Thermodynamic Properties of Rare Earth Complexes

VIII. Stability Constants for Oxalate Complexes of Sc(III)

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The stability constants for the formation of four mononuclear
scandium(III) oxalato complexes have been determined at 20°C in an
aqueous sodium perchlorate medium with ionic strength 1 M. Three
different methods were used, *viz.* solvent extraction with thenoyltri-
fluoroacetone as the auxiliary ligand, solubility measurements by
using $Na_3Sc(C_2O_4)_3 \cdot x\,H_2O$ as the solid phase, and potentiometric
measurements of the hydrogen ion concentration.

The chemical properties of scandium(III) are very similar to those of the
tervalent lanthanoids. A comparison of the values of ΔG_j°, ΔH_j° and ΔS_j°
for the formation of some scandium(III) and lanthanoid(III) complexes
has previously been published in this series.[1] The differences between the
complexes could be discussed in terms of the ionic radius of the central ion
and the special geometrical requirements of the ligand used. This investiga-
tion is an extension of the previous study to include the ligand oxalate.

The complex formation between oxalate and some lanthanoid(III) ions
(Ce, Eu, Tb, and Lu) has previously been studied (Part VI in this series [2]),
mainly by solubility measurements. Only a few incomplete investigations of
scandium oxalato complexes have been published so far. These include two
spectrophotometric studies,[3,4] one solvent extraction study using oxine (8-
hydroxyquinoline) as auxiliary ligand [5] and one ion-exchange investigation.[6]
In one of the spectrophotometric studies [3] only the complex ScA^+ (A denotes
oxalate) was studied, while in the other [4] the presence of three complexes
ScA_j^{3-2j} $(j=1-3)$ was reported. The results of the latter investigation are
doubtful, because the range of oxalate concentration investigated was very
narrow (3×10^{-5} M to 1.4×10^{-4} M). The solvent extraction study took only the
complex ScA_3^{3-} into account. The ion-exchange study is also incomplete, as
no information about complexes higher than ScA_2^- was obtained.

In the present study three different methods have been used. All measure-
ments have been performed in a medium with ionic strength 1 M, using sodium
perchlorate as the inert electrolyte. The temperature was 20°C. The protona-

tion constants of oxalic acid in this medium and at this temperature have been determined before (Part VI, p. 102). The symbols not defined below have been given in Part I in this series.[7] ([H$^+$] in Ref. 7 is here replaced with h.)

SOLVENT EXTRACTION MEASUREMENTS

The distribution of scandium(III) between an organic and an aqueous phase was studied by using xylene as the organic solvent and thenoyltrifluoroacetone (TTA) as the extracting agent. The aqueous phase consisted of solutions with different oxalate concentrations and with ionic strength 1.00 M.

Calculations

The distribution equilibrium can be written

$$Sc^{3+}(aq) + 3\ HB(org) \rightleftharpoons ScB_3(org) + 3\ H^+(aq)$$
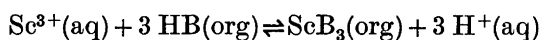
with an equilibrium constant equal to K_{ex}. The distribution ratio, D, of Sc(III) between the two phases is equal to

$$D = \frac{[ScB_3]_{org}}{[Sc^{3+}] \cdot X} \tag{1}$$

if the only scandium complexes in the aqueous phase have the composition ScA_j^{3-2j}, and the only species in the organic phase can be represented by $ScB_3(Xylene)_n$. The existence of species of the type $Sc_iA_jH_k^{3i+k-2j}$ $(i>1,\ k \neq 0)$ are discussed below (*vide infra* p. 167). The complex formation between scandium and the auxiliary ligand is probably of little importance in the aqueous phase.[8]

The corresponding distribution ratio when no oxalate is present is given by

$$D_0 = \frac{[ScB_3]_{org}}{[Sc^{3+}]} = \frac{K_{HB}}{h^3} \tag{2}$$

where $K_{HB} = K_{ex} \cdot [HB]_{org}^3 \cdot f_{HB}^3 \cdot f_{ScB_3}^{-1}$. Here f_{HB} and f_{ScB_3} are the activity coefficients for the species HB and ScB$_3$ in the organic phase.

