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The Formation of Polynuclear Complexes

I. The Determination of the Composition and Formation Constants of Polynuclear Complexes

BROR SKYTTE JENSEN

Danish Atomic Energy Commission, Risø, Denmark

The composition and the formation constant of the primary polymerisation product in the reaction between a central atom B and ligand atom A are determined from log-log plots of the average number of ligands bound per central atom *versus* the free ligand concentration for different total concentrations C_B of central atom B.

The composition and the formation constant of the final product in the same reaction may under certain circumstances be obtained from a log-log plot of the average number of ligand atoms not bound to B *versus* the free ligand concentration for different total concentrations C_B of central atom B.

The method set forth in this paper is applied to available data on the hydrolysis of the vanadium(IV), vanadium(V) and aluminium(III) ions.

In recent years the formation of polynuclear complexes has been intensively investigated. Special and general methods for the treatment of the complex data have been published [1–8].

Most of the data obtained experimentally have been treated according to a "core-link" theory set forth by Sillén *et al.*[1–4] where complexes of composition $A_r(AB_t)_N$ or $B_s(A_tB)_N$ are assumed to be the most probable being formed.

Mainly the hydrolysis of metal salts has been investigated. An excellent review of this field has been presented recently [9].

In the present paper another approach to the problem of analysis of the experimental data will be presented. This approach is in some respects similar to those published previously; however, the solutions of the present set of formulas need not be presented in the "core-link" formulation of Sillén.

In the derivation of the formulas some simplifications had to be introduced as is almost always the case when very complex systems are considered. This naturally also introduces some restrictions with regard to the cases which can be treated by the method. The solutions to the equations will therefore only be approximate and their deviation from the true solutions are difficult to estimate.

In the derivation of the formulas real equilibria are assumed, *i.e.* the law of mass-action is assumed to apply.

LIST OF SYMBOLS

$[B]$	concentration of species B.
C_B	total concentration of B.
$[A]$	concentration of free ligand.
A_b	number per volume of moles of A bound in complexes with B.
C_A	total concentration of species A.
$[B_rA_x]$, $[B_qA_y]$,	concentrations of complexes of composition B_rA_x, B_qA_y.
$Z =$	A_b/C_B *i.e.* the average number of ligands bound to B.
Z_t	The final value of Z corresponding to a defined product.

$\beta_{rx} = \dfrac{[B_rA_x]}{[B]^r[A]^x}$, the formation constant for the species B_rA_x

$\beta_{0,y} = 0$

$\beta_{1,0} = 1$

$\varkappa_{rx} = \dfrac{[B_rA_x][H]^x}{[B]^r[HA]^x}$

$K_w = [H][OH]$, the ion product of water.

$$n = \left(\frac{\partial \log Z)}{\partial \log [A]}\right)_{C_B}$$

$$n' = \left(\frac{\partial \log (Z_t - Z)}{\partial \log [A]}\right)_{C_B}$$

$$t = t' = \left(\frac{\partial \log C_B}{\partial \log [A]}\right)_Z$$

DERIVATION OF THE FORMULAS

In the solution the species B, A and $B_iA_u(i,u = 0,1,2,4\ldots)$ are assumed to exist.

The total concentration of B, C_B, can then be expressed as

$$C_b = \Sigma\Sigma i[B_iA_u] = \Sigma\Sigma i\beta_{i,u}[B]^i[A]^u \qquad (1)$$

where the summation include i and u equal to zero when $\beta_{1,0}$ is set equal to unity.

Similarly the concentration of A bound to B can be expressed as

$$A_b = \Sigma\Sigma u[B_iA_u] = \Sigma\Sigma u\beta_{i,u}[B]^i[A]^u \qquad (2)$$

with $\beta_{0,u}$ equal to zero. $\beta_{0,0}$ need not to be defined.

In eqns. 1 and 2 concentrations are used instead of activities, which is permissible if certain restrictions are put on the actual conditions under which the experiments are performed.

