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Studies of Scandium in Various Solutions. I. An Ion-Exchange Study of Scandium(III) Chloride and Nitrate Complexes

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The complex formation of scandium(III) with chloride and nitrate ions has been investigated at 25°C. Scandium-46 was employed in conjunction with a cation-exchange resin (Dowex 50W X-12, 100—200 mesh) in the H$^+$-form and the ionic strength was maintained at 4.0 M with perchloric acid. The stability constants have been obtained graphically by a curve-fitting method and the following results were obtained.

$$\beta_n=[\mathrm{ScL}_n{}^{3-n}]/[\mathrm{Sc}^{3+}][\mathrm{L}^-]^n$$

	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
Chloride	-0.12	-0.84	-1.40
Nitrate	0.28	-0.28	—

The chemical properties of trivalent scandium are known to be somewhat similar to those of trivalent lanthanides and yttrium. Scandium(III) is often included among the rare earth elements.

However, its smaller ionic size and its higher electronegativity sometimes make this ion different from the other rare earth ions. Actually, the scandium ion in solutions is believed to be a better acceptor of various complex-forming ligands than the other rare earth ions.

This series will report on our studies of the chemical behavior of scandium in various solutions. Paper I will report on a study of scandium(III) complexes with chloride or nitrate ions.

The complex formation of scandium(III) in concentrated hydrochloric acid and nitric acid may easily be supposed from the ion-exchange adsorption or the solvent extraction of this ion from these acid media.[1-3] However, because of the low stability of these complexes, no quantitative data on the stabilities have been presented until quite recently.

The stability constants of scandium(III) chloride complexes were first studied by Paul[4] by potentiometry in perchlorate solutions at 0.5 M. The stability constants were also determined by Reed, Sutton and Morris[5] from an ion-exchange study in perchloric acid media at 0.691 M. However, no report on the stability constants of scandium(III) nitrate complexes seems to have been presented.

In the present work, the cation-exchange equilibria of scandium(III) at a tracer concentration were determined radiometrically at 25°C between an ion-exchange resin and 4.0 M H(Cl, ClO$_4$) or 4.0 M H(NO$_3$, ClO$_4$). These ionic media were chosen in order to make it possible to compare the results with those on trivalent lanthanide and americium complexes obtained in other work.[6]

The stability constants were determined graphically by a curve-fitting method[7] from the decrease in the ion-exchange adsorption with the increase in the ligand concentration in the aqueous phase.

Statistical Treatment

The distribution ratio of scandium(III) in equilibrium between a cation-exchange resin phase and an aqueous phase is defined as:

$$\left.\begin{aligned} D&=\frac{[\mathrm{Sc(III)}]_\mathrm{R}}{[\mathrm{Sc(III)}]}\\ &=\frac{\mathrm{Sc(III)\ per\ g.\ resin}}{\mathrm{Sc(III)\ per\ ml.\ solution}}\end{aligned}\right\} \tag{1}$$

where the subscript "R" denotes a species in the resin phase.

This can be calculated by radioactivity measurements as:

$$D=(T-vA)/(G\times A) \tag{2}$$

where T is the total radioactivity in the whole

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[1] K. A. Kraus and F. Nelson, "Proceedings International Conference on Peaceful Uses of Atomic Energy Geneva, 1955, Vol. VII," United Nations Publication, New York (1956), p. 837.

[2] D. F. Peppard, G. W. Mason and J. L. Maier, *J. Inorg. Nucl. Chem.* **3**, 215 (1956).

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[4] A. D. Paul, *J. Phys. Chem.*, **66**, 1248 (1962).

[5] G. L. Reed, K. J. Sutton and D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **26**, 1463 (1964).

[6] T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 1463 (1964); *Acta Chem. Scand.*, **19**, 1435 (1965).

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

system; A is the radioactivity per ml. of the aqueous phase in equilibrium with the resin; v is the volume of the aqueous phase (ml.), and G is the weight of the resin (g.).

When no complex-forming ligand exists in the system, the distribution constant, K_{d_0}, can be written as:

$$K_{d_0}=[\mathrm{Sc}^{3+}]_\mathrm{R}/[\mathrm{Sc}^{3+}] \tag{3}$$

where the subscript "0" denotes the absence of the ligand.