In the present case the volume ratio between the two phases is constant. The total concentration of scandium is very small compared with the initial concentration of auxiliary ligand, $[HB]_{org}'$. When $[HB]_{org}'$ is kept constant, $[HB]_{org}$ (the equilibrium concentration) and K_{HB} are constant.[9-11] K_{HB} can be determined by distribution measurements with $C_A = 0$ and with $[HB]_{org}'$ kept constant; *cf.* eqn. (2).

The function X is calculated from corresponding values of D, K_{HB}, and h:

$$X = \frac{D_0}{D} = \frac{K_{HB}}{h^3 \cdot D} \tag{3}$$

Experimental

Chemicals. A stock solution of scandium perchlorate was prepared by dissolving scandium oxide (Johnson, Matthey & Co.; 99.99 %) in warm perchloric acid (Baker's Analysed). A 0.2 M solution was prepared and analysed for scandium with EDTA using xylenolorange as an indicator. The concentration of free hydrogen ions, which was determined potentiometrically, was kept as high as 0.4 M in order to avoid hydrolysis.[12,13] Stock solutions of sodium perchlorate were prepared and analysed as described earlier.[14] Stock solutions of oxalic acid and sodium oxalate (both Merck *p.a.*) were analysed as before.[2] TTA (Baker's Analysed) was used as received. Xylene was of analytical grade with a boiling range of $138-139°C$. The radioactive tracer ([46]Sc) was obtained from New England Nuclear Corp. A radioactive stock solution of scandium perchlorate in water was prepared by mixing the inactive solution of scandium perchlorate with the original [46]Sc solution.

Distribution measurements. Radioactive scandium solutions in xylene were prepared by extraction from the active water stock solution into the organic TTA-phase. Three different concentrations of TTA (0.400 M, 0.698 M, and 1.400 M) were used. The scandium concentration in these organic stock solutions ranged between 2×10^{-5} M and 1×10^{-4} M. Equal volumes (5 ml) of an active organic phase and an aqueous phase containing oxalate were then agitated vigorously for 2 h at $20 \pm 1°C$. The compositions of the oxalate solutions are given in Table 2. Equilibrium was attained in less than 30 min. The phases were separated by centrifugation, and the distribution value, D, was determined by γ-activity measurements [2,p.98] on 3 ml samples of the two phases.

Results

Determination of K_{HB}-values. Values of K_{HB} were obtained from eqn. (2) from the experimental data of D_0 and h given in Table 1. K_{HB} was equal to $(8.17 \pm 0.46) \times 10^{-3}$ M³, $(3.98 \pm 0.15) \times 10^{-2}$ M³, and 0.291 ± 0.008 M³ for TTA

Table 1. The determination of different K_{HB} from eqn. (4). Every K_{HB} represents one separately determined distribution.

    I. $[HB]_{org}' = 0.400$ M.
              $h = 0.1225$ M: $K_{HB} \times 10^5/M^3 = 758, 855, 733, 782.$
              $h = 0.245$ M: $K_{HB} \times 10^5/M^3 = 800, 794, 877, 789, 798, 799, 822, 890, 779.$
              $h = 0.493$ M: $K_{HB} \times 10^5/M^3 = 794, 820, 749, 881, 887, 861, 842, 847.$

    II. $[HB]_{org}' = 0.698$ M.
              $h = 0.245$ M: $K_{HB} \times 10^4/M^3 = 386, 376, 398, 386.$
              $h = 0.493$ M: $K_{HB} \times 10^4/M^3 = 382, 405, 422, 410.$
              $h = 0.986$ M: $K_{HB} \times 10^4/M^3 = 398, 418.$

    III. $[HB]_{org}' = 1.400$ M.
              $h = 0.493$ M: $K_{HB} \times 10^3/M^3 = 291, 290, 277.$
              $h = 0.739$ M: $K_{HB} \times 10^3/M^3 = 291, 294.$
              $h = 0.986$ M: $K_{HB} \times 10^3/M^3 = 303, 282, 299.$

concentrations equal to 0.400 M, 0.698 M, and 1.400 M, respectively. The errors quoted are equal to the standard deviation of the means.