The expression for Z, the average ligand number per central atom then becomes

$$Z = \frac{\Sigma\Sigma u[\mathrm{B}_i\mathrm{A}_u]}{\Sigma\Sigma i[\mathrm{B}_i\mathrm{A}_u]} = \frac{\Sigma\Sigma u\beta_{i,u}[\mathrm{B}]^i[\mathrm{A}]^u}{\Sigma\Sigma i\beta_{i,u}[\mathrm{B}]^i[\mathrm{A}]^u} \tag{3}$$

To simplify eqn. 3 one may imagine certain concentration ranges where only two complexes exist simultaneously, *e.g.*, $\mathrm{B}_q\mathrm{A}_y$ and $\mathrm{B}_r\mathrm{A}_x$ where $\mathrm{B}_r\mathrm{A}_x$ is considered the product in a reaction of $\mathrm{B}_q\mathrm{A}_y$ with B and A, so that

$$x/r > y/q$$

This leads to

$$C_\mathrm{B} = r[\mathrm{B}_r\mathrm{A}_x] + q[\mathrm{B}_q\mathrm{A}_y] \tag{4}$$

and

$$Z \simeq \frac{x[\mathrm{B}_r\mathrm{A}_x] + y[\mathrm{B}_q\mathrm{A}_y]}{C_\mathrm{B}} \simeq \frac{x[\mathrm{B}_r\mathrm{A}_x]}{r[\mathrm{B}_r\mathrm{A}_x] + q[\mathrm{B}_q\mathrm{A}_y]} \tag{5}$$

From eqn. 5 is then derived

$$\frac{Z}{x/r - Z} = \frac{r[\mathrm{B}_r\mathrm{A}_x]}{q[\mathrm{B}_q\mathrm{A}_y]} \tag{6}$$

Two limiting cases are immediatedly discernible. The one that $Z \ll x/r$ and the other that $Z \simeq x/r$. In the former case we get

$$Z = \frac{x[\mathrm{B}_r\mathrm{A}_x]}{q[\mathrm{B}_q\mathrm{A}_y]} = \frac{x\beta_{r,x}[\mathrm{B}]^r[\mathrm{A}]^x}{q\beta_{q,y}[\mathrm{B}]^q\,[\mathrm{A}]^y} = \frac{x\beta_{r,x}}{q\beta_{q,y}}\,[\mathrm{B}]^{r-q}[\mathrm{A}]^{x-y} \tag{7}$$

As we have assumed C_B to be expressed as

$$C_\mathrm{B} = q\beta_{q,y}[\mathrm{B}]^q[\mathrm{A}]^y \tag{8}$$

[B] can be found as a function of C_B and [A]. Thus

$$[\mathrm{B}] = \sqrt[q]{C_\mathrm{B}/q\beta_{q,y}[\mathrm{A}]^y} \tag{9}$$

which when inserted into eqn. 7 gives

$$Z = \frac{x\beta_{r,x}}{(q\,\beta_{q,y})^{r/q}}\,C_\mathrm{B}{}^{(r-q)/q}[\mathrm{A}]^{(qx-ry)/q} \tag{10}$$

or

$$\log Z = \log\left(\frac{x\beta_{r,x}}{(q\beta_{q,y})^{r/q}}\right) + \left(\frac{r-q}{q}\right)\log C_\mathrm{B} + \left(\frac{qx-ry}{q}\right)\log\,[\mathrm{A}] \tag{11}$$

From this expression can be found

$$\left(\frac{\partial\,\log\,Z}{\partial\,\log\,C_\mathrm{B}}\right)_{[\mathrm{A}]} = \frac{r-q}{q} \tag{12}$$

$$\left(\frac{\partial\,\log\,Z}{\partial\,\log\,[\mathrm{A}]}\right)_{C_\mathrm{B}} = \frac{qx-ry}{q} = x - \frac{r}{q}\,y = n \tag{13}$$

$$\left(\frac{\partial \log C_{\mathrm{B}}}{\partial \log [\mathrm{A}]}\right)_Z = \frac{qx—ry}{q-r} = \frac{x—\frac{r}{q}y}{1—\frac{r}{q}} = t \tag{14}$$

If the above mentioned conditions are satisfied, *e.g.* that a complex $\mathrm{B}_r\mathrm{A}_x$ dominates in the expression for A_b and at the same time a complex of composition $\mathrm{B}_q\mathrm{A}_y$ dominates in the expression for C_{B} a linear relationship for a plot of log Z *versus* log [A] and in the same concentration range a linear relationship for a plot of, *e.g.*, log Z *versus* log C_{B} is to be expected, as in this case r, q, x, and y can be considered constants.