When the metal ion forms complexes with a mono-negative ligand, L^-, the net distribution ratio of the metal ion between the resin and the aqueous phase can be written as:

$$D=\frac{[\mathrm{Sc}^{3+}]_\mathrm{R}+[\mathrm{ScL}^{2+}]_\mathrm{R}+[\mathrm{ScL}_2{}^+]_\mathrm{R}}{[\mathrm{Sc}^{3+}]+[\mathrm{ScL}^{2+}]+[\mathrm{ScL}_2{}^+]+[\mathrm{ScL}_3]+\cdots} \tag{4}$$

The ion-exchange equilibrium constant for the "nth" complex may be defined as:

$$K_{d_n}=[\mathrm{ScL}_n{}^{3-n}]_\mathrm{R}/[\mathrm{ScL}_n{}^{3-n}] \tag{5}$$

The formation and the over-all stability constant, β_n, of the "nth" complex can be described as:

$$\mathrm{Sc}^{3+}+n\mathrm{L}^- \rightleftarrows \mathrm{ScL}_n{}^{3-n} \tag{6}$$

$$\beta_n=[\mathrm{Sc}_n{}^{3-n}]/[\mathrm{Sc}^{3+}][\mathrm{L}^-]^n \tag{7}$$

By introducing Eqs. 3, 5 and 7 into Eq. 4, the following equation is obtained:

$$\frac{D}{K_{d_0}}=\frac{1+(K_{d_1}/K_{d_0})\beta_1[\mathrm{L}^-]+(K_{d_2}/K_{d_0})\beta_2[\mathrm{L}^-]^2}{1+\beta_1[\mathrm{L}^-]+\beta_2[\mathrm{L}^-]^2+\beta_3[\mathrm{L}^-]^3+\cdots} \tag{8}$$

The constants in Eq. 8 can be determined by a curve-fitting method.[7)]

In order to obtain a simpler function, a variable, a, and two parameters, R and B, are introduced into Eq. 8. Here a, R and B are $\beta_2{}^{1/2}$ $[\mathrm{L}^-]$, $\beta_1\beta_2{}^{-1/2}$ and K_{d_1}/K_{d_0} respectively. Then:

$$\frac{D}{K_{d_0}}=\frac{1+BRa+(K_{d_2}/K_{d_0})a^2}{1+Ra+a^2+\beta_3\beta_2{}^{-3/2}a^3+\cdots} \tag{9}$$

It may be possible to discuss the problem more generally, but here the following assumptions are made as the first approximation:

(i) K_{d_2} is negligible compared to K_{d_1}.

(ii) Only the first and the second complexes exist in the solution.

On the basis of these assumptions, Eq. 9 can be written as:

$$y=(1+BRa)/(1+Ra+a^2) \tag{10}$$

By introducing various sets of values into R and B in Eq. 10, families of standard curves represented by the following equations are obtained:

$$\left.\begin{aligned} &Y=\log y=-\log(1+Ra+a^2)+\log(1+BRa) \\ &X=\log a \end{aligned}\right\} \tag{11}$$

One of these curves will be found to fit the plot of the experimental data, $\log(D/K_{d_0})$ vs. $\log[\mathrm{L}^-]$.

The equilibrium constants can be determined from the parameters of this particular standard curve as follows:

From the definition,

$$\log a=\frac{1}{2}\log\beta_2+\log[\mathrm{L}^-]$$

The value of $1/2\log\beta_2$ can be determined graphically from the difference between the value on the abscissa of the standard curve ($X=\log a$) and the value on the abscissa of the experimental data ($X=\log[\mathrm{L}^-]$).

For example, one may compare the abscissa of the experimental data (plotted as $\log D/K_{d_0}$ vs. $\log[\mathrm{L}^-]$) with that of the best-fitted curve (plotted as $\log y$ vs. $\log a$ (Eq. 11)). Then one can read the $\log[\mathrm{L}^-]_0$ value on the abscissa of the experimental plot which coincides with the point, $\log a=0$, on the abscissa of the standard curve; this $\log[\mathrm{L}^-]_0$ value should give the $\log a$—$\log[\mathrm{L}^-]$ value.