Determination of stability constants. Experimental values of D and X are given in Table 2, and a plot lg X *versus* lg($[A]/M$) is shown in Fig. 1. The stability constants were obtained by the graphical standard methods of Leden and Fronæus.[15] The values were then refined by a least squares method.

Table 2. Experimental values from the solvent extraction measurements.

$\dfrac{[HB]_{org}'}{M}$	$-\lg \dfrac{[A]}{M}$	$-\lg \dfrac{h}{M}$	$\lg D$	$\lg X$	$\lg \dfrac{X}{X_{calc.}}$
1.4	7.585	0.006	-0.627	0.109	-0.024
1.4	7.585	0.006	-0.650	0.132	-0.001
1.4	7.585	0.006	-0.668	0.150	0.017
1.4	7.347	0.131	-0.340	0.198	-0.013
1.4	7.347	0.131	-0.337	0.196	-0.015
0.7	7.199	0.210	-1.055	0.286	0.010
0.7	7.199	0.210	-1.053	0.284	0.008
0.7	7.020	0.307	-0.856	0.377	0.005
0.7	7.020	0.307	-0.862	0.384	0.012
0.7	6.790	0.434	-0.650	0.551	0.026
0.7	6.790	0.434	-0.633	0.535	0.010
0.7	6.790	0.434	-0.622	0.524	-0.001
0.7	6.648	0.514	-0.529	0.672	0.036
0.7	6.648	0.514	-0.521	0.665	0.029
0.7	6.480	0.611	-0.348	0.780	-0.003
0.7	6.480	0.611	-0.351	0.783	0.000
0.7	6.272	0.735	-0.201	1.005	0.017
0.7	6.272	0.735	-0.206	1.011	0.023
0.7	5.990	0.910	0.011	1.320	0.016
0.7	5.990	0.910	-0.007	1.337	0.033
0.7	5.990	0.910	0.011	1.320	0.016
1.4	5.750	0.460	-0.749	1.592	-0.020
1.4	5.750	0.460	-0.733	1.576	-0.036
1.4	5.750	0.460	-0.773	1.616	0.004
0.7	5.553	1.208	0.306	1.919	0.028
0.7	5.553	1.208	0.300	1.924	0.033
1.4	5.500	0.603	-0.648	1.924	-0.047
1.4	5.500	0.603	-0.673	1.948	-0.023
1.4	5.500	0.603	-0.709	1.984	0.013
0.7	5.267	1.424	0.562	2.308	-0.033
0.7	5.267	1.424	0.573	2.297	-0.044
1.4	5.250	0.752	-0.674	2.395	0.026
1.4	5.250	0.752	-0.672	2.393	0.024
1.4	5.250	0.752	-0.670	2.391	0.022
0.7	5.058	1.593	0.707	2.674	-0.024
0.7	5.058	1.593	0.669	2.711	0.013
1.4	5.000	0.908	-0.640	2.829	0.028
1.4	5.000	0.908	-0.627	2.816	0.015
1.4	4.750	1.074	-0.583	3.268	0.008
1.4	4.750	1.074	-0.578	3.264	0.004
0.7	4.750	1.074	-1.417	3.238	-0.022
0.7	4.750	1.074	-1.425	3.246	-0.014
0.7	4.729	1.881	0.942	3.301	0.001
0.7	4.729	1.881	0.947	3.295	-0.005
1.4	4.500	1.251	-0.538	3.755	0.016
1.4	4.500	1.251	-0.539	3.756	0.017
0.7	4.500	1.251	-1.378	3.731	-0.008
0.7	4.500	1.251	-1.374	3.726	-0.013
0.7	4.445	2.149	1.191	3.854	0.007
0.7	4.445	2.149	1.206	3.840	-0.007
0.7	4.250	1.442	-1.277	4.205	-0.029
0.7	4.250	1.442	-1.304	4.232	-0.002
0.7	4.250	1.442	-1.293	4.220	-0.014

Table 2. Continued.