One may determine the slopes n and t defined by eqns. 13 and 14 from the linear parts of the experimental curves. From the two equations thus obtained only two independent ratios among the four variables r, q, x, and y can be determined.

From eqns. 13 and 14 are found

$$r = \frac{t—n}{t} q \tag{15}$$

and

$$x = \frac{t—n}{t} y + n \tag{16}$$

When Z approaches Z_{f} a new set of complexes $\mathrm{B}_{r'}\mathrm{A}_{x'}$ and $\mathrm{B}_{q'}\mathrm{A}_{y'}$ not necessarily identical with $\mathrm{B}_r\mathrm{A}_x$ and $\mathrm{B}_q\mathrm{A}_y$ might dominate in the expression 3.

In the case $Z \simeq x'/r'$ an equation similar to eqn. 10 is found from eqn. 6. Thus

$$(Z_{\mathrm{f}} — Z) = \frac{x'q'\beta_{q'y'}}{r'(r'\beta_{r'x'})q^{q'/r'}} C_{\mathrm{B}}{}^{(q'-r')/r'}[\mathrm{A}]^{(r'y'-q'x')/r'} \tag{17}$$

We next define the slopes n' and t'

$$\left(\frac{\partial \log(Z_{\mathrm{f}}—Z)}{\partial \log[\mathrm{A}]}\right)_{C_{\mathrm{B}}} = \frac{r'y'—q'x'}{r'} = n' \tag{18}$$

$$\left(\frac{\partial \log C_{\mathrm{B}}}{\partial \log [\mathrm{A}]}\right)_Z = \frac{r'y—q'x'}{r'-q'} = t' \tag{19}$$

from which is found

$$r' = \frac{t'}{t'—n} q' \tag{20}$$

$$x' = \frac{t'}{t'—n'} (y'—n') \tag{21}$$

$$x'/r' = y'/q'—n'/q' = Z_{\mathrm{f}} \tag{22}$$

DISCUSSION OF THE FORMULAS

The formulas 15, 16, 20, and 21 naturally determine an infinite number of sets of values (r,x), (q,y), (r',x'), and (q',y'). In order to chose among these sets, independent data are necessary. In the following will be shown how the data contained in a plot of $\log Z$ or $\log(Z_{\mathfrak{t}}-Z)$ *versus* $\log[\mathrm{A}]$ can be applied.

Because of the following inequalities

$$Z=\frac{\Sigma\Sigma u[\mathrm{B}_i\mathrm{A}_u]}{C_{\mathrm{B}}}=\frac{\Sigma\Sigma\frac{u}{i}i[\mathrm{B}_i\mathrm{A}_u]}{C_{\mathrm{B}}}<\frac{x}{r}\frac{\Sigma\Sigma i[\mathrm{B}_i\mathrm{A}_u]}{C_{\mathrm{B}}}=\frac{x}{r} \tag{23}$$

$$Z=\frac{\mathrm{A}_b}{\Sigma\Sigma i[\mathrm{B}_i\mathrm{A}_v]}=\frac{\mathrm{A}_b}{\Sigma\Sigma\frac{i}{u}u[\mathrm{B}_i\mathrm{A}_u]}>\frac{y}{q}\frac{\mathrm{A}_b}{\Sigma\Sigma u[\mathrm{B}_i\mathrm{A}_u]}=\frac{y}{q} \tag{24}$$

$$\frac{y}{q}<Z<\frac{x}{r} \tag{25a}$$

$$\frac{y'}{q'}<Z<\frac{x'}{r'} \tag{25b}$$

the measured Z values must be near in magnitude to the u/i values of the compounds actually existing in the solution. By the use of this fact all but a few possible sets of values for (r,x), (q,y), (r',x'), (q',y') will usually be excluded.

