Studies on the Hydrolysis of Metal Ions

XII. The Hydrolysis of the Vanadium(IV)ion

F. J. C. ROSSOTTI and H. S. ROSSOTTI

Department of Inorganic Chemistry, the Royal Institute of Technology, Stockholm 70, Sweden

Spectrophotometric and potentiometric measurements made in a 3 M perchlorate medium at 25° C indicate that vanadium(IV) exists as the vanadyl ion, VO^{2+} (or $V(OH)_2^{2+}$), in the range of acidity
3 M $>[H^+]>0.002$ M. Potentiometric data for the hydrolysis of the vanadyl ion, for total concentrations of vanadium in the range
0.05 M$>$M$>$0.005 M, may be explained by assuming that only two further complexes are formed in solution. For convenience these will be written as $VO.OH^+$ and $(VO)_2(OH)_2^{2+}$, although they may be combined with water molecules, or sodium or perchlorate ions. The following values of the equilibrium constants were obtained:
$$\varkappa_{1,1} = [VO.OH^+][H^+]/[VO^{2+}] = 10^{-6.0\pm0.1}$$
$$\varkappa_{2,2} = [(VO)_2(OH)_2^{2+}][H^+]^2/[VO^{2+}]^2 = 10^{-6.88\pm0.04}$$
Precipitation occurred when approximately 10 % of the vanadyl ions were further hydrolysed.

L ittle quantitative work on the hydrolysis of tetravalent vanadium has been reported. Britton and Welford [1] (*cf.* Ref.[2]) have measured the changes in pH which occur when a solution of vanadyl sulphate, $VOSO_4$, is titrated with alkali, but as both the total concentration of vanadium, and the ionic strength, varied throughout the titration, no detailed interpretation of these data is possible. Their results do, however, indicate that, in strongly acidic solutions, vanadium(IV) exists as the "vanadyl" ion, VO^{2+}. A precipitate of composition $VO(OH)_2$ is formed on addition of alkali. It is somewhat soluble in excess of alkali to give "vanadites", which are readily oxidised by air.

Jones and Ray [3] measured the pH of solutions of pure vanadyl sulphate of concentrations 0.5 M to 0.0001 M. Their data have subsequently been used to calculate the equilibrium constant, $\varkappa_{1,1} = 4.4 \cdot 10^{-6}$ for the reaction

$$VO^{2+} + H_2O \rightleftharpoons VO(OH)^+ + H^+$$
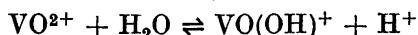
at infinite dilution [4]. It was assumed that $VO(OH)^+$ was the only hydroxyl complex formed, and that the presence of HSO_4^- ions and vanadium sulphate complexes could be neglected.

The influence of the hydrogen ion concentration on the formal redox potential V(IV)/V(V) has been investigated by several authors (Ref.[5] and refs. therein,[6]). The data obtained in strongly acidic solution indicate that vanadium (IV) exists as the vanadyl ion, VO^{2+}. Measurements at higher values of pH are difficult to interpret, as hydrolysis products of both valency states are undoubtedly present. As would be expected, the value of the half-wave oxidation potential[7] of vanadium(IV) also varies with pH.

As a large number of metal ions react with water to form polynuclear hydrolysis products, investigation of equilibria in systems of this type requires accurate data at a number of different total concentrations of metal. The hydrolysis of tetravalent vanadium was therefore studied using the techniques previously developed in this laboratory (*cf.* previous papers in this series, *e. g.*[8–15]).

List of symbols

The symbols adopted are mainly those used in the previous papers in this series.

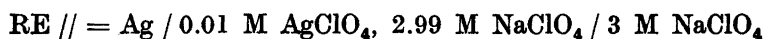|	
A_s	optical absorbancy
c_n	concentration of complex $VO((OH)_tVO)_n$
E	measured potential in mV
E'	$= E - 59.16 \log h$ (1)
g	$= k_n u^n$ (11)
H	total analytical concentration of hydrogen ions in the system, assuming that all vanadium is in the form VO^{2+} (4)
H'	total analytical concentration of hydrogen ions in the system, assuming that all vanadium is in the form V^{4+} (3)
h	concentration of free hydrogen ions
k	equilibrium constant, defined by $k = k_{n+1}k_n^{-1}$ (hypothesis IIIa)
k_0	$= k_n k^{-n}$ (hypothesis IIIa)
k_n	$=$ equilibrium constant for the reaction $(n+1)VO^{2+} + tn\ H_2O = VO((OH)_t)_n^{2+} + tn\ H^+$
K_w	ionic product of water $= [H^+]\ [OH^-]$
M	total concentration of vanadium
M	mole/l
m	concentration of free vanadyl ions, VO^{2+}
N	number of $(OH)_tVO$ links in a unique complex
n	variable number of $(OH)_tVO$ links in the complex $VO((OH)_tVO)_n$
$\bar{n}$	average number of links per complex
p	number of hydroxyl groups in complex $(VO)_q(OH)_p$
q	number of vanadyl groups in complex $(VO)_q(OH)_p$
s, s'	hydration numbers
t	number of hydroxyl group per vanadyl group in link
u	$= mh^{-t}$ (10)
x	$= \log M - t \log h$ (7)
y	$= Z/t$ (6)
Z	average number of hydroxyl groups per vanadyl group $= (H-h)/M$ (2)
$\varkappa_{p,q}$	equilibrium constant for the reaction $q\ VO^{2+} + p\ H_2O \rightleftharpoons (VO)_q(OH)_p + p\ H^+$

All species may be combined with the medium ions, Na^+ and ClO_4^-, or with molecules of the solvent; thus it is impossible to distinguish between two hydroxyl groups, and one oxo-group, $-O-$.