From this $\log[\mathrm{L}^-]_0$, $\log\beta_2$ can be determined as:

$$\log\beta_2=-2\log[\mathrm{L}^-]_0$$

The $\log\beta_1$ value can then be determined as:

$$\log\beta_1=\log R+\frac{1}{2}\log\beta_2$$

and K_{d_1} can be determined as:

$$K_{d_1}=BK_{d_0}$$

If the assumptions i and ii cannot be adopted, the terms K_{d_2}/K_{d_0} and/or $\beta_3\beta_2{}^{-3/2}a^3$, etc., should be introduced into Eq. 11. Then the followings are obtained:

$$\begin{aligned}\log y=&-\log(1+Ra+a^2+\beta_3\beta_2{}^{-3/2}a^3)\\ &+\log(1+BRa)\end{aligned} \tag{12}$$

$$\begin{aligned}\log y=&-\log(1+Ra+a^2)\\ &+\log\{1+BRa+(K_{d_2}/K_{d_0})a^2\}\end{aligned} \tag{12$'$}$$

$$\begin{aligned}\log y=&-\log(1+Ra+a^2+\beta_3\beta_2{}^{-3/2}a^3)\\ &+\log\{1+BRa+(K_{d_2}/K_{d_0})a^2\}\end{aligned} \tag{12$''$}$$

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and the curve-fitting can be continued as above.

More details of this method may be found in other articles (for instance, Ref. 7).

Experimental

Reagents.—The perchloric acid, the hydrochloric acid and the nitric acid used were of a reagent grade. The concentration of the acids was determined by titrations using potassium acid carbonate as the standard substance.

Radioactive Tracer.—Scandium-46 was used as the tracer. It was obtained from the Radiochemical Center, Amersham, England, as a hydrochloric acid solution. This tracer was purified by a solvent extraction method and diluted with 4.00 M hydrochloric acid, nitric acid or perchloric acid. These solutions were then used as the stock solutions.

Cation-exchange Regin.—A Dowex 50 W X-12, 100—200 mesh, was used. The resin was conditioned alternately with 4 M hydrochloric acid and 4 M sodium chloride solution several times. The resin was finally made into a H^+-form and dried in an air-bath at 60°C overnight. Then it was equilibrated in the open air for several days and stored in a closed bottle. The exchange capacities of this resin were 3.62 meq./g. for Na^+ and 3.60 meq./g. for H^+.

Procedures.—All of the procedures were carried out in a thermostatted room at 25 ± 0.5°C. About 100 mg. of resin was placed in glass-stoppered tubes (volume, 20 ml.) and weighed. The tracer solution and various amounts of hydrochloric acid or nitric acid were placed in the tubes, and then perchloric acid was added to make the aqueous phase 5.0 ml. and the ionic strength 4.0 M. The tubes with the contents were agitated by a mechanical rotator for about four hours in order to ensure an equilibrium. It was found in the preliminary experiments that the ion-exchange equilibrium was reached within two hours by the rotation. After the rotation was finished, the substances were centrifuged at 2000 r.p.m. for about three minutes. A two-milliliter aliquot of the solution was then pipetted out and transferred into a small test tube, and the γ-radioactivity of the aqueous phase was measured with a well-type (NaI) scintillation counter.

Results

The distribution ratios of scandium(III) between the resin and the aqueous perchlorate solutions with various amounts of chloride ions or nitrate ions are given in Table I. The plots of $\log (D/K_{d_0})$ against $\log [Cl^-]$ and $\log [NO_3^-]$ are shown in Fig. 1.

The stability constants of the complexes were determined by the curve-fitting as follows. The plots in Fig. 1 were first compared with the families of the standard curves defined by Eq. 11. The plot of the data in the nitrate system was found to be well fitted by a standard curve which was obtained with the parameters $R=2.5$ and $B=0$. The stability constants were therefore determined from these values and $\log[L^-]_0=-0.14$. However, it was not possible to find a standard curve for the chloride system among the curves defined by Eq. 11, which fits the plot over all the ligand concentration region. The standard curve obtained by introducing $R=2$ and $B=0$ into Eq. 11 fits the plot in the lower concentration region when $\log[L^-]_0$ was 0.42, but it deviated from the plot upward as the ligand concentration increased. This seemed to indicate the formation of the third complex, $ScCl_3$. After many trials, a curve given by Eq. 12 was found to fits best when $R=2$, $B=0$ and $\beta_3\beta_2^{-3/2}=0.6$ were introduced into the equation. The $\log [L^-]_0$ value was found to be 0.42 even after the introduction of the third term. The equilibrium constants were calculated from these values.

