Studies on the Hydrolysis of Metal Ions

18. The Scandium Ion, Sc^{3+}

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The data of Kilpatrick and Pokras concerning the hydrolysis of Sc^{3+} have been recalculated by using general methods for polynuclear complexes [3-5]. At all temperatures and ionic media studied, the data could be explained assuming the formation of "core + links" complexes of the general formula $Sc((OH)_2Sc)_n^{(3+n)+}$.

From a "direct analysis" of the data it was found that at least the complexes with $n=1$ and $n=2$, $Sc_2(OH)_2^{4+}$ and $Sc_3(OH)_4^{5+}$ must exist; there were also indications of the formation of higher complexes. By comparison with the calculated curves from AB II [4], a good approximation was obtained with "hypothesis IIIa". The equilibrium constants obtained with this hypothesis are listed in Table 2. Here $k_0 k$ is the equilibrium constant of the reaction $Sc^{3+} + 2\ H_2O + Sc^{3+} \rightleftharpoons Sc(OH)_2Sc^{4+} + 2\ H^+$; k is the equilibrium constant for all following steps $Sc((OH)_2Sc)_n^{(3+n)+} + 2\ H_2O + Sc^{3+} \rightleftharpoons Sc((OH)_2Sc)_{n+1}^{(4+n)+} + 2\ H^+$.

At the lowest total scandium concentration used, a small correction was necessary for the formation of the mononuclear complexes $ScOH^{2+}$ and $Sc(OH)_2^+$. For 25°C and $I = 1.0$ M, the following values of the equilibrium constants were calculated: for $Sc^{3+} + H_2O \rightleftharpoons ScOH^{2+} + H^+$ log $\beta_1 = -5.1 \pm 0.2$, and for $Sc^{3+} + 2\ H_2O \rightleftharpoons Sc(OH)_2^+ + 2\ H^+$ log $\beta_2 = -10.2 \pm 0.5$.

Some time ago, Kilpatrick and Pokras published the results of a very careful investigation on the hydrolysis of the Sc^{3+} ion. The most extensive measurements [1] were made at 25°C with an ionic strength 1.0 M (with $NaClO_4$). In a following paper [2], data were also given at other ionic strengths (0.01 M, 0.1 M, and 0.5 M at 25°C) and for 10°C and 40°C at ionic strength 1.0 M.

The hydrogen ion concentration at equilibrium was determined with a quinhydrone electrode since spectrophotometric studies had indicated no complex formation between Sc^{3+} and quinhydrone. The equilibria were found to be established rapidly.

Kilpatrick and Pokras concluded from their data that the chief products of the hydrolysis are $ScOH^{2+}$ and $Sc_2(OH)_2^{4+}$, and that higher polynuclear complexes are probably formed.

In the meantime, general methods for treating polynuclear complex equilibria have been given (AB I[3], AB II[4], AB IV[5]), and applied to the hydrolysis of a number of ions (parts VIII—XIV of this series [7-11]). In the present paper, the same methods have been applied to Kilpatrick and Pokras' data for scandium [1,2], the treatment on the whole confirming the conclusions of these authors and providing, in addition, some information on the higher complexes.

Notation

We shall use the following notation: h is the equilibrium concentration of H^+, b the concentration of free Sc^{3+}, B the total scandium concentration (denoted by C in [1,2]) and Z the average number of hydrogen ions set free per Sc. The ionic strength (as defined in [1,2]) is denoted by I. Instead of Z, the original papers [1,2] give the "hydroxyl number" n. The connection between Z and n is easily shown. Since the solutions are always acidic, the total number of bound OH groups per litre, $BZ = nB + h$, or $Z = n + hB^{-1}$. All concentrations are in M (mole/l) if not otherwise stated.

THE DATA FOR 25°C and $I = 1.0$ M

Formula of the complexes

The mathematical analysis of the data will be based chiefly on the data for 25°C and $I = 1.0$ since they are much more extensive than those for other temperatures and ionic strengths.