Concentrations and equilibrium constants will be expressed in M (mole/l) throughout.
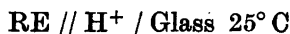
METHOD

The main investigation consisted of a series of potentiometric titrations at 25° C. In each titration, the total concentration of vanadium, M, was kept constant, while the total concentration of acid in the system was varied. All solutions were made 3 M with respect to the perchlorate ion by the addition of sodium perchlorate. Since the concentrations of hydrogen ions and metal ions never exceeded 0.4 % and 1.7 %, respectively, of the concentration of perchlorate ions, it can be assumed that the activity coefficients of all species remain constant [8], and hence that true stoichiometric constants may be calculated from the measurements.

Now as trivalent vanadium is oxidised by the perchlorate ion [20], and as no reliable data on the hydrolysis of pentavalent vanadium in 3 M perchlorate solutions were available, the concentration of free vanadyl ions could not be measured with a redox electrode; neither is another electrode which is reversible to vanadium(IV) known. The titrations were therefore followed only by measurement of the free hydrogen ion concentration, h. A glass electrode was used, in combination with the half-cell

$$RE \,/\!/ = Ag \,/\, 0.01 \; M \; AgClO_4, \; 2.99 \; M \; NaClO_4 \,/\, 3 \; M \; NaClO_4$$

For the cell

$$RE \,/\!/ \, H^+ \,/\, Glass \;\; 25° \, C$$

the relationship between the measured potential, E, and the concentration of free hydrogen ions, is given by

$$E = E_0' + 59.16 \, \log h \tag{1}$$

The term E_0' includes the standard potentials of the two electrodes, the asymmetry potential of the glass electrode, and the liquid junction potential. In the range of acidity studied ($h \ll 0.01$ M), the value of E_0' was found to be independent of h within the limits of experimental error. The value of E_0' was determined for each titration, either by a preliminary acid-base titration in the absence of metal, or by titration in the presence of metal, in the range $0.01 \; M \gg h \gg 0.002$ M. As no hydrolysis occurs in this region (see below), h is identical with the total analytical hydrogen ion concentration, H, defined by equation (4). For each point, H is known from the composition of the solutions, and E_0' is calculated from the measured value of E, using equation (1).

When E_0' is known, and E is measured, h can be obtained from equation (1). As both H and M are known, the average ligand number of the hydroxy complexes, Z, may be calculated for any point of the titration, using the relationship

$$Z = (h - H) \,/\, M \tag{2}$$

The data may conveniently be discussed in terms of the variation of Z with $\log h$.

The vanadium(IV) species present in strongly acidic solution were investigated spectrophotometrically.

EXPERIMENTAL DETAILS

R e a g e n t s

Vanadium (IV) perchlorate solutions were prepared by adding a solution of saturated ammonium carbonate (*p. a.*) dropwise to an aqueous solution of vanadyl sulphate (Merck, *p. a.*) until there was no further precipitation. The precipitate was centrifuged, washed free from sulphate ions, and dissolved in a slight excess of perchloric acid (*p. a.*). The washing was carried out as quickly as possible to avoid aerial oxidation of the neutral precipitate (*cf.* Ref.[2]). The concentration of vanadium(IV) in the solution was determined by titration with aqueous potassium permanganate, which had been standardised against sodium oxalate (*p. a.*), dried at 120° C. In order to test for the possible presence of any vanadium(V), the solution was then reduced with sulphur dioxide. When the excess of sulphur dioxide had been expelled by passing carbon dioxide through the boiling solution, the solution was again titrated with permanganate. Since the amount of permanganate required after this reduction was the same as that used in the first titration, the stock solution contained only tetravalent vanadium. The total concentration of perchlorate ion was found by passing the solution through a column containing the resin Amberlite IR 120, in the hydrogen form, washing with water, and titrating the eluate to the methyl red end-point with standard sodium hydroxide. Dilute solutions of vanadium (IV) perchlorate for titration were prepared by weight.

Perchloric acid solutions were prepared from perchloric acid (*p. a.*) and standardised against potassium hydrogen carbonate (Merck, *p. a.*) which was free from sodium ions, and had been dried in an atmosphere of carbon dioxide.
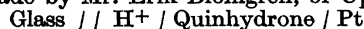
Sodium hydrogen carbonate solutions were prepared by weighing out the "AnalaR" solid. The concentrations were checked by potentiometric titration against standard perchloric acid, using Gran's method for calculating the end-point [21].

Silver perchlorate solutions were prepared by adding an excess of silver oxide to a boiling solution of perchloric acid. The solution was filtered, and the concentration of silver determined by Volhard's method.

Sodium perchlorate was prepared by neutralising a solution of perchloric acid with sodium hydrogen carbonate. The solutions were analysed both by using a cation exchange resin (see above), and by evaporating and drying to constant weight at 125° C. Good agreement was found between the two methods. No chloride or chlorate ions could be detected in the product.

A p p a r a t u s

The titration cell was of the type described by Forsling, Hietanen, and Sillén [9]. The glass electrode was made by Mr. Erik Blomgren, of Uppsala. The potential of the cell
$$\text{Glass} \mid \mid \text{H}^+ \mid \text{Quinhydrone} \mid \text{Pt}$$
was found to be constant, ± 0.1 mV, in the range $-1.0 \gg \log h \gg -6.0$, showing that equation (1) is valid. Thus, in the range $h < 0.01$ M, where the term E'_0 is effectively independent of h (see p. 1179), the behaviour of the glass electrode can be described by the Nernst equation. The silver reference electrodes were prepared as recommended by Brown [22] and coated with silver chloride by electrolysis for half an hour in 0.1 M hydrochloric acid with a current of 0.3 milliampere per electrode. Potentials were measured to ± 0.1 mV with a Radiometer PHM3i valve potentiometer.

Solutions were introduced into the titration cell from burettes which had been calibrated by the method of weighing, using 3 M sodium perchlorate. The titration solution was stirred by a stream of nitrogen which had been passed through a 3 M sodium perchlorate solution.

Spectrophotometric measurements were made at 25 ± 1° C with a Beckman DU Spectrophotometer, using matched 1.00 cm Corex cells, and minimum slit widths.

