossotti, "The Determination of Stability Constants in Solution," McGraw-Hill Book Co., Inc., New York (1961).

10) T. Sekine and Y. Hasegawa, This Bulletin, **39**, 240 (1966).

$$\left.\begin{aligned} X &= \log v \\ Y &= -\log(1+\sum_{n=1}^{n} p_n v^n) \end{aligned}\right\} \qquad (16)$$

After several trials, it was found that both of the plots in Figs. 3 and 4 fit the standard curve $X=\log v$; $Y=\log(1+v)$. The best-fit constants obtained from the curve-fitting are listed in Table II. The solid curves in Figs. 3 and 4 show the statistical curves calculated from these constants.

Discussion

In the present study, the aqueous phase was always 0.1 M (Na, H)ClO_4, and the hydrogen ion concentration was larger than 10^{-4} M. Therefore, the hydrolysis of Sc^{3+} in the aqueous phase may not be very much, because the hydrolysis constant of scandium in 0.1 M ($NaClO_4$) at 25°C was reported to be $[ScOH^{2+}][H^+][Sc^{3+}]=10^{-4.74}$.[11] The formation of polynuclear complexes may be negligible because the total concentration of scandium in the aqueous phase is less than 6×10^{-5} M; thus, Assumption i described in the previous section, may be valid in the present systems. The scandium complexes in the organic phase may be in the ScA_3 form in both the AA and TTA systems, because no remarkable deviation of the plot in Figs. 2 to 4 is observed even when the organic concentration of the chelating acid is larger or smaller than 0.1 M (cf. Ref. 5). Thus, it may be concluded that Assumption ii is also valid in the present systems. The distribution ratios obtained both by the extraction from the aqueous phase and by the back-extraction from the organic phase agree within the range of experimental error; this may indicate that the distribution equilibrium of scandium is established under the present experimental conditions.

The plots in Figs. 3 and 4 scatter somewhat from the fitted curve given by a solid curve, and as a result the limit of the error of the constants will be rather large. Therefore, the $\log K_{ex}$ are given to three figures, while the $\log\beta_1$ are given to only two figures.

Starý[12] listed the extraction constants of scandium(III) into benzene with AA ($\log K_{ex}=-5.83$) and TTA ($\log K_{ex}=-0.77$).

Wakahayashi, Oki, Omori and Suzuki[13] studied the distribution of scandium(III) chelate into various solvents. They reported that the net distribution ratio of scandium(III) between chloroform and 0.1 M (Na, H)ClO_4 was $\log D=0.41$ for the AA chelate and $\log D=-0.54$ for the TTA chelate when $-\log[A^-]=7.80$. Their figure for the TTA chelate seems to agree with the present results, but their value for the AA chelate seems to be a little higher. They did not give any constants for the complex formation in the aqueous phase.

Izatt and his co-workers[14] gave the stability constants for the AA complexes of scandium(III) at zero ionic strength and at 30°C as $\log K_1=8.0$ and $\log K_2=7.2$ ($\log\beta_2=15.2$). The $\log K_1$ in their work is of the same order as that in the present work, but the formation of a secondary complex of the $\log\beta_2$ around 15 can not be concluded from the present results (cf. Fig. 3).

No stability constant for scandium TTA complexes seems to have been reported.

Part of this work was carried out at the Laboratory of Nuclear Chemistry, the Institute of Physical and Chemical Research, Tokyo. The authors are very grateful to Professor Nobufusa Saito, the head of that Laboratory. The authors are also very grateful to Mr. Ichiro Kobayashi and Mr. Ichiro Sakamoto of the present laboratory for their experimental aid.

---

[11] M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **101**, 39 (1954).

[12] J. Starý, "The Solvent Extraction of Metal Chelates," Pergamon Press Ltd., Oxford (1964), p. 42.

[13] T. Wakahayashi, S. Oki, T. Omori and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2265 (1964).

[14] R. M. Izatt, W. C. Fernerius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59** 170 (1955).