|					
0.7	4.205	2.388	1.410	4.354	0.030
0.7	4.205	2.388	1.423	4.340	0.016
0.7	4.000	1.648	−1.191	4.734	−0.008
0.7	4.000	1.648	−1.194	4.738	−0.004
0.7	4.000	1.648	−1.202	4.746	0.004
0.7	3.750	1.868	−1.065	5.269	0.003
0.7	3.750	1.868	−1.074	5.278	0.012
0.7	3.500	2.101	−0.915	5.819	0.007
0.7	3.500	2.101	−0.918	5.822	0.010
0.7	3.250	2.349	−0.744	6.389	0.003
0.7	3.250	2.349	−0.727	6.373	−0.013
0.4	3.250	2.349	−1.444	6.401	0.015
0.7	3.000	2.611	−0.559	6.992	−0.004
0.7	3.000	2.611	−0.573	7.005	0.009
0.4	3.000	2.611	−1.255	7.000	0.004
0.4	3.000	2.611	−1.237	6.982	−0.014
0.4	3.000	2.611	−1.299	7.045	0.049
0.4	2.750	2.895	−1.046	7.643	−0.005
0.4	2.750	2.895	−1.039	7.637	−0.011
0.4	2.500	3.223	−0.661	8.243	−0.101
0.4	2.500	3.223	−0.640	8.221	−0.123
0.4	2.250	3.668	−0.186	9.101	0.019
0.4	2.250	3.668	−0.181	9.096	0.014
0.4	2.000	4.000	0.035	9.877	0.014
0.4	2.000	4.000	0.035	9.877	0.014
0.4	1.750	4.000	−0.762	10.674	−0.012
0.4	1.750	4.000	−0.740	10.652	−0.034
0.4	1.750	4.000	−0.753	10.666	−0.020
0.4	1.500	4.000	−1.559	11.471	−0.081
0.4	1.500	4.000	−1.542	11.453	−0.099
0.7	1.500	4.000	−0.840	11.439	−0.113
0.7	1.500	4.000	−0.842	11.442	−0.110
0.7	1.250	4.000	−1.721	12.320	−0.138
0.7	1.250	4.000	−1.714	12.314	−0.144

The various constants are given in Table 5. One check of the validity of eqn. (3) was made by measuring D at such low [A]-values that an accurate extrapolation of the X *versus* [A] curve to [A] = 0 could be made. The extrapolated value was equal to 0.98 ± 0.04, in good agreement with the expected value of unity. (The error is an estimated maximum error.)

SOLUBILITY MEASUREMENTS

Scandium(III) forms sparingly soluble oxalates of the general formula $N_p Sc_q A_r \cdot x\ H_2O$ (*cf.* Ref. 2). N = Na, K, or NH_4. For N = Na, the three following compounds have been described: $Sc_2A_3 \cdot x\ H_2O$, $NaScA_2 \cdot x\ H_2O$, and $Na_3ScA_3 \cdot x\ H_2O$.[16] The existence of $Na_4Sc_2A_5 \cdot x\ H_2O$ is doubtful.[16] The various phases are stable in different oxalate concentration ranges, *viz.* Sc_2A_3 at the lowest and Na_3ScA_3 at the highest.

In the lanthanoid oxalate study,[2] solubility data from more than one solid phase were obtained. This method was tried in the present study too. However, it was only possible to get reliable results from the solid Na_3ScA_3.

Fig. 1. a. The $\bar{n}$-curve as a function of $-\lg([A]/M)$ calculated from the final set of constants given in Table 5. The filled circles represent $\bar{n}$-values from the potentiometric measurements. *b.* The corresponding X- and $-\lg([A]/M)$-values from the extraction measurements (open circles). The full-drawn curve has been calculated from the final set of constants in Table 5.
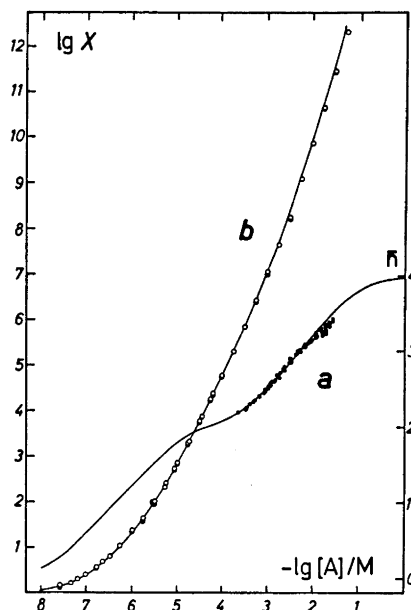
Calculations