Titration procedure

Titrations were carried out in a paraffin oil thermostat at 25.0 ± 0.1° C. 20.0 ml of a solution, A, containing vanadium(IV) perchlorate (concentration 2 *M*) in perchloric acid (~0.005 M) was added to 20.0 ml of perchloric acid (~0.012 M). This mixture, solu-

tion B, was titrated with equal volumes of sodium hydrogen carbonate (~0.03 M) and of solution A. The total concentration of metal, M, then remained constant throughout the titration. Series of measurements were made with M~0.05 M, ~0.02 M, ~0.01 M and ~0.005 M.

Sodium hydrogen carbonate was used as a base in preference to sodium hydroxide to avoid local precipitation (cf. Ref.[10]). Values of h <0.0001 M were not required as vanadium(IV) precipitates in this region. Near the end of one titration, the equilibrium potential was noted, and the stream of nitrogen exchanged for a rapid stream of carbon dioxide. The system was left for an hour, and then nitrogen was bubbled through the solution for one minute. The potential was the same as before, indicating that the measurements are not invalidated by complex formation between vanadium(IV) and carbonate ions.

In the early stages of hydrolysis (e. g. Z ~0.05, for M ~0.01 M) a steady potential was reached in 2 to 5 minutes. When slightly hydrolysed solutions were back-titrated with acid, the points Z(log h) fell on the same curves as points obtained by forward titration with alkali, indicating that equilibria are reversible in this region. In solutions of rather higher pH (e. g. Z ~0.08, for M~ 0.01 M), equilibrium was reached more slowly. A steady potential was obtained in about half an hour, and remained constant for at least three hours. As the emf. measurements in this region did not seem to be quite reversible, it is possible that some invisible precipitate was present. When visible precipitation occured, no steady potential could be obtained, and the titration was discontinued.

It is well-known that solutions of tetravalent vanadium are readily oxidised by air [2]. Preliminary work on the ageing of hydrolysed solutions of vanadium(IV) perchlorate in the absence of air shows that the perchlorate ion is slowly reduced at room temperature. The reaction takes place rapidly on boiling. After each titration the metal solution was acidified, and analysed for vanadium(IV) and (V), but no oxidation was found to have occurred during the course of the titrations.

VANADIUM (IV) PERCHLORATE IN ACIDIC SOLUTION

The total analytical hydrogen ion concentration, H', was first calculated assuming that the ion V^{4+} is completely unhydrolysed. Then for the stock metal solution, which contains only vanadium (IV) perchlorate and perchloric acid

$$H' = [ClO_4^-] - 4M \tag{3}$$

Preliminary titrations based on this assumption indicated that, in the range 0.03 $M \gg h \gg$ 0.002 M, two hydroxyl groups are bound to each metal atom, i. e. that the species $[V(OH)_2^{2+}]_X$ or $(VO^{2+})_X$ is present.

The effect of higher acidities and metal concentrations on the nature of the species present was investigated by comparing the optical absorbancy, A_s, of different solutions. The ratio A_s/M is shown as a function of wavelength in Fig. 1, and is seen to be independent of M in the range 0.936 M $\gg M \gg$ 0.023 M, and of h in the range 2.953 M $\gg h \gg$ 0.027 M. Fig. 1 is similar to that obtained by Furman and Garner [23], who showed that the absorption spectrum of vanadium(IV) perchlorate is independent of h in the range 1 M $\gg h \gg$ 0.02 M. The slight[differences between the[present results, and those obtained by Furman and Garner in a 2 M perchlorate medium may be due to the large difference in the concentration of the perchlorate ion. The absorbancies of solutions of iron (III) perchlorate are also influenced by the concentration of perchlorate ions [24].

As the ratio $A/_sM$ is independent of the value of M, the species is probably monomeric. For convenience it will be written as VO^{2+}, although it may be
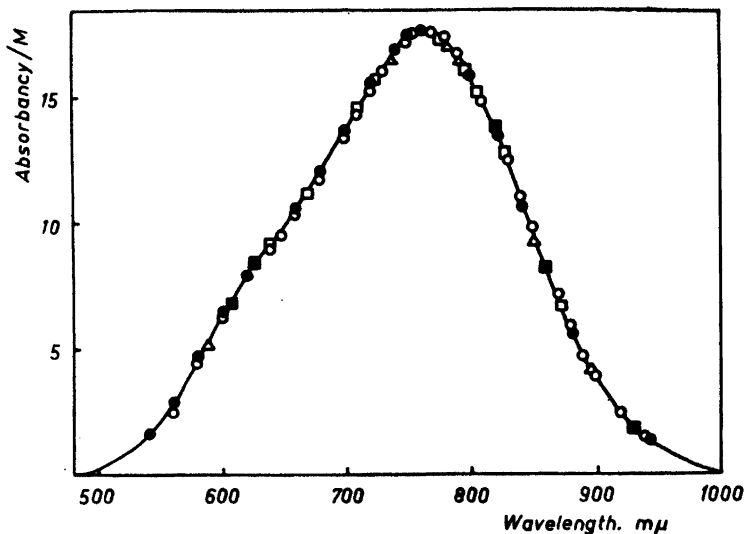
Fig. 1. Visual absorption spectrum of vanadium (IV) perchlorate in acidic solution (3 M perchlorate medium).

	M	h
O	0.0234 M	0.0266 M
●	0.0234 M	2.935 M
□	0.0094 M	0.700 M
■	0.0468 M	0.700 M
△	0.0936 M	0.700 M

combined either with water molecules, or with sodium or perchlorate ions [11]. As the ion showed no tendency to combine with protons, even at the highest acidity studied ($h = 2.95$ M), the subsequent results will be discussed in terms of the addition of hydroxyl groups to a central vanadyl ion. H is then defined as the total analytical concentration of hydrogen ions, assuming that all the vanadium is in the form of VO^{2+}. Thus, for the stock solution of vanadium(IV) perchlorate

$$H = [ClO_4^-] - 2M \tag{4}$$

Similarly, Z is defined as the average number of hydroxyl groups bound to' or protons dissociated from, a vanadyl ion. An analogous approach has been used [12] in the study of the uranyl ion, UO_2^{2+}.