TABLE I. THE DISTRIBUTION RATIO OF Sc(III) AT 25°C
Ion-exchange resin: Dowex 50 W X-12

(A) 4.0 M $H(Cl, ClO_4)$

$[Cl^-]$	D	$[Cl^-]$	D
4.00	3.90×10	1.44	1.31×10^2
4.00	3.86×10	1.36	1.33×10^2
3.84	4.09×10	1.36	1.39×10^2
3.68	3.90×10	1.28	1.40×10^2
3.52	4.56×10	1.20	1.47×10^2
3.36	4.98×10	1.12	1.48×10^2
3.20	5.30×10	1.04	1.56×10^2
3.20	5.63×10	0.96	1.57×10^2
3.04	5.81×10	0.88	1.74×10^2
2.88	6.21×10	0.80	1.60×10^2
2.72	6.89×10	0.72	1.86×10^2
2.56	6.80×10	0.64	1.94×10^2
2.40	7.75×10	0.56	2.00×10^2
2.40	7.91×10	0.48	2.08×10^2
2.08	9.26×10	0.48	2.13×10^2
2.00	9.76×10	0.40	2.32×10^2
1.92	1.08×10^2	0.32	2.31×10^2
1.76	1.11×10^2	0.28	2.50×10^2
1.76	1.11×10^2	0.24	2.51×10^2
1.68	1.11×10^2	0.20	2.43×10^2
1.60	1.12×10^2	0.16	2.72×10^2
1.60	1.18×10^2	0.12	2.69×10^2
1.52	1.27×10^2	0.08	2.84×10^2
1.44	1.19×10^2	0.04	2.85×10^2

(B) 4.0 M $H(NO_3, ClO_4)$

$[NO_3^-]$	D	$[NO_3^-]$	D
4.00	1.83×10	1.20	7.63×10
3.84	1.94×10	1.12	7.50×10
3.68	1.99×10	1.04	8.05×10
3.52	1.98×10	0.96	8.64×10
3.20	2.37×10	0.80	1.03×10^2
3.04	2.43×10	0.68	1.16×10^2
2.88	2.70×10	0.56	1.30×10^2
2.72	2.79×10	0.52	1.43×10^2
2.56	3.19×10	0.48	1.38×10^2
2.40	3.40×10	0.40	1.59×10^2
2.24	3.46×10	0.32	1.72×10^2
2.08	3.81×10	0.28	1.86×10^2
2.00	4.51×10	0.24	1.96×10^2
1.92	4.59×10	0.22	2.14×10^2
1.84	4.82×10	0.20	2.23×10^2
1.68	5.41×10	0.20	2.21×10^2
1.60	5.74×10	0.12	2.54×10^2
1.52	5.92×10	0.08	2.55×10^2
1.44	6.15×10	0.04	2.65×10^2
1.28	6.66×10		

From these results, the constants were determined to be as shown in Table II.

Conclusion

From the results, the following conclusions may be drawn:

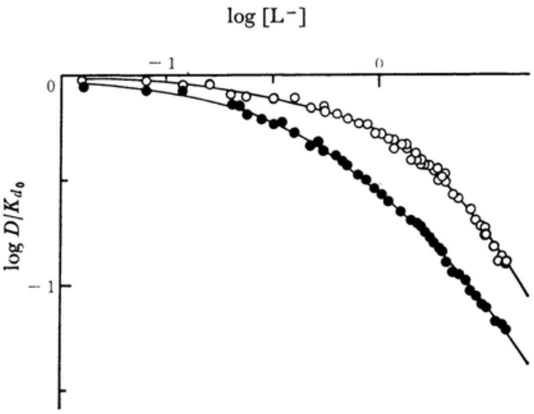

Fig. 1. The plot $\log D/K_{d_0}$ vs. $\log [L^-]$ of scandium(III) in nitrate and chloride media.
Ion-exchange resin: Dowex 50 W X-12 100—200 mesh
Aqueous phase: 4.0 M $H(Cl, ClO_4)$ -○-
4.0 M $H(NO_3, ClO_4)$ -●-
The curves drawn for the plots are
$\log D/299 = -\log(1+1.9[NO_3^-]+0.53[NO_3^-]^2)$
$\log D/299 = -\log(1+0.76[Cl^-]+0.14[Cl^-]^2 +0.04[Cl^-]^3)$