First of all, the original data n (log h)$_B$ were recalculated and plotted in the form $Z(\log h)_B$. In the resulting diagram, Fig. 1, the points for each of the values of B used (1.25, 2.5, 5, 10, and 20 mM) are given with different symbols. Since the curves for different values of B do not coincide, the process cannot be explained assuming only mononuclear complexes; polynuclear species must also be formed. Moreover, the points are seen to lie on practically parallel curves. From the spacing of the curves, the derivative

$$\left(\frac{\partial \log B}{\partial \log h} \right)_Z \tag{1}$$

is found to be roughly 2.2. The value 2.0 was tested by plotting $y = \frac{1}{2} Z$ as a function of

$$x = \log B - 2 \log h \tag{2}$$

(cf. part VIII[7], 14—15 a). The ordinate was taken as

$$y = \frac{Z}{2} \tag{3}$$

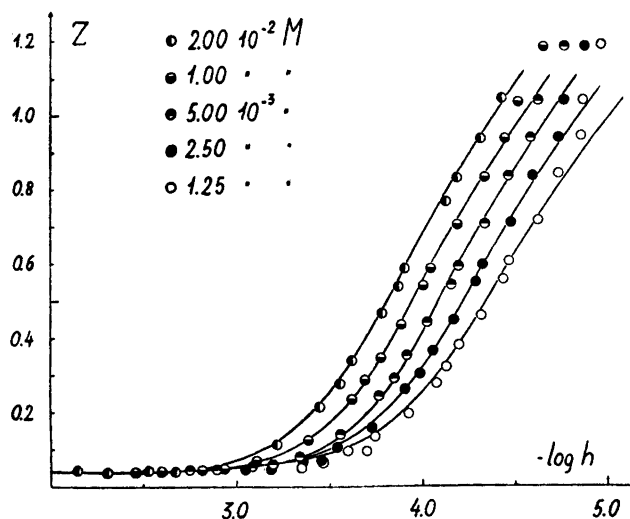to facilitate a comparison with the calculated curves from AB II[4].

Fig. 1. Hydrolysis of Sc^{3+}. Z (average number of OH bound per Sc) as a function of log h, for five different total concentrations B. Experimental data[1]: symbols, see figure. Curves calculated assuming a polynuclear unlimited mechanism (14) (IIIa, with $k_0 = 5$, log k = -6.8), together with a mononuclear reaction with log $\beta_1 = -4.9$; a correction of $+0.04$ has been added to the calculated Z values.

From the diagram $y(x)$, Fig. 2, it is seen that the points fall on practically the same curve; only for the very lowest B value (1.25 mM) is a slight positive deviation noted while, for $x > 7$, all the data are seen to diverge.

Disregarding for a moment these small deviations, we would find that Z is a function of log $B - 2$ log h which, according to AB I[3] and VIII[7], implies
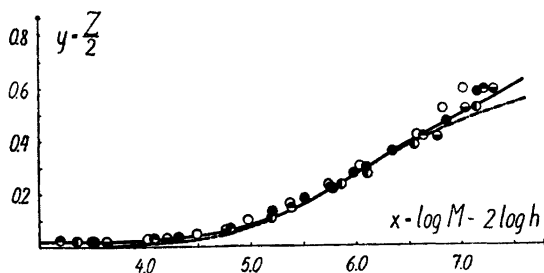

Fig. 2. Hydrolysis of Sc^{3+}. $y = \frac{1}{2}Z$ as a function of $x = \log B - 2 \log h$. Points: experimental data[1], symbols as in Fig. 1. Full drawn curve calculated with mechanism IIIa, $k_0 = 5$, log k = -6.8, adding $+0.02$ to the calculated y values. Dotted curve: only two complexes, log $k_1 = -6.1$, log $k_2 = -12.9$; y corrected; for $x < 6.4$ it practically coincides with the full-drawn curve. Broken curve: IIIa, $k_0 = 5$, log k = -6.7, no correction to y. For $x > 5.2$, it practically coincides with the full-drawn curve.

that all the predominating complex species can be written in the general "core + links" form

$$Sc((OH)_2Sc)_n^{(3+n)+} \hspace{3cm} (4)$$

The deviations at the lowest B values can be ascribed to the formation of mononuclear complexes, especially $ScOH^{2+}$ (see below), whereas the irregular behavior around $x = 7.0$ may be caused by some slow process, *e.g.* irreversible precipitation.

To the left in Fig. 2 it is seen that, with decreasing x, y approaches a value of 0.02 rather than 0. Similarly Z in Fig. 1 approaches 0.04 instead of 0. This behavior indicates a small systematic error, perhaps in the analysis of the perchlorate concentration in the scandium stock solution.