The value of H was found using equation (4). For each titration, the total analytical concentration of hydrogen ions in solution A was checked by potentiometric titration with sodium hydrogen carbonate. The titrations were discontinued before any hydrolysis of the vanadyl ion occured ($h > 0.002$ M), and the end-point was found by Gran's method of extrapolation[21] . Similarly, the total analytical concentration of hydrogen ions in solution B was checked by extrapolating the first few points of the actual hydrolysis titration ($h > 0.002$ M) to the end-point. Very satisfactory agreement was found between the inter-related values of the total analytical hydrogen ion concentrations.

THE HYDROLYSIS OF THE VANADYL ION, VO^{2+}.

The data Z (log h)$_M$ were obtained from the potentiometric measurements, using equations (1) and (2). They are shown in Table 1 and plotted in Fig. 2. If only mononuclear complexes were formed, Z would be a function of h only,
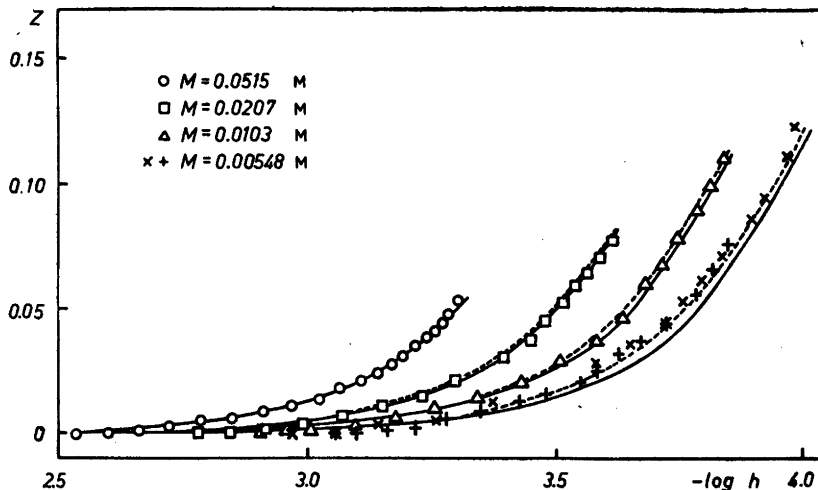

Fig. 2. Average number, Z, of hydroxyl groups bound to each vanadyl ion as a function of log h. O, □, △, +, ×, are experimental points for different total concentrations, M, of vanadium. Full curves calculated for $\varkappa_{1,1} = 0$, $\varkappa_{2,2} = 10^{-6.88}$. Dashes calculated for
$$\varkappa_{1,1} = 10^{-6.0}, \varkappa_{2,2} = 10^{-6.88}$$

Table 1. Data Z, log h

| $M = 0.0515$ M		$M = 0.0207$ M		$M = 0.0103$ M		$M = 0.00548$ M			
$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z	$-\log h$	Z
2.534	0.000	2.721	0.000	2.904	0.000	3.053	0.000	2.972	0.001
2.598	0.000	2.781	0.000	2.958	0.001	3.101	0.000	3.053	0.0015
2.661	0.001	2.845	0.001	3.027	0.002	3.159	0.001	3.144	0.004
2.721	0.003	2.917	0.002	3.095	0.004	3.218	0.0025	3.259	0.005
2.784	0.005	2.992	0.004	3.174	0.007	3.278	0.006	3.374	0.013
2.850	0.006	3.073	0.007	3.253	0.011	3.348	0.009	3.582	0.028
2.912	0.009	3.152	0.011	3.343	0.015	3.425	0.013	3.653	0.036
2.970	0.011	3.232	0.015	3.430	0.021	3.472	0.016	3.720	0.044
3.024	0.014	3.301	0.021	3.507	0.029	3.544	0.021	3.763	0.053
3.068	0.018	3.396	0.030	3.582	0.037	3.883	0.025	3.798	0.061
3.107	0.021	3.443	0.037	3.636	0.047	3.626	0.032	3.847	0.071
3.139	0.024	3.479	0.045	3.683	0.061	3.671	0.037	3.900	0.085
3.171	0.028	3.516	0.052	3.717	0.068	3.722	0.044	3.927	0.094
3.190	0.031	3.541	0.059	3.751	0.079	3.781	0.056	3.974	0.111
3.217	0.035	3.558	0.063	3.785	0.089	3.815	0.066	3.986	0.123
3.239	0.038	3.589	0.070	3.813	0.100	3.847	0.076		
3.256	0.041	3.612	0.077	3.841	0.111				
3.262	0.044								
3.277	0.047								
3.303	0.053								
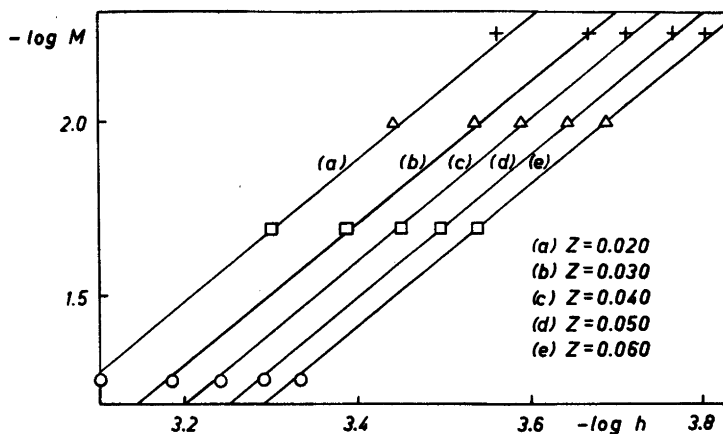
Fig. 3. *Log* M *as a function of log* h, *for different values of* Z. *The best lines of slope 2.0*
are shown.

and all points would lie on the same Z (log h) curve, regardless of the value of M. As this is not the case, at least one polynuclear hydroxyl complex must be formed.