The calculation of stability constants from solubility data has been given before.[2,p.95] If only complexes of the type ScA_j^{3-2j} are formed, and the sodium ion concentration is kept constant, the solubility of Na_3ScA_3 is equal to

$$S = K_{III} \cdot [A]^{-3} \cdot \sum_{j=0}^{J} \beta_j \cdot [A]^j \qquad (4)$$

where $K_{III} = K_{III} \times [Na]^{-3}$; K_{III} is the solubility product of Na_3ScA_3.

If the solubility products of Sc_2A_3 and $NaScA_2$ are denoted K_I and K_{II}, the following relationships will be obtained:

$$K_I = K_{II}^2[A]_t^{-1} \qquad (5)$$

and

$$K_{II} = K_{III} \ [A]_T^{-1} \qquad (6)$$

$K_{II} = K_{II}[Na]^{-1}$; $[A]_t$ and $[A]_T$ are the oxalate concentrations at the two phase-transition points (*cf.* Ref. 2).

Experimental

Chemicals. The compound Na_3ScA_3 was obtained from stock solutions of $NaClO_4$, $Na_2C_2O_4$, and $Sc(ClO_4)_3$ with $[Na] = 1.00$ M at equilibrium. The free oxalate concentration was kept higher than about 10^{-3} M all the time to avoid the formation of the solids Sc_2A_3 and $NaScA_2$. The compound $NaScA_2$ was prepared as described above, except that the free oxalate concentration was kept between 10^{-5} M and 10^{-4} M. Sc_2A_3 was obtained from $Sc(ClO_4)_3$- and $H_2C_2O_4$-solutions. The radioactive salts were prepared from Sc-solutions

of known specific activity. The stock solutions and the tracer were the same as described in the previous section.

Analyses of the solid phases. The solids were analysed for scandium and oxalate. The scandium content was determined by oxidation with $(NH_4)_2S_2O_8$ followed by titration with EDTA, while the oxalate content was determined as described before.[2] The results of the analyses are collected in Table 3.

Table 3. Analyses of the solid phases.

Solid phase	Scandium, %		Oxalate, %		Mol oxalate/ mol Sc (exp.)
	Exp.	Calc.	Exp.	Calc.	
$Sc_2A_3 \cdot 11.6\ H_2O$	16.01	15.97	46.9	46.9	1.50
$NaScA_2 \cdot 3.4\ H_2O$	14.75	14.73	57.8	57.7	2.00
$Na_3ScA_3 \cdot 5.7\ H_2O$	9.38	9.35	54.5	54.9	2.97

Solubility measurements. The methods have been described in a previous paper.[2,p.98] The temperature was $20.0 \pm 0.1°C$. The various oxalate buffer solutions were prepared as in Ref. 2, with the sodium ion concentration constant $= 1.00$ M. The compositions of the solutions are given in Table 4.

Table 4. The solubility measurements. h' and C_A' denote concentration values before any solid phase was added. [A] and S are equilibrium values.

h' varying, $C_A' = 9.92$ mM
$-\lg(h'/M)$, $-\lg([A]/M)$, $-\lg(S/M)$: 2.611, 2.985, *3.135*; 2.611, 2.985, *3.129*; 2.611, 2.985, *3.131*; 2.895, 2.742, *3.223*; 2.895, 2.742, *3.225*; 2.895, 2.742, *3.223*; 3.223, 2.497, *3.278*; 3.223, 2.497, *3.283* 3.223, 2.497, *3.272*; 3.668, 2.251, *3.286*; 3.668, 2.251, *3.279*; 3.668, 2.251, *3.283*.