In the case $Z < 0.1$, this must therefore mean

$$\frac{y}{q}<0.1 \tag{26}$$

a very improbable case if y is not zero. Hence we must conclude that in the majority of cases y is equal to zero for Z smaller than 0.1.

The inserting of this value into eqn. 16 leads to

$$x=n \tag{27}$$

Therefore for $\mathrm{B}_r\mathrm{A}_x(=\mathrm{B}_r\mathrm{A}_n)$ to be a chemical entity we must have

$$n=\text{integer for } Z<0.1 \tag{28}$$

As q most often is equal to unity for very low values of Z inspection of eqn. 15 shows that in this case the ratio n/t must also be an integer for r to be so. Thus

$$n/t=\text{integer for } Z<0.1 \tag{29}$$

This fact often makes a choice of the exact value of a slope possible in cases where a slope is ill defined due to experimental error.

As the condition $Z < 0.1$ is easily realised experimentally the composition of the primary polymerisation product may very often be determined with great certainty.

Regarding the case where $Z-Z_{\mathfrak{t}}=x'/r'$ we find from eqns. 20 and 21

$$Z_{\mathfrak{t}}=x'/r'=\frac{y'-n'}{q'} \tag{30}$$

Here also an infinite number of sets (q',y') can be found which satisfy eqn. 30 within experimental error. If, however, the linearity of a $\log Z$ and a $\log(Z_f—Z)$ plot is approximately conserved for the same value of Z in the intermediate region, the only reasonable values of q' and y' are

$$q' = r \tag{31}$$

$$y' = x \tag{32}$$

If eqns. 31 and 32 are consistent with eqn. 30 with the experimentally determined values Z_f and n', the following main reactions can be considered identified.

$$r\mathrm{B} + x\mathrm{A} \rightarrow \mathrm{B}_r\mathrm{A}_x$$

and

$$\mathrm{B}_r\mathrm{A}_x—n'\mathrm{A} \rightarrow \mathrm{B}_r\mathrm{A}_{x-n'} = \frac{r}{r'}\mathrm{B}_{r'}\mathrm{A}_{x'}$$

where $\mathrm{B}_r\mathrm{A}_{x-n'}$ must not be considered a chemical entity.

To perform an analysis it is practical to identify the primary polymerisation product at first from a $\log Z$ *versus* $\log$ [A] diagram. On the same plot it should be possible to estimate the magnitude of Z_f.

One next makes the plot of $\log (Z_f—Z)$ *versus* $\log$[A] and determines the slopes n' and t'.

The insertion of the values of Z_f and n' and substitution of r,x for q',y' into eqn. 30 is the next step. If the equation is consistent the values of q' and y' can be considered identified and r' and x' can be determined from eqn. 20 and 21.

THE DETERMINATION OF FORMATION CONSTANTS

If experimental data have allowed the determination of r, q, x, and y, the ratio $\beta_{r,x}/(\beta_{q,y})^{r/q}$ can be determined from eqn. 10.

The point where the line $Z = 1$ intersects the line described by eqn. 11 for a given value of C_B determines a corresponding log[A′] value.

The rearrangement of eqn. 10 leads to

$$\beta_{r,x}/(\beta_{q,y})^{r/q} = \frac{[\mathrm{A}']^{(ry-qx)/q}q^{r/q}}{xC_\mathrm{B}{}^{(r-q)/q}} = \left(\frac{[\mathrm{A}']^{-n}}{n\ C_\mathrm{B}{}^{-n/t}}\right)_{(q,y=1,0)} \tag{33}$$

In the case $\beta_{q,y} = \beta_{1,0} = 1$, $\beta_{r,x}$ can be determined immediately.

When considering hydrolysis equilibria the constants $\varkappa_{r,x}$ used by Sillén *et al.* are related to $\beta_{r,x}$ by the relation

$$\varkappa_{r,x} = \beta_{r,x}\ (K_\mathrm{w})^n \tag{34}$$

where K_w is the ion-product of water.