Now the system may contain any species of the general formula $(VO)_q(OH)_p{}^{(2q-p)+}$, where p and q may have any positive integral values. A quite general method for computing the hydrolysis constants

$$\varkappa_{p,q} = [(VO)_q(OH)_p{}^{(2q-p)+}][H^+]^p/[VO^{2+}]^q$$

in systems of this type has been developed by Hedström [25]. Unfortunately, as measurements of the concentration of free VO^{2+} could not be made, measurements at a very large number of concentrations of total metal would be needed. Hedström's approach was therefore not used in the present work, and the data were analysed to see if they could be explained by imposing certain restrictions on the values of p and q. It has previously been found that the hydrolysis products of a number of metal ions, Me, have the general "core+links" formula $Me[(OH)_tMe]_n$, here t and n are integers, such that t is a constant, but that n may vary. The treatment of systems of this type, in which p is a linear function of q, has been developed by Sillén [26,27] (*cf.* parts VIII—XII of this series [11-15]).

If all the complexes present in appreciable amounts can be written in a "core+links" form, a set of parallel Z (log $h)_M$ curves should be obtained. The value of t is then given by

$$t = (\partial \log M/\partial \log h)_Z \qquad (5)$$

It is seen in Fig. 2 that the data for the hydrolysis of vanadium(IV) do lie on parallel Z (log $h)_M$ curves. A value of $t = 2$ was obtained from Fig. 3, in which log M is plotted against log h for several values of Z. Again, if only the species
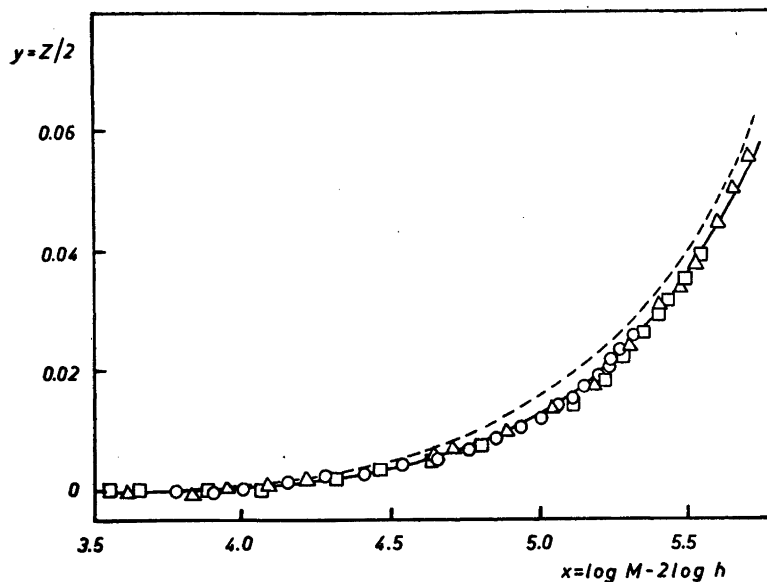
Fig. 4. y $(= Z/2)$ *as a function of* x $(= log \, M - 2 \, log \, h)$.
The symbols are those used in Fig. 2. Dashes represent the experimental curve for
M $= 0.005$ M. *The full curve is calculated for* $x_{1,1} = 0$, $x_{2,2} = 10^{-6.88}$.

$VO((OH)_t VO)_n$ are formed, all experimental points should lie on the same curve $y(x)$, where

$$y = Z/t \tag{6}$$

and

$$x = \log \, M - t \, \log \, h \tag{7}$$

The experimental curve, $Z/2$, $(\log \, M - 2\log \, h)$ is shown in Fig. 4, and it is seen that points for 0.05 M $\gg M \gg$ 0.01 M do lie on a single curve. The small deviations which are observed for the points at the lowest concentration of vanadium (broken curve in Fig. 4) may indicate the presence of mononuclear complexes (see p. 1189). However, on account of the limited accuracy of the glass electrode, and of the very low values of Z (< 0.1) obtained, it was not considered practicable to investigate the behaviour of more dilute solutions of vanadium(IV).

Now as y is a function of x only, and as $t = 2$, any complexes formed in appreciable amounts are of the type $VO((OH)_2 VO)_n$ or $VO(O.VO)_n$. Direct analysis of the curve $y(x)$ should indicate whether n is a constant or a variable.

Direct analysis of the curve $y(x)$

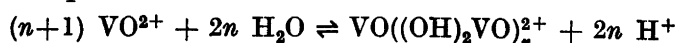It has been shown (Ref.[27], equations 14 and 15) that the function $y(x)$ may be used to calculate

$$\log \, (1 + g) = \int_{-\infty}^{x} y \, dx + \log \, (1-y) + y \, \log \, e \tag{8}$$

and $\qquad \log u = x - y \log e - \int_{-\infty}^{x} y \, dx$ $\qquad$ (9)

Here $\qquad\qquad u = [VO^{2+}]h^{-2}$ $\qquad\qquad$ (10)

$$g = \sum k_n u^n \qquad\qquad (11)$$

and k_n is the equilibrium constant for the reaction

$$(n+1) \; VO^{2+} + 2n \; H_2O \rightleftharpoons VO((OH)_2VO)_n^{2+} + 2n \; H^+$$

The average number of $((OH)_2VO)$ or $(O.VO)$ "links" per complex is given by

$$\bar{n} = d \log g / d \log u = \sum n \; c_n / \sum c_n \qquad (12)$$

where c_n is the equilibrium concentration of the complex $VO((OH)_2VO)_n^{2+}$.

A smooth curve was drawn through the experimental points y, x for 0.05 M $\gg$ M $\gg$ 0.01 M, and a set of values of $\int_{-\infty}^{x} y \, dx$ was obtained by graphical integration. Values of $\log(1+g)$ and $\log u$ were calculated using equations (8) and (9), and are shown in Table 2.