We shall first treat the main reaction, which leads to the formation of polynuclear complexes $Sc((OH)_2Sc)_n^{(3+n)+}$, and then consider the correction for the mononuclear reaction.
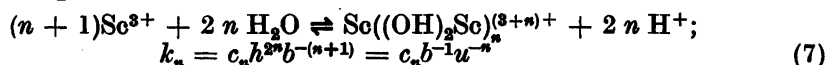
Direct analysis of $y(x)$

We could now draw a smooth curve through the data $y(x)$ and apply equations (AB II, 14 and 15) which yield the function $g(u)$ where

$$u = bh^{-2} = [Sc^{3+}]h^{-2} \hspace{3cm} (5)$$

$$g = \sum k_n u^n = k_1 u + k_2 u^2 + \ldots \hspace{2cm} (6)$$

and k_n is the equilibrium constant of the reaction:

$$(n + 1)Sc^{3+} + 2 n H_2O \rightleftharpoons Sc((OH)_2Sc)_n^{(3+n)+} + 2 n H^+;$$
$$k_n = c_n h^{2n} b^{-(n+1)} = c_n b^{-1} u^{-n} \hspace{2cm} (7)$$

(c_n = concentration of n:th complex).

This procedure involves no additional assumptions besides the one, corroborated by the fitting of the data with a single $y(x)$ curve, that all complexes present in appreciable amounts can be written in the "core + links" form (4).

Fig. 3 gives the results, recalculated to

$$gu^{-1} = k_1 + k_2 u + k_3 u^2 + \ldots \hspace{2cm} (8)$$

as a function of u. The points marked ◐ were calculated from a smooth curve, rather similar to the dashed curve in Fig. 2; corrections applied to the integration constant could not eliminate the irregular behavior for low x.

For the dots O, the experimental y values were corrected by subtracting 0.02 (assuming a systematic error). Disregarding deviations at the lowest values of u, which are very sensitive to small errors in y, the points are seen to lie approximately on a straight line, from the intercept and slope of which we estimate

$$k_1 = 10^{-6.1\pm0.1} \text{ M}; \hspace{1cm} k_2 = 10^{-12.9\pm0.4} \text{ M}^2 \hspace{1cm} (9)$$

At the highest u values the points are seen to deviate upwards, indicating the formation of higher complexes; it did not seem possible to estimate k_3 accurately.

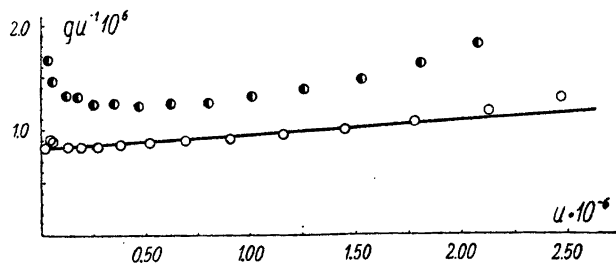The $y(x)$ curve, calculated for the values (9) of k_1 and k_2, is given as a dotted line in Fig. 2.

Fig. 3. gu^{-1} as a function of u calculated by "direct analysis" of y(x). Circles ◖ calculated without correction to y, circles ○ by correcting the experimental y with -0.02. Line: $gu^{-1} = 0.8 \cdot 10^{-6} + 1.25 \cdot 10^{-13}$ u $= 10^{-6.1} + $ u $\cdot 10^{-12.9}$.

From the $g(u)$ data we can calculate also the average number of links per complex

$$\bar{n} = \frac{d \log g}{d \log u} \tag{10}$$

To compute $\bar{n}$ it is convenient to apply the equation

$$\bar{n} = y(1 - y - F^{-1})^{-1} \tag{11}$$

where

$$\log F = y \log e + \int_{-\infty}^{x} y \, dx \tag{12}$$

Eqn. (11) can be obtained by combining (10) with eqns. (14) and (15) of AB II[4].

In Fig. 4 $\bar{n}$ is plotted as a function of log u. $\bar{n}$ is seen to start at about 0.90 instead of unity; this is explained by the inaccuracy of the numerical integration for low u values. As u increases, $\bar{n}$ rises monotonically, attaining the maximum value 1.84. Thus the conclusion can be drawn, in agreement with the preceding calculation, that complexes with $n = 1$ and 2 predominate in the u range studied.
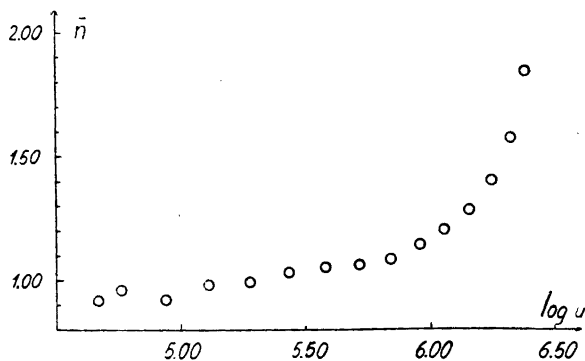

Fig. 4. $\bar{n}$ (equation 10) as a function of log u. A correction of -0.02 has been added to the experimental y values.

