The Hydrolysis of Metal Ions. Part 6.[1] Scandium(III)

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The potentiometric titration technique has been used to study the hydrolytic behaviour of the scandium(III) ion in 0.10 mol dm^{-3} potassium nitrate at 25 °C. Data treatment indicates the presence of the species $[Sc(OH)]^{2+}$, $[Sc_2(OH)_2]^{4+}$, and $[Sc_3(OH)_5]^{4+}$, the $-\log \beta_{pq}$ values being 4.840 (0.008), 6.096 (0.004), and 17.567 (0.006) respectively; the estimated standard deviations are given in parentheses.

The hydrolysis of the scandium(III) ion has received little attention. The most extensive work is that of Kilpatrick and Pokras [2,3] who studied the hydrolytic behaviour at different temperatures and ionic strengths and, later, that of Aveston.[4] Both these studies yielded limited data and therefore the reported interpretations may be questionable. Thus, in keeping with the aims of the present series, this system was investigated in 0.10 mol dm^{-3} potassium nitrate at 25 °C.

Experimental

Reagents.—Unless otherwise stated, all reagents were Merck Suprapur. The source of scandium was scandium oxide (Spec. Pure; Johnson Matthey Ltd.). Sodium hydroxide was used as the base. The scandium(III) nitrate stock solution was analysed by atomic absorption spectroscopy.

Procedure.—The procedure used has been described.[5] The value of λ in the expression $[H^+] = 10^{-pH}/\lambda$ was found to be 0.701, and the ionisation reaction of water was ignored. All titrations were carried out using 0.10 mol dm^{-3} KNO_3 as the ionic medium, at 25.0 ± 0.1 °C. A summary of the titrations is given in Table 1; full details are available on request.

Results

The convention previously adopted [1,5] for the reactions (1) defines the stoicheiometric equilibrium constants as in (2). Each species will be represented by its formula or by a (p,q) pair.

$$pSc^{3+} + qH_2O \rightleftharpoons [Sc_p(OH)_q]^{(3p-q)+} + qH^+ \quad (1)$$

$$\beta_{pq} = [Sc_p(OH)_q{}^{(3p-q)+}][H^+]^q/[Sc^{3+}]^p \quad (2)$$

The three species (1,1), (2,2), and (3,5) are the major species documented.[2-4,6,7] Aveston [4] found no evidence for the existence of any species containing more than three scandium atoms.

Our data can be interpreted by using a model containing the above three species. This model meets the conditions of our acceptance criteria (R = 0.001 6, see Table 2).[1] Further calculations using the additional species (1,2), (2,3), (3,4), (4,6), (4,7), (5,8), and (5,9), taken singly and in pairs with the (1,1), (2,2), and (3,5) species as the base model (28 models), demonstrated that no alternate explanation was acceptable.

Thus, in agreement with Aveston,[4] we were unable to detect any species higher than a trimer. However, we failed to detect $[Sc_3(OH)_4]^{5+}$, a species suggested by Aveston: the formation constant of this species became negative on refinement with the base model.

Table 1. Summary of titrations of scandium(III) at 25 °C and in 0.10 dm^{-3} KNO_3

Total initial scandium(III) concentration (10^{-3} mol dm^{-3})	pH range	Number of points
2.110	3.695—4.929	107
1.055	3.813—4.939	105
0.527	3.906—5.097	122
0.211	3.965—5.084	151

Discussion

Some previous potentiometric studies of the hydrolysis of the scandium(III) ion are compared with the results of the present study in Table 2. For those models containing the (1,1), (2,2), and (3,5) species the (2,2) species is notable for the invariance of its formation constant (25 °C) with ionic strength. The only variation is in 0.01 mol dm^{-3} $NaClO_4$ (Kilpatrick and Pokras [3]) but the formation constants determined are questionable because of the unavoidable changes in the ionic medium at this low value.

In the concentration ranges studied the (2,2) dimer is important at all pH values. The monomer becomes more important at low metal-ion concentrations. The trimer is important at high pH values and all metal-ion concentrations. The relative percentage of each species present at 0.5 mmol dm^{-3} metal ion is given in the Figure.