C_A' varying, $\lg(h'/M) = -3.000$
$C_A' \cdot mM^{-1}$, $-\lg([A]/M)$, $-\lg(S/M)$: 6.37, 2.841, *3.194*; 6.37, 2.841, *3.188*; 10.19, 2.648, *3.244*; 10.19, 2.648, *3.257*; 22.6, 2.307, *3.287*; 22.6, 2.307, *3.282*; 36.9, 2.095, *3.267*; 36.9, 2.095, *3.270*.

C_A' varying, $\lg(h'/M) = -4.000$
$C_A' \cdot mM^{-1}$, $-\lg([A]/M)$, $-\lg(S/M)$: 13.55, 2.004, *3.260*; 13.55, 2.004, *3.267*; 13.55, 2.004, *3.256*; 19.73, 1.841, *3.197*; 19.73, 1.841, *3.195*; 24.1, 1.755, *3.174*; 24.1, 1.755, *3.185*; 24.1, 1.755, *3.180*; 28.4, 1.683, *3.140*; 28.4, 1.683, *3.151*; 42.8, 1.505, *3.069*; 42.8, 1.505, *3.068* 42.8, 1.505, *3.064*; 57.1, 1.380, *2.997*; 57.1, 1.380, *2.987*; 76.2, 1.255, *2.911*; 76.2, 1.255, *2.899*; 76.2, 1.255, *2.898*.

The solubility of Na_3ScA_3 was determined by the column method. The solubility equilibrium was established after only one passage of solution. The solubility was no longer constant when [A] was below about 10^{-3} M and decreased after every passage through the column. A phase-transition probably occurs here.

It was not possible to get any reproducible solubility values for the other two phases, either by using the column method or the agitation method. For the solid Sc_2A_3 some attempts were made to study the solubility in oxalate solutions where no sodium perchlorate had been added. These solutions were about 1.00 M in respect of $HClO_4$. The reproducibility was poor here, too. The only possible explanations for this lack of repro-

ducibility seems to be either a very long time of equilibration or some changes in the solid phase.

Determination of the phase-transition points. The method has been described before.[2,p.101] (Method *b.* was used.)

Rate of phase-transitions. The rates for the two phase-transformations are very slow; an agitation time of about four weeks is not sufficient to attain complete equilibrium (*cf.* Ref. 2, p. 101). Because of this, the determinations of the phase-transition points are rather uncertain, but can nevertheless be used for a rough estimation of the solubility products for the solids Sc_2A_3 and $NaScA_2$.

Results

Values of the phase-transition points. The concentration of oxalate ions at the transformations $Sc_2A_3 \rightarrow NaScA_2$ and $NaScA_2 \rightarrow Na_3ScA_3$ are equal to $(8\pm1)\times10^{-6}$ M and $(8\pm1)\times10^{-4}$ M, respectively. (The errors are estimated maximum errors.)

Solubility measurements. The solubility data for the solid Na_3ScA_3 are collected in Table 4. The corresponding solubility curve is shown in Fig. 2.
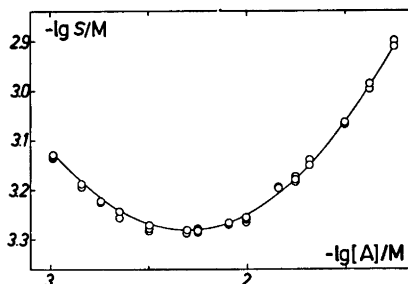
Fig. 2. Experimental values of the solubility for the solid Na_3ScA_3. The full-drawn curve has been calculated with the final set of solubility product (K_{III}) and stability constants given in Table 5.

The constants $\beta_j K_{III}$ were determined in a similar way, as described in the extraction part. The results are given in Table 5. As the measurements were restricted to rather high [A]-values, only the constants with $j = 2-4$ could be obtained. The value of $\beta_2 K_{III}$ is rather uncertain, because the second complex is present in very small amounts in the oxalate concentration range investigated. The solubility product, K_{III}, could consequently not be determined directly. The "best" value of the solubility product is probably obtained by dividing $K_{III}\beta_{3(sol)}$ by $\beta_{3(extr)}$. The corresponding solubility products for the solids Sc_2A_3 and $NaScA_2$ (K_I and K_{II}) were calculated by using eqns. (5) and (6). The results are given in Table 5.