Comparison with $y(x)$ curves for simple mechanisms

Another way of treating the data is to compare the experimental $y(x)$ data with the $y(X)$ curves calculated for various simple mechanisms in AB II[4]. With mechanism I (precipitate formed, in this case *e.g.* $Sc(OH)_2ClO_4$), no good fit could be found. With hypothesis II (only one complex $Sc((OH)_2Sc)_N^{3+N}$ formed), an approximate agreement was found with $N = 1$ for low values of x. With increasing x, y became systematically higher than the calculated curve, showing that complexes higher than $Sc_2(OH)_2^{4+}$ are also formed.
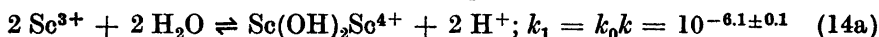
Good agreement could, however, be obtained with the hypotheses IIIa—c assuming a repeated reaction, with the formation of complexes with all n values $n = 1, 2 \ldots$ Since the accuracy did not permit a distinction between IIIa, IIIb, and IIIc, only the simplest hypothesis IIIa was considered in detail:

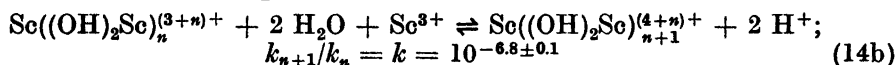$$\text{IIIa: } k_n = k_0 k^n \qquad (13)$$

This hypothesis has been found satisfactory with Th^{4+}, UO_2^{2+}, and In^{3+} (parts IX[8], X[9], XIV[11]). Except for the lowest y, a good agreement was obtained with hypothesis IIIa, assuming $k_0 = 5$ and $\log k = -6.7 \pm 0.1$; this is the broken curve in Fig. 2.

A still better agreement in the whole range was obtained after correcting the calculated y with $+0.02$, assuming $k_0 = 5$ and $\log k = -6.8 \pm 0.1$ (full-drawn curve in Fig. 2). In the range $x > 5.2$ the curves practically coincide.

We would thus have the reactions and equilibrium constants

$$2\,Sc^{3+} + 2\,H_2O \rightleftharpoons Sc(OH)_2Sc^{4+} + 2\,H^+; \; k_1 = k_0k = 10^{-6.1\pm0.1} \quad (14a)$$

and for all consecutive steps

$$Sc((OH)_2Sc)_n^{(3+n)+} + 2\,H_2O + Sc^{3+} \rightleftharpoons Sc((OH)_2Sc)_{n+1}^{(4+n)+} + 2\,H^+;$$
$$k_{n+1}/k_n = k = 10^{-6.8\pm0.1} \qquad (14b)$$

This result, as far as the first two constants are concerned ($k_1 = 10^{-6.1}$, $k_2 = 10^{-12.9}$) is identical with that obtained by the direct analysis (9), and the first one agrees well with the value $k_1 = 10^{-6.0}$ given by Kilpatrick and Pokras [2] (Table IV, where the present k_1 is denoted by "K_0").

In fact, Kilpatrick and Pokras' mechanism, the one (9) obtained by direct analysis, and IIIa (13, 14) may be regarded as three successive approximations to the real mechanism. Kilpatrick and Pokras considered only the first complex, $Sc_2(OH)_2^{4+}$, whereas the data force us to assume also a second complex $Sc_3(OH)_4^{5+}$. Moreover the data indicate that higher complexes are formed, as implied by IIIa. Assuming IIIa and the constants (14) one may calculate the fraction of all Sc present in the form of the various complexes

$$\alpha_0 = [Sc^{3+}]/B; \; \alpha_1 = 2\,c_1/B; \ldots \alpha_n = (n+1)\,c_n/B \qquad (15)$$

where c_n is the concentration of the n:th complex. One finds

for $u = 1.5 \cdot 10^6 (Z = 0.9)$, $\alpha_0 = 0.20$, $\alpha_1 = 0.51$, $\alpha_2 = 0.19$, $\alpha_3 = 0.06$ (16a)
for $u = 2.4 \cdot 10^6 (Z = 1.2)$, $\alpha_0 = 0.11$, $\alpha_1 = 0.41$, $\alpha_2 = 0.24$, $\alpha_3 = 0.13$ (16b)

Thus the complexes with n higher than 2 would be appreciable only in the region where the data begin to diverge.

Mononuclear complexes

In order to explain the deviations of the experimental data for the lowest B, 1.25 mM, in the $y(x)$ diagram (Fig. 2), it will be assumed that, besides the main hydrolysis products, $Sc((OH)_2Sc)_n$, *mononuclear* species are also present in appreciable concentrations.