(1) The adsorption of scandium(III) from 4 M $H(Cl, ClO_4)$ or 4 M $H(NO_3, ClO_4)$ to Dowex 50W X-12 decrease with the increase in the ligand concentration. When the ligand concentration is the same, the decrease is always larger in the nitrate system.

(2) The change in the distribution ratio is explained by Eq. 4, together with the equilibrium constants in Table II.

(3) The constants in Table II seem to indicate that:

(a) The ScL^{2+} and ScL_2^+ species are formed both in the nitrate and in the chloride system.

(b) The ScL_3 species is negligible in the nitrate system, but it is formed in the chloride system.

(c) The adsorption of the ScL^{2+} or ScL_2^+ complexes to the ion-exchange resin is negligible.

TABLE II. EQUILIBRIUM CONSTANTS FOR THE ION-EXCHANGE ADSORPTION AND THE STABILITY CONSTANTS FOR THE CHLORIDE AND THE NITRATE COMPLEXES OF SCANDIUM(III) IN 4.0 M $H(Cl, ClO_4)$ AND 4.0 M $H(NO_3, ClO_4)$ AT 25°C
Ion-exchange resin: Dowex 50 W X-12
$K_{d_0}=[Sc^{3+}]_R/[Sc^{3+}]$, $K_{d_1}=[ScL^{2+}]_R/[ScL^{2+}]$
$\beta_n=[ScL_n^{3-n}]/[Sc^{3+}][L^-]^n$

	Chloride	Nitrate
K_{d_0}	299	
K_{d_1}	0	0
$\log \beta_1$	−0.12	0.28
$\log \beta_2$	−0.84	−0.28
$\log \beta_3$	−1.40	—

In the present study, the above conclusions were reached by assuming the constancy of the activity coefficients of the chemical species. More precise argument will be possible when many more thermodynamical data are available.

The stability constants reported by Paul[4] and by Reed et al.[5] are summarized in Table III. The present results may not, however, be compared directly with those results because those experiments were carried out in aqueous solutions of a lower ionic concentration.

Table IV summarizes the stability constants of chloride complexes of lanthanum(III), europium(III), lutetium(III) and americium(III) in 4 M $Na(Cl, ClO_4)$.[6]

From Tables II and IV, it may be concluded that the stability constants for the complexes MCl^{2+} and MCl_2^+ of these five metal ions are in the same order, but that only scandium(III) forms a MCl_3 complex under these experimental conditions.

Some part of the work was carried out at the Laboratory of Nuclear Chemistry, Institute o Physical and Chemical Research, Tokyo. The authors are so grateful to Professor Nobufusa Saito, the head of the laboratory.

TABLE III. SUMMARY OF STABILITY CONSTANTS OF SCANDIUM(III) CHLORIDE COMPLEXES IN PREVIOUS WORK

Temp. °C	Ionic medium	β_1	β_2	K_1	K_2	Ref.
25°C	$I=0.50$	(11.7)	(128)	11.7±0.5	10.9±1.0	4
20°C	$I=0.691$	1.1±0.1	0.75±0.1	(1.1)	(0.7)	5

$K_n=\beta_n/\beta_{n-1}$

TABLE IV. SUMMARY OF THE STABILITY CONSTANTS OF CHLORIDE COMPLEXES OF SOME LANTHANIDES AND AMERICIUM IN Ref. 6

Ionic medium 4 M $Na(Cl, ClO_4)$
Temp., 25°C

	La(III)	Eu(III)	Lu(III)	Am(III)
$\log \beta_1$	−0.22±0.11	−0.15±0.10	−0.35±0.07	−0.15±0.07
$\log \beta_2$	−0.64±0.11	−0.72±0.17	−0.57±0.05	−0.69±0.10