Table 2. *Direct analysis of the curve* y(x).

y	x	$10^3 \int_{-\infty}^{x} y \, dx$	$\log u$	$\log (1+g)$
0.01	4.895	3.389	4.887	0.00337
0.015	5.080	5.696	5.068	0.00565
0.02	5.210	7.957	5.194	0.00787
0.025	5.310	10.219	5.289	0.01008
0.03	5.400	12.690	5.375	0.01249
0.035	5.478	15.230	5.448	0.01496
0.04	5.540	17.541	5.505	0.01718
0.045	5.592	19.742	5.553	0.01928
0.05	5.640	22.019	5.596	0.02145
0.055	5.685	24.374	5.633	0.02369
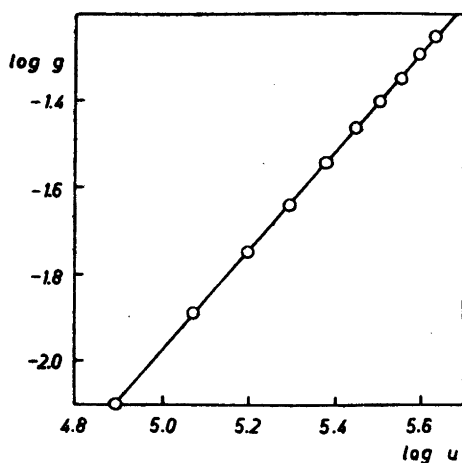
Fig. 5. *Direct analysis of the curve* y(x); *log* u (= *log* [VO²⁺]h⁻²) *as a function of log* g (= *log* $k_n u^n$).

The residual integral $\int_{-\infty}^{3.9} y \cdot dx$ was assumed to be zero (*cf.* Fig. 4). The function $\log g$ ($\log u$) was calculated, and is plotted in Fig. 5. A straight line of slope 1.1 was obtained over the whole range studied ($0 \leqslant y \leqslant 0.05$). A slope of 1.0 would indicate that only the first complex, $VO((OH)_2VO)^{2+}$ is formed. The slightly higher value obtained is not considered to be significant; as Hietanen [13] has emphasized, $\bar{n}$ is very sensitive to small errors in y in the range $y < 0.2$. If higher complexes were formed, the value of d $\log g$/d $\log u$ would be expected to increase with increasing u. No such curvature was observed.

If only the first complex is formed, then from equation (11)

$$\log g - \log u = \log k_n \tag{13}$$

and the value of $\log k_n$ may be obtained from equation (13) for each of the points $\log g$, $\log u$. The value

$$\log k_1 = \log \varkappa_{2,2} = -6.90 \pm 0.02$$

was obtained using points in the range $0.02 < y < 0.05$ (see below).

Other methods for calculating the hydrolysis constant

If, as indicated by direct analysis of the curve $y(x)$, only the first "core + links" complex is formed, then p and q are constants, such that $p = t$, and $q = 2$. For a system containing only one complex, $Me_Q(OH)_P$, it may be shown that

$$\log \{P^{Q-1}Z(P-QZ)^{-Q}\} = \log \varkappa_{P,Q} + (Q-1)\log M - P \log h \tag{14}$$

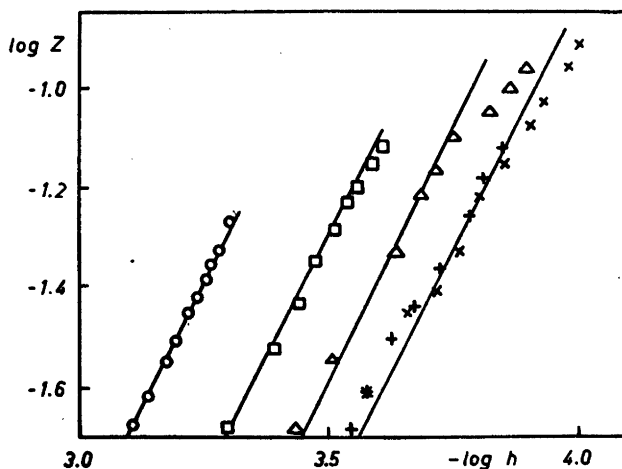Whence $(\partial \log M/\partial \log h)_Z = P(Q-1)$ (15) (*cf.* Ref.[26] equation 29).

Fig. 6. Log Z *as a function of* log h, *showing the best straight lines of slope 2.0. The symbols for experimental points are those used in Fig. 2.*

Combining equations (5) and (15),

$$P \,/\, (Q-1) = t$$

Furthermore, $\lim\limits_{z \to 0} (\partial \log Z \,/\, \partial \log h)_M = -P$ (17)

Plots of $\log Z$ against $\log h$ are shown in Fig. 6. Points for very low values of Z (<0.02) are omitted, as the value of $\log Z$ is very sensitive to small experimental errors in Z over this range. Limiting slopes of -2 were obtained for the concentrations of metal $0.05 \text{ M} \ll M \ll 0.01$ M, indicating that $P = 2$. As $t = 2$ (see p. 1184), equation (16) gives $Q = 2$.

When $P = 2$ and $Q = 2$, equation (14) reduces to

$$\log \ \{Z \,/\, 2 \ (1-Z)^2\} = \log \varkappa_{2,2} + \log \ M - 2 \log h \qquad (14a)$$

Thus, if $Me_2(OH)_2$ is the only complex formed, a plot of $\log Z/2(1-Z)^2$ against $(\log \ M - 2 \log h)$ should be a straight line of unit slope and of intercept $\log \varkappa_{2,2}$. The data for the hydrolysis of the vanadyl ion are plotted in fig. 7, and it is seen that points for $0.05 \text{ M} \gg M \gg 0.01$ M do lie on a straight line of unit slope. This is further strong indication that the only complex formed in appreciable amounts is $(VO)_2(OH)_2^{2+}$ or $(VO)_2O^{2+}$. The intercept gives $\log \varkappa_{2,2} = -6.87 \pm 0.02$. Deviations are again observed for points at the lowest concentration of vanadium.