It may be inferred from the $y(x)$ diagram that, even for the lowest B, the concentration of the mononuclear ions may amount only to a few percent of the total concentration of the hydrolysis products. Therefore it would not be practical to compute the formation constants of the mononuclear species by using some type of deviation function; this would be inevitably too strongly influenced by the uncertainty in k.

To find simultaneously the equilibrium constants of the polynuclear and mononuclear mechanisms, we shall use an approach [5] which has been worked out especially for such an unfavorable case.

This method is based on the consideration of the function $\log B(x)_Z$, where $x = \log B$—$t \log h$, as in (2). When only polynuclear complexes of the "core + links" type are formed, the family of functions $\log B(x)_Z$ is represented by lines parallel with the $\log B$ axis, since $x = $ const. for $Z = $ const. When mononuclear ions are present exclusively, $\log B(x)_Z$ consists of lines with a slope of unity, since $h = $ const. for $Z = $ const. In the intermediate range where both mononuclear and polynuclear species exist in comparable amounts, $\log B(x)_Z$ forms curves with continuously increasing slope.

Thus if the plot $\log B(x)_Z$ is made from the experimental data, a deviation of the points from a vertical line at low B values indicates that mononuclear ions begin to be formed in appreciable amounts. Such a deviation is more conspicuous than deviations of the data for low B from the $y(x)$ curve valid for high B.

The $\log B(x)_Z$ diagram calculated from Kilpatrick and Pokras' data is shown in Fig. 5; points for low B clearly indicate the presence of mononuclear ions.

In order to calculate the formation constants of the mononuclear complexes and a more accurate value for $\log k$, the $\log B(x)_Z$ data will be compared with the calculated curves

$$\log B(X)_Z$$

where $X = x + \log k$, $\log B = \log B + \log k$—$t \log \beta_1$ (*cf.* eqns. (13) and (14) of [5]). β_1 is the equilibrium constant of the reaction

$$Sc^{3+} + H_2O \rightleftharpoons ScOH^{2+} + H^+ \quad \beta_1 = [ScOH^{2+}]h[Sc^{3+}]^{-1}$$
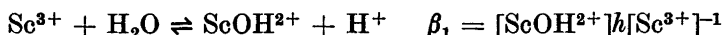
If the data are superimposed on the calculated curves $\log B(X)_Z$, the differences X—x and $\log B - \log B$ give in the position of best agreement the most probable values of $\log k$ and $\log \beta_1$.

In the first instance, $\log B(X)_Z$ was calculated by assuming that only one mononuclear species is formed, namely $ScOH^{2+}$. The fit obtained is shown in Fig. 5a. Up to $Z = 0.6$, the agreement is satisfactory but, for higher values of Z, the deviations increase gradually.
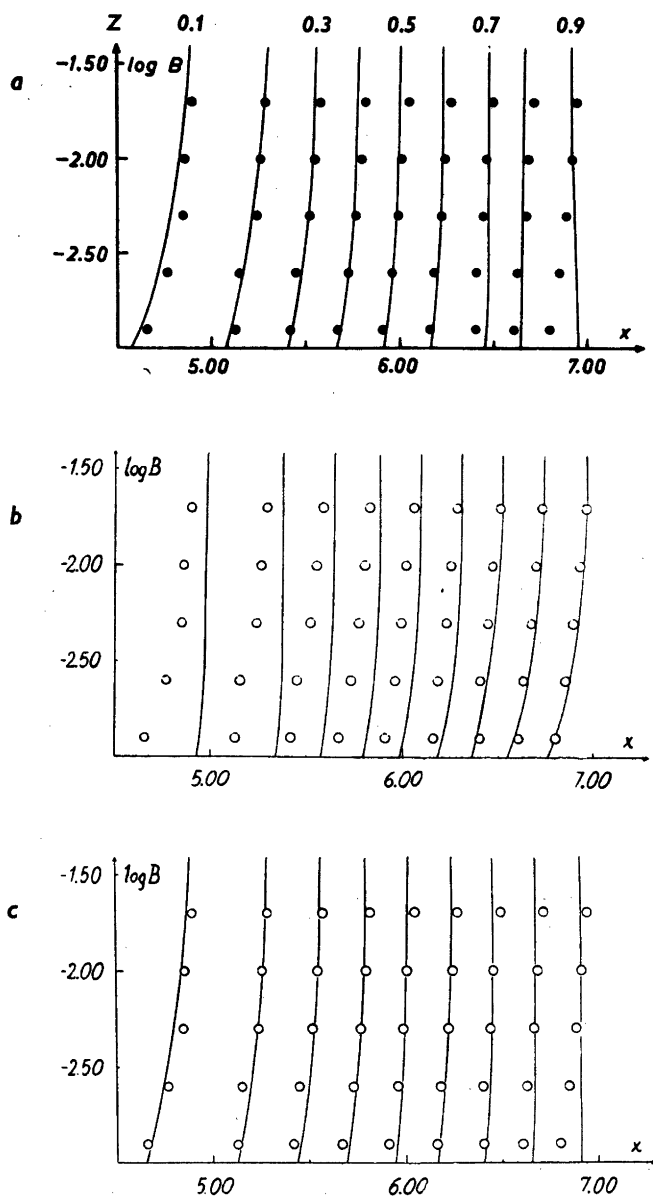
Fig. 5 a, b, c. log B as a function of x for Z values of 0.1 — 0.9. Circles: experimental points.
The curves have been calculated assuming the equilibrium constants given in Table 1.