POTENTIOMETRIC MEASUREMENTS

At high ligand concentrations it was possible to obtain supersaturated solutions with scandium concentrations sufficiently large for potentiometric measurements. The method used was the standard method of obtaining corresponding values of $\bar{n}$ and [A] by emf-measurements of h.

Table 5. Results from the extraction and solubility studies and the final stability constants and solubility products. The errors are given as three standard deviations. $K^* = K_{III}^{-1} \times 10^{-19}$ (K_I, K_{II}, and K_{III} are defined on p. 163).

Constant	Extraction measurements	Solubility measurements	Final set
$\beta_1 \times 10^{-7}$ M	1.37 ± 0.07	—	1.37 ± 0.07
$\beta_2 \times 10^{-12}$ M²	4.9 ± 0.3	$(3.2 \pm 2.4) \times K^*$	4.9 ± 0.3
$\beta_3 \times 10^{-15}$ M³	4.8 ± 0.5	$(3.7 \pm 0.3) \times K^*$	4.8 ± 0.5
$\beta_4 \times 10^{-17}$ M⁴	1.3 ± 0.3	$(1.55 \pm 0.08) \times K^*$	2.0 ± 0.5
$K_3 \times 10^{-2}$ M	9.8 ± 1.4	11.6 ± 9.6	—
K_4 M	28 ± 8	42 ± 6	—
$K_{III} \times 10^{20}$ M⁻⁷	—	—	7.7 ± 1.4
K_I M⁻⁵	—	—	$\sim 1 \times 10^{-27}$
K_{II} M⁻⁴	—	—	$\sim 1 \times 10^{-16}$

Experimental

The type of cells used and the experimental technique have been described previously.[1] (Glass electrode was used.) The ionic strength was 1.00 M and the temperature $20.0 \pm 0.1°C$. Titrations were made at three different scandium concentrations, *viz.* 2.4 mM, 5.0 mM, and 10.0 mM, while the total ligand concentration varied between 28 mM and 76 mM. The value of h was in the range 10^{-2} to 10^{-5} M. All the titrations were started at high ligand concentration which was decreased until a solid phase was formed. The reproducibility was sometimes rather poor. Emf-values which could not be reproduced within 0.5 mV were not used to determine $\bar{n}$.

Results

Satisfactory potentiometric measurements have been made over a fairly narrow range of free oxalate concentration. The results have not been used to compute stability constants. However, a comparison has been made between the potentiometric $\bar{n}$-values and those calculated from the final stability constants obtained from the two other methods. In the concentration range 10^{-3} M $< [A] < 10^{-2}$ M the differences between these $\bar{n}$-values are usually within 0.02 units. In solutions where the free oxalate concentration exceeds 10^{-2} M, the value of $\bar{n}_{final} - \bar{n}_{pot}$ is positive and rapidly increasing with increasing oxalate concentration. In some cases, especially when h is very low at the beginning of the series, the calculated $\bar{n}_{pot}$-curve passes through a maximum. This seems to indicate some experimental errors or some wrong assumptions; *e.g.* some hydrolysed species may be formed.

Some $\bar{n}$-values from the potentiometric measurements are shown in Fig. 1 together with the final $\bar{n}$-curve. Six titration series are here represented in the range $h > 10^{-4}$ M. (Data are thus omitted in the beginning of some series.)

DISCUSSION

The final set of stability constants is chosen from the extraction and solubility measurements. The values $\beta_1 - \beta_3$ are directly taken from the extraction study. The value of $K_4 = \beta_4 \beta_3^{-1}$ determined with this method seems to be more

uncertain than the value obtained in the solubility investigation. The final value of β_4 is thus calculated from $K_{4(\text{sol})} \cdot \beta_{3(\text{extr})}$. The "best" stability constants with their estimated maximum errors are given in Table 5. The full-drawn curves in Figs. 1 and 2 are calculated by using this set of constants. From the figures it is obvious that a good description of the experimental findings is obtained.