The experimental curve $y(x)$ may also be compared with theoretical curves, calculated for different values of $\log \varkappa_{2,2}$, using equation (14a). A good fit was
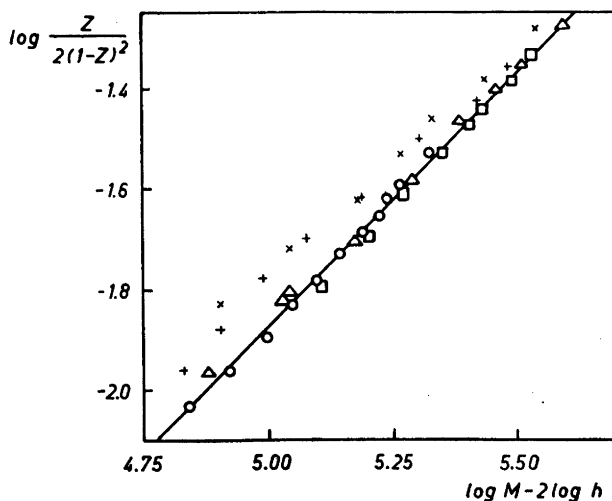

Fig. 7.   Log $\{(Z/2\,(1-Z)^2\}$ as a function of $(\log M - 2 \log h)$. The best straight line of unit slope is drawn through the experimental points for $0.05 \ M \ll M \ll 0.01$ M. The symbols are those used in Fig. 2.

obtained with $\log \varkappa_{2,2} = -6.88$ (see Fig. 4). It may be shown that equation (14a) is identical to that used by Sillén ([27], equation 23) for the case where only one complex, $Me((OH)_xMe)$ is formed (hypothesis II, $N = 1$).

The possible presence of hydrolysis products other than $(VO)_2(OH)_2^{2+}$

(a) Higher polymeric species. In order to test whether higher polymers, e. g. $VO((OH)_2VO)_2^{2+}$, are present in appreciable amounts, the shape and position of the experimental curve $y(x)$ was compared with curves calculated for the simplified cases suggested by Sillén [27]. A good fit was obtained with some of the curves calculated assuming that n may vary, and that the ratio k_{n+1}/k_n is independent of the value of n ([27], hypothesis IIIa). It was found that $k_0 \geqslant 0.5$, where $k_0 = k_n k^{-n}$, and $k = k_{n+1} k_n^{-1}$. For a given value of k_0, the value of k may be calculated from the experimental data. Combination of equations given previously (Ref.[27], equations 33, 36, 37) leads to

$$k^2 [y^2 \, 10^{2x} \, (1-y)^2] - k[2y^2 10^x (1-y) - k_0 10^x (1-2y)^2] + y^2 = 0 \qquad (18)$$

Using equation (18), values of $k_1 = k_0 k$ were calculated for some of the possible values of k_0, and are given below.

k_0	$\log k_1 = \log \varkappa_{2,2}$	mean $\log \varkappa_{2,2}$
0.5	-6.90 ± 0.02	
1.0	-6.88 ± 0.03	-6.88 ± 0.04
2.0	-6.86 ± 0.02	
20.0	-6.90 ± 0.02	

Thus for $k_0 \geqslant 0.5$, the value of k_1 is independent of the value of k_0 within the limits of experimental error. The very good agreement between this value of k_1, and the values obtained by other methods, indicates that no higher hydroxyl polymers are present in appreciable amounts. (*i. e.* $\sum_{n=2}^{n=\infty} c_n \, M^{-1} \leq 0.3 \%$) This would be expected at the very low values of Z (<0.1) studied.

(b) Mononuclear species. Figs. 2, 4, 6 and 7 indicate that the experimental data for $M \sim 0.005$ M cannot be explained satisfactorily by assuming that only the complex $(VO)_2(OH)_2^{2+}$ is present. The observed deviations may be explained in terms of the formation of appreciable amounts of the mononuclear complex, $VO.OH^+$, at this concentration of vanadium. If the species $(VO)_2 (OH)_2^{2+}$ and $VO.OH^+$ are the only two complexes in solution, it may be shown that

$$h = \left(\frac{1-Z}{2Z}\right) \left\{ \varkappa_{1,1} + \sqrt{\varkappa_{1,1}^2 + 8Z\varkappa_{2,2}M} \right\} \qquad (19)$$

Sets of curves $Z(\log h)_M$ were calculated for different values of $\varkappa_{1,1}$ using equation (19), and assuming that $\log \varkappa_{2,2} = -6.88$. The experimental data agree satisfactorily with the curves calculated assuming that $\log \varkappa_{1,1} = -6.0 \pm 0.1$ (*cf.* broken curves in Fig. 2).

DISCUSSION

Potentiometric and absorptiometric studies indicate that vanadium (IV) exists as the vanadyl ion, VO^{2+}, in the range of acidity 2.95 $M \gg h \gg 0.002$ M. The potentiometric titration data for $h < 0.002$ M can be explained by assuming that only two further complexes, $VO.OH^+$ and $(VO)_2(OH)_2^{2+}$, are formed. As might be expected for the low values of Z (< 0.1) at which precipitation occurs, there is no evidence for the formation of higher polymeric species in solution. Values of the equilibrium constant, $\varkappa_{2,2}$, for the reaction

$$2VO^{2+} + 2H_2O \rightleftharpoons (VO)_2(OH)_2^{2+} + 2H^+$$
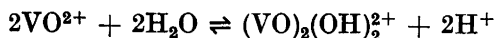
have been calculated by a number of methods, and are shown below.

Method	$\log \varkappa_{2,2}$
Direct analysis of curve $y(x)$	-6.90 ± 0.02
Equation (14a)	-6.87 ± 0.02
Curve-fitting. Hypothesis II	-6.88 ± 0.02
Hypothesis IIIa, $k_0 \gg 0.5$	-6.88 ± 0.04

The good agreement obtained using different methods of calculation is further evidence that no higher complexes are formed in appreciable amounts.

The equilibrium constant for the reaction

$$VO^{2+} + H_2O \rightleftharpoons VO.OH^+ + H^+$$
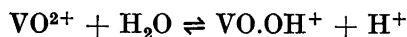
was calculated primarily from the data for $M \sim 0.005$ M. The value obtained ($\log \varkappa_{1,1} = -6.0 \pm 0.1$) indicates that, even at this low concentration of metal, only 0.2 % of the total vanadium is present as $VO.OH^+$ when $Z = 0.05$. Unfortunately, the value of $\varkappa_{1,1}$ could not be calculated from data for lower concentrations of vanadium, as Z and h could not be measured sufficiently accurately in the range $M < 0.005$ M. The constant obtained is of the same order as that calculated by Meites [4] for infinite dilution.