Fig. 5 d, e. log B as a function of x for Z values of 0.1—0.9. Circles: experimental points. The curves have been calculated assuming the equilibrium constants given in Table 1.
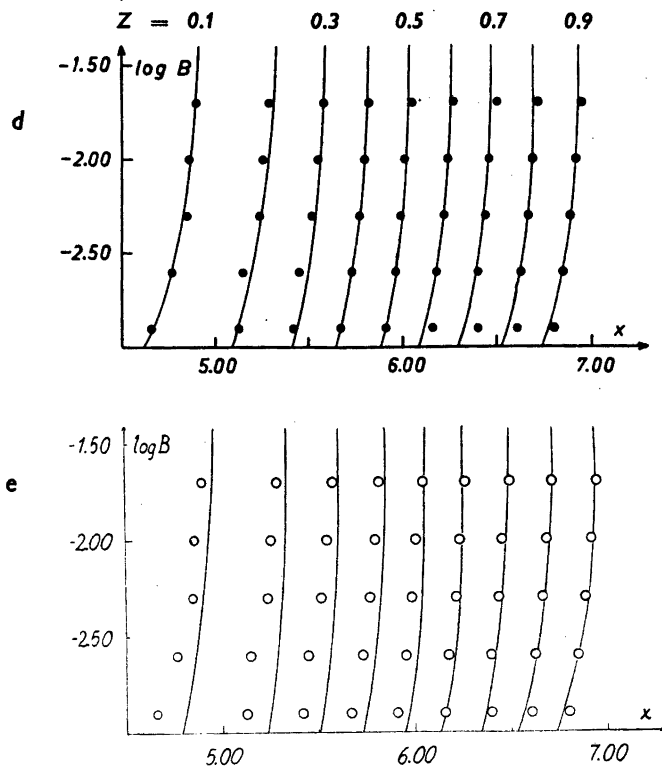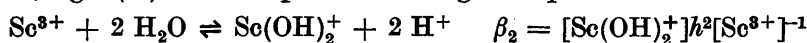
Next, $\log B(X)_Z$ was computed assuming the equilibrium

$$\text{Sc}^{3+} + 2\,\text{H}_2\text{O} \rightleftharpoons \text{Sc(OH)}_2^+ + 2\,\text{H}^+ \qquad \beta_2 = [\text{Sc(OH)}_2^+]h^2[\text{Sc}^{3+}]^{-1}$$

In this case we have *

$$\log B = \log B + \log k - \frac{t}{2} \log \beta_2$$
$$X = x + \log k$$

As Fig. 5b shows, the agreement is acceptable for $Z > 0.6$ but, as Z is decreased, the deviations rapidly increase.

To obtain an agreement for the whole range of Z investigated, we must thus assume that ScOH^{2+} and Sc(OH)_2^+ are both present in appreciable amounts.

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* Introducing the auxiliary normalized variable $a = \beta_2 h^{-2}$ we get by eqn. (8) of [5] $\log B = \log v - \log k - \frac{t}{2} (\log a - \log \beta_2) + \log(1 + a + g + vg')$ where $v = k\,u$ and $g = \sum k_n u^n$.

Thus for a constant value of Z $\log B = \log B + \log k - \frac{t}{2} \log \beta_2$ is a function of v only.

In this case where three constants, β_1, β_2 and k, should be determined, some assumption must be made on the ratio

$$\beta_2 \beta_1^{-2} = l$$

in order to calculate log $B(X)_Z$. With $l = 1$, the agreement is very satisfactory (Fig. 5d). With $l = 0.1$ (Fig. 5c), the deviations at the highest Z values indicate that l was chosen somewhat too low, on the other hand, with $l = 10$ (Fig. 5e) a reasonable fit is obtained only for $Z > 0.6$, indicating that a too high value of l was taken.