The existence of polynuclear species has been examined by varying the total scandium concentration in the extraction measurements. No differences outside the expected experimental errors could be detected. At high oxalate concentrations ($[A] > 10^{-3}$ M) data are available from all the methods. The scandium concentration is here varied from about 10^{-6} M (extraction) to 10^{-3} M (solubility) and 10^{-2} M (potentiometry). The fact that these measurements can be described with the same set of stability constants is a good indication that no polynuclear species are formed in this oxalate concentration range.

In the range 10^{-6} M $< [A] < 10^{-4}$ M the distribution ratios were determined at varying values of $[A]$ and h. Similar variations were also made in the other two methods in the range $[A] > 10^{-3}$ M. As the various properties X, S, or $\bar{n}$ did not vary with h for a given value of $[A]$, one could conclude that no acid or hydroxo complexes were formed. (Some deviations in the potentiometric study have been discussed above.) The good description of the experimental material with species of the type $\text{ScA}_j{}^{3-2j}$ only, is of course also a good indication that no mixed complexes are formed in larger amounts in the concentration ranges used. The existence of a complex ScHA^{2+} could hardly be established even in the most acid solutions if the constant $[\text{ScHA}] \cdot [\text{Sc}]^{-1} \cdot [\text{HA}]^{-1}$ is smaller than about 10^3 M. The value of this constant is probably about the same as the β_1-value of the scandium acetate system. The latter constant is equal to 1.4×10^3 M^{-1} in a medium with ionic strength 0.1 M (NaClO$_4$) and at 25°C.[17]

The over-all stability constants for the scandium oxalato complexes are larger than the corresponding constants for the lanthanoid complexes.[2] This might be caused by the smaller ionic radius of scandium. The stepwise stability constants also show that the two last complexes are relatively weak compared to the two first ones. The K_1-value of scandium is about 70 times larger than the corresponding value of lutetium. The K_2-value is about 20 times larger. The values of K_3 and K_4 for scandium are on the other hand smaller than the corresponding Lu-values (1/2 and 1/3, respectively). The relative weakness of the two highest complexes is also seen from the presence of a weak plateau around $\bar{n}$ equal to 2 in the curve of Fig. 1. Similar trends, sometimes said to be caused by "steric hindrance", have been discussed previously for other ligands (cf. Ref. 1, p. 626).

REFERENCES

1. Grenthe, I. and Hansson, E. *Acta Chem. Scand.* **23** (1969) 611.
2. Grenthe, I., Gårdhammar, G. and Rundcrantz, E. *Acta Chem. Scand.* **23** (1969) 93.

3. Korenman, I. M. and Zaglyadimova, N. V. *Zh. Neorg. Khim.* **11** (1966) 2774.
4. Kumok, V. N., Skorik, N. A. and Serebrennikov, V. V. *Tr. Tomsk. Gos. Univ. Ser. Khim.* **185** (1965) 129.
5. Starý, J. *Anal. Chim. Acta* **28** (1963) 132.
6. Gridasova, R. K., Kolosov, I. V. and Ivanov-Emin, B. N. *Radiokhimiya* **10** (1968) 37.
7. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
8. Taft, R. W., Jr. and Cook, E. H. *J. Am. Chem. Soc.* **81** (1959) 46.
9. Reid, J. C. and Calvin, M. *J. Am. Chem. Soc.* **72** (1950) 2948.
10. King, E. L. and Reas, W. H. *J. Am. Chem. Soc.* **73** (1951) 1804.
11. Norén, B. *Acta Chem. Scand.* **21** (1967) 2435.
12. Bidermann, G., Kilpatrick, M., Pokras, L. and Sillén, L.-G. *Acta Chem. Scand.* **10** (1956) 1327.
13. Aveston, J. *J. Chem. Soc.* **1966** 1599.
14. Grenthe, I. and Williams, D. R. *Acta Chem. Scand.* **21** (1967) 341.
15. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
16. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1932, Band VI, Abteilung 2, p. 688.
17. Kaleeva, V. A., Kumok, V. N. and Serebrennikov, V. V. *Tr. Tomsk. Gos. Univ. Ser. Khim.* **185** (1965) 141.