As two hydroxyl groups cannot be distinguished from one $-O-$ group by equilibrium measurements in a constant ionic medium, the vanadyl ion may be either VO^{2+} or $V(OH)_2^{2+}$. Similarly, there are a number of possible structures of the hydrolysis products $[V(OH)_3 + sH_2O]^+$ and $[V_2(OH)_6 + s'H_2O]^{2+}$, where s and s' are positive or negative integers, such that $s \gg -1$, and $s' \gg -3$. Thus several complexes with different values of s and s' may coexist, and isomers may also be formed. Although it has been found that the vanadyl ion is monomeric in solid vanadyl sulphate [28], no crystallographic data on the structures of basic vanadyl salts are available. It is therefore difficult to assign probable structures to the hydroxyl complexes formed in solution.

The hydrolysis products of several metals may be written as $Me((OH)_2Me)_n$, (i. e. as ''core + links'' complexes, with $t = 2$). When Me represents the iron (III) [10,11], copper (II) [18], or vanadyl ion, only the first complex,

Me((OH)$_2$ Me, has been detected. In the case of scandium [15], indium (III) [16], bismuth [11,19] and uranyl [12] ions, a series of complexes is formed. Values of the equilibrium constant, $\varkappa_{2,2}$ for the reaction

$$2 \, Me^{2+} + 2H_2O \rightleftharpoons Me((OH)_2Me)^{2+} + 2H^+$$

are listed below for cases where Me is a doubly charged ion.

Ion	$\log \varkappa_{2,2}$
UO^{2+}	$-\ 6.05$
Cu^{2+}	-10.6
VO^{2+}	$-\ 6.88$

The product of hydrolysis of the vanadyl ion is somewhat less stable than that of the uranyl ion, but is very much more stable than the corresponding copper complex. As would be expected, the hydroxyl complexes derived from doubly charged ions are much less stable than those derived from the trivalent ions of the B sub-group metals indium [16] and bismuth [11,19], and of the transition metal, iron [10,11].

The dimerisation constant for the species VO.OH$^+$ is given by

$$[(VO_2(OH)_2^{2+}] / [VO.OH^+]^2 = \varkappa_{2,2} / \varkappa_{1,1}^2 = 10^{5.1 \pm 0.1}$$

Dimerisation constants for the hydroxyl complexes, MeOH, of some other metal ions are given below.

MeOH	$\log (\varkappa_{2,2}/\varkappa_{1,1}^2)$	Ref.
CuOH$^+$	$+ 5.4$	18
FeOH^{2+}	$+ 3.2$	10
InOH^{2+}	$+ 3.7$	16
ScOH^{2+}	$+ 3.8$	15

It is seen that the dimerisation constant of the singly charged vanadium(IV) complex, VO.OH$^+$, is of the same order of magnitude as that of the analogous copper(II) complex, but is considerably higher than the dimerisation constants of the doubly charged species derived from iron(III), indium(III) and scandium.

It is of interest that, for the copper(II), uranyl, and vanadyl complexes, the Me(OH)$_2$ "link" of the polynuclear species is uncharged, and the ratio of metal ions to hydroxyl groups is the same as in the precipitate. An approximate value of the solubility product, S.P., of the vanadium (IV) precipitate was obtained from the values of Z and h at which visible precipitation first occurred. At this point, the value of the term $[VO^{2+}]h^{-2} = M(1-Z)h^{-2}$ was found to be 10 $^{5.5 \pm 0.3}$, and the solubility product is given by

$$S.P. = M(1-Z)h^{-2}K_w^2$$

where K_w is the ionic product of water. Then as $K_w = 10^{-14.2}$ in a 3 M perchlorate medium[29] S.P.$\sim 10^{-23.0}$.

REFERENCES

1. Britton, H. T. S. and Welford, G. *J. Chem. Soc.* **1940.** 758.
2. Britton, H. T. S. *J. Chem. Soc.* **1934** 1842.
3. Jones, G. and Ray, W. A. *J. Am. Chem. Soc.* **66** (1944) 1571.
4. Meites, L. *J. Am. Chem. Soc.* **75** (1953) 6059.
5. Hart, A. B. and Partington, J. R. *J. Chem. Soc.* **1940** 1532.
6. Willard, H. H. and Manola, G. D. *Anal. Chem.* **19** (1947) 463.
7. Lingane, J. J. and Meites, L. *J. Am. Chem. Soc.* **69** (1947) 1883.
8. Biedermann, G. and Sillén, L.G. *Arkiv Kemi* **5** (1953) 425.
9. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 901.
10. Hedström, B.O.A. *Arkiv Kemi* **6** (1953) 1.
11. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1607.
12. Ahrland, S., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1907.
13. Hietanen, S. *Acta Chem. Scand.* **8** (1954) 1626.
14. Brosset, C., Biedermann, G. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1917.
15. Biedermann, G., Pokras, L., Kilpatrick, M. and Sillén, L. G. *To be published.*
16. Biedermann, G. *To be published.*
17. Sillén, L. G. and Biedermann, G. *To be published.*
18. Berecki-Biedermann, C. *To be published.*
19. Granér, F. and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 631.
20. King, W. R. and Garner, C. S. *J. Phys. Chem.* **58** (1954) 29.
21. Gran, G. *Analyst* **77** (1952) 661.
22. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
23. Furman, S. C. and Garner, C. S. *J. Am. Chem. Soc.* **72** (1950) 1785.
24. Sykes, K. W. in *"The Kinetics and Mechanism of Inorganic Reactions in Solution"* Chemical Society, London 1954.
25. Hedström, B. O. A. *Acta Chem. Scand.* **9** (1955) 613.
26. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 299.
27. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 318.
28. Lundgren, G. *Private communication.*
29. Frydman, M., Lagerström, G., Sillén, L. G. and Ulfvarson, U. *Private communication.*