The constants obtained using different assumptions are summarized in Table 1.

Table 1.

l	0	0.1	1	10	infinite
log k	−6.85	−6.84	−6.87	−6.88	−6.90
log β_1	−5.0	−5.1	−5.1	(−5.6)	—
log β_2	—	(−11.2)	−10.2	−10.2	−10.2
	Fig. 5a	Fig. 5c	Fig. 5d	Fig. 5e	Fig. 5b

We can estimate as the most probable values

$$\log k = -6.87 \pm 0.10$$
$$\log \beta_1 = -5.1 \pm 0.2$$
$$\log \beta_2 = -10.2 \pm 0.5$$

This log β_1 value is in good agreement with that given by Kilpatrick and Pokras [1]: −4.9 ± 0.1.

We have found previously, assuming a pure polynuclear mechanism, that log $k = -6.8 \pm 0.1$; thus no serious error was introduced by neglecting the mononuclear mechanism at $B \geq 2.5$ mM.

DATA AT OTHER TEMPERATURES AND IONIC STRENGTHS

For the other temperatures and ionic strengths, the data for only two values of log B were generally available. The data were plotted as before, giving $y = Z/2$ as a function of $x = \log B - 2 \log h$ (Fig. 6a, b; Fig. 7a, b). The points for $B = 1.25$ mM were in general found to be somewhat higher (especially for 40° C) than those for the higher concentration (usually 10 mM). Since the effect is rather small, no attempt was made to use these data for calculating accurately the variation of β_1 or β_2 with ionic strength and temperature.

The shape of the curves could be well explained with mechanism IIIa in all cases, assuming $k_0 = 5$ (10 for the lower values of I). The correction $+0.02$ was made to the calculated y, to account for a possible small analytical error (see above). The results are summarized in Table 2.
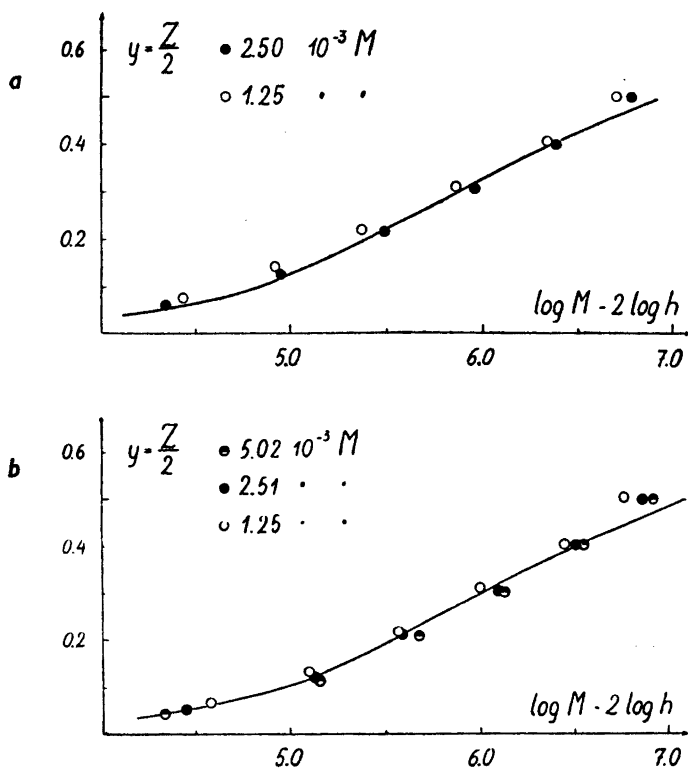
Fig. 6. *Hydrolysis of* Sc^{3+}. *Data[2] for 25°C and ionic strengths 0.5 and 0.1 M plotted in the form* y(x), *assuming* t = 2. *Fig. 6a:* I = 0.1 M; *curve:* IIIa, k_0 = 10, log k = −6.8. *Fig. 6b:* I = 0.5 M; *curve:IIIa*, k_0 = 10, log k = −6.9.

Table 2

Temperature °C	I M	k_0	log k	log $k_0 k$ = log k_1	log k_1[a]
25	1.00	5	−6.87 ± 0.1	−6.17 ± 0.1	−6.00
25	0.50	10	−6.9 ± 0.2	−5.9 ± 0.2	−5.90
25	0.10	10	−6.8 ± 0.2	−5.8 ± 0.2	−5.67
10	1.00	5	−7.3 ± 0.2	−6.6 ± 0.2	−6.66
40	1.00	5	−6.2 ± 0.2	−5.5 ± 0.2	−5.50

The last column gives the log k_1 ("log K_0") values given by Kilpatrick and Pokras [2] who, however, considered only the first polynuclear complex. The agreement is very satisfactory.