In the work of Kilpatrick and Pokras [2,3] the results at various temperatures and ionic strengths were interpreted by assuming the formation of $[Sc(OH)]^{2+}$ and $[Sc_2(OH)_2]^{4+}$. They found, however, that the agreement between the experimental and calculated values worsened progressively as $\bar{n}$ (the ratio of number of hydroxyl groups per scandium ion) increased. The authors suggested that further polymerisation to species such as (3,4) and (4,6) could explain the increasing deviation. Indeed, a recalculation of these results by Biedermann *et al.*[8] showed that the polymerisation reactions could be accounted for by assuming formation of the ' core-plus-links ' series $Sc[(OH)_2Sc]_n{}^{(3+n)+}$. The formation of such a series, however, has since been questioned by the Sillén school.[9] A further recalculation of these results [2,3] by Aveston [4] showed that the hydrolysis could best be explained by assuming the three species $[Sc(OH)]^{2+}$, $[Sc_2(OH)_2]^{4+}$, and $[Sc_3(OH)_5]^{4+}$.

Aveston interpreted the results of additional measurements

Table 2. Survey of potentiometric investigations of the hydrolysis of scandium(III)

Medium	Temperature (°C)	Total scandium concentration (10^{-3} mol dm^{-3})	$-\log \beta_{pq}$ (1,1)	(2,2)	(3,5)	Ref.
$NaClO_4$	25	1.25—10.0	4.93	5.97		2
(1 mol dm^{-3})			5.15	6.11	17.47	4[a]
	10	1.25—10.0	5.09	6.66		3
			5.6	6.63	18.77	10[a]
	40	1.25—10.0	4.41	5.49		3
			4.53	5.54	15.87	10[a]
$NaClO_4$	25	1.254—5.016	4.90	5.90		3
(0.5 mol dm^{-3})			4.68	6.08	17.26	10[a]
$NaClO_4$	25	1.25—2.50	4.74	5.67		3
(0.1 mol dm^{-3})			4.47	6.03	17.02	10[a]
$NaClO_4$	25	1.25	4.61	5.35		3
(0.01 mol dm^{-3})			4.48	5.45	16.02	10[a]
$NaClO_4$	25	1.25—80	5.11	6.14	17.47	4
(1 mol dm^{-3})			5.18	6.06[b]	17.33	4
KNO_3	25	0.26—2.6	4.47	5.86		6
(0.1 mol dm^{-3})						
	25	0.211—2.110	4.840	6.096	17.567	This work

[a] Recalculation in cited reference. [b] $-\log \beta_{3,4} = 13.00$.

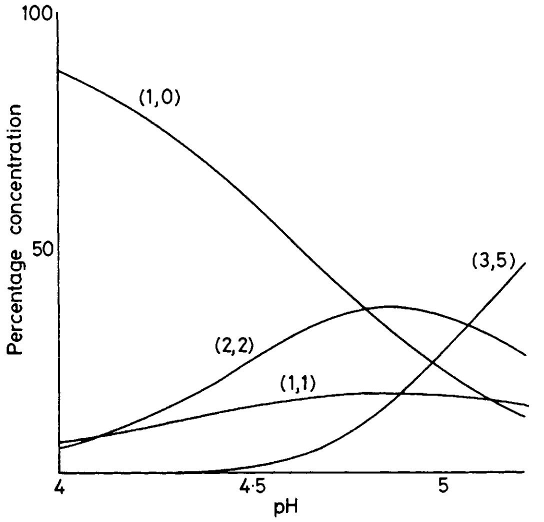

Figure. Percentage of scandium(III) hydrolysis products present at total $[Sc^{3+}] = 5 \times 10^{-4}$ mol dm^{-3}, assuming $[H^+] = 10^{-pH}$ ($\lambda = 1$)

by assuming the same three species, as well as $[Sc_3(OH)_4]^{5+}$. The view has been expressed,[10] however, that the formation of the latter is doubtful; furthermore, we can find no evidence in our data for the existence of this species. Attempts at identifying further species have similarly met with no success.

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