The formation of the polynuclear complexes is favored by increasing the temperature. From the temperature variation of the constants we may calculate, both for the first step (14a) and for the following (14b), values for ΔH of about 15 kcal, and values for ΔS of about 20 cal degree^{-1}, in good agreement with Kilpatrick and Pokras [2].
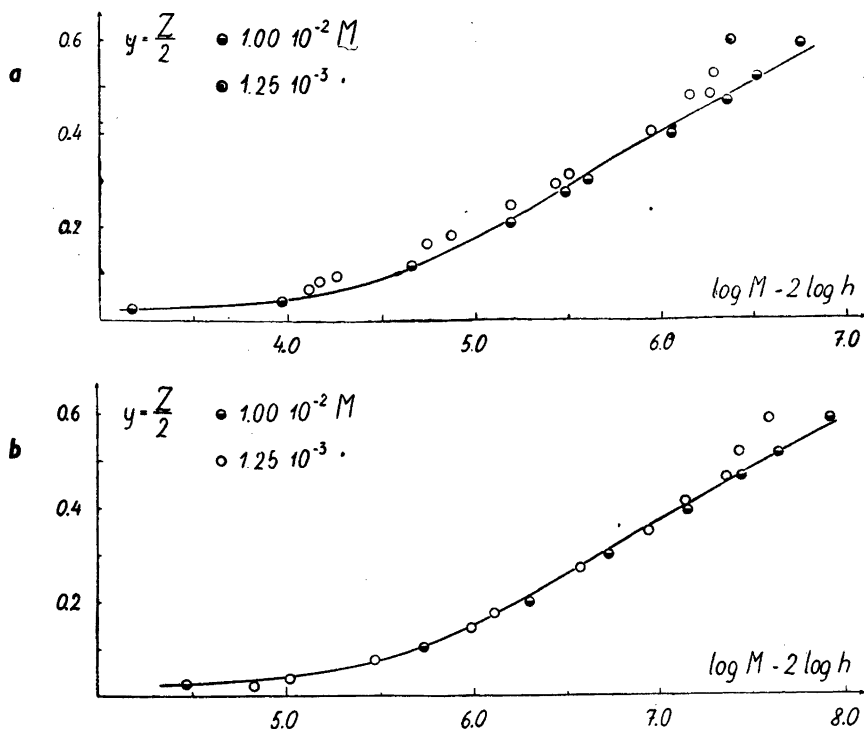
Fig. 7. Hydrolysis of Sc^{3+}. Data[2] for $10°C$ and $40°C$ plotted in the form y(x), assuming $t = 2$. Fig. 7a: $40°C$, $I = 1.00$ M; curve: IIIa, $k_0 = 5$, $\log k = -6.2$. Fig .7b: $10°C$, $I = 1.00$ M; curve: IIIa, $k_0 = 5$, $\log k = -7.3$.

From Table 2 it seems that $\log k$ is not much affected by changes in I. The increase in $\log k_0k$ would imply an increasing predominance of the first complex, $Sc_2(OH)_2^{4+}$, with decreasing I.

DISCUSSION

We may thus conclude that, for all temperatures and ionic media studied by Kilpatrick and Pokras, the data can be explained by the same mechanism, namely the formation of a series of "core+links" complexes, $Sc((OH)_2Sc)_n^{(3+n)+}$, with a small correction for the mononuclear complexes $ScOH^{2+}$ and $Sc(OH)_2^{+}$.

Complexes of the same general formula have been found for Fe^{3+} (part VII[6]), UO_2^{2+} (part X[9]), and In^{3+} (part XIV[11]). Scandium is seen to take an intermediate place in the range in the following respect. For Fe^{3+}, the data could be explained assuming only one polynuclear complex, with $n = 1$. For Sc^{3+}, we have found that at least two complexes, with $n = 1$ and 2, must be considered. For UO_2^{2+} and In^{3+} at least $n = 3$ must also be considered. However, it seems that the differences are only gradual. One may imagine

that in all cases an unlimited series of complexes may be formed but that the higher complexes do not reach appreciable concentrations within the experimental range which is limited by the precipitation of the hydroxide or some other solid phase at a sufficiently high value of Z.

Another type of reaction seems to be found for Al^{3+}, where the rather scarce data are best explained assuming only one complex, of some complicated composition like $Al_6(OH)_{15}^{3+}$ (part XI[10]). Recent crystal structure data suggest the existence of complexes $Al_{13}(OH)_{32}^{7+}$ [12].

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