From eqn. 17 is similarly found for $Z_f—Z = 1$

$$(\beta_{r',x'})^{q'/r'}/\beta_{q',y'} = C_\mathrm{B}{}^{-n'/t'}[\mathrm{A}'']^{n'}\frac{q}{r^{q'/r'}}\frac{x'}{r'} \tag{35}$$

This can be considered the equilibrium constant for a reaction

$$\mathrm{B}_{q'}\mathrm{A}_{y'} + \frac{q'x'-r'y'}{r}\,\mathrm{A} \rightarrow \frac{q'}{r'}\,\mathrm{B}_{r'}\mathrm{A}_{x'}$$

or

$$\mathrm{B}_{q'}\mathrm{A}_{y'} + (-n')\,\mathrm{A} \rightarrow \frac{t'-n'}{t'}\,\mathrm{B}_{r'}\,\mathrm{A}_{x'} = B_{q'}\,\mathrm{A}_{y'-n'}$$

Even in the case r' and x' are infinite can the formation constant of the repeating unit ($= \mathrm{B}_{q'}\mathrm{A}_{y'-n'}$) be found as the expression $r'^{q'/r'}$ in the denominator in eqn. 35 in this case can be replaced by unity.

Eqns. 33 and 35 have been used to determine the formation constants for several polymeric species in systems which will be discussed in the following pages.

THE EVALUATION OF EXPERIMENTAL ERRORS

The preceding discussion has shown that an analysis of experimental data by the present method is possible only when q and y are known with certainty. If we therefore presume that no uncertainties are connected with the magnitudes of q and y the effect of experimental errors in n and t on the magnitudes of r,x and β_{r_x} can be estimated by means of eqns. 15, 16, and 33.

From eqns. 15 and 16 are obtained

$$r = \frac{t-n}{t}\left(1 \pm \sqrt{\left(\frac{n\,\Delta\,t}{t(t-n)}\right)^2 + \left(\frac{\Delta\,n}{t-n}\right)^2}\right) \tag{36}$$

and approximately

$$x = \left(\frac{t-n}{t}\,y + n\right)\left(1 \pm \sqrt{\left(\frac{n\,\Delta\,t}{t(t-n}\right)^2 + \left(\frac{\Delta\,n}{t-n}\right)^2}\right) \tag{37}$$

As r and x are known to be integers even data of moderate precision allow the determination of the most probable primary polymerisation product with great certainty.

From eqn. 33 is similarly found

$$\begin{aligned}\Delta\,\beta_{r,x} &= \beta_{r,x}\left[\left(\frac{n\,\Delta\,[\mathrm{A}']}{[\mathrm{A}']}\right)^2 + \left(\frac{n\,\Delta\,C_{\mathrm{B}}}{tC_{\mathrm{B}}}\right)^2 + \left(\log\,[\mathrm{A}'] + \frac{1}{t}\log\frac{q\beta_{qy}}{C_{\mathrm{B}}} + \frac{1}{n}\right)^2\Delta^2 n\right. \\ &\quad \left. + \left(\frac{n}{t^2}\log\frac{q\beta_{qy}}{C_{\mathrm{B}}}\right)^2\Delta^2\,t\right]^{\frac{1}{2}} \simeq \beta_{r,x}\left[(\log[\mathrm{A}'] - \frac{1}{t}\log\,C_{\mathrm{B}})^2\Delta^2 n + \left(\frac{n}{t^2}\log\,C_{\mathrm{B}}\right)^2\Delta^2\,t\right]^{\frac{1}{2}} \\ &= \beta_{r,x}\;k\end{aligned} \tag{38}$$

The result will therefore be formulated as

$$\beta_{r,x}(1 \pm k) \simeq \beta_{r,x}(1 + k)^{\pm 1} = 10^{\log\,\beta_{r,x}\,\pm\,\log\,(1+k)} \tag{39}$$

Similar equations are found for r', x', and $\beta_{r',x'}$. Thus

$$r' = \frac{t'}{t'-n'}\,q'\left(1 \pm \sqrt{\left(\frac{n'\,\Delta\,t'}{t'(t'-n')}\right)^2 + \left(\frac{n'}{t'-n'}\right)^2}\right) \tag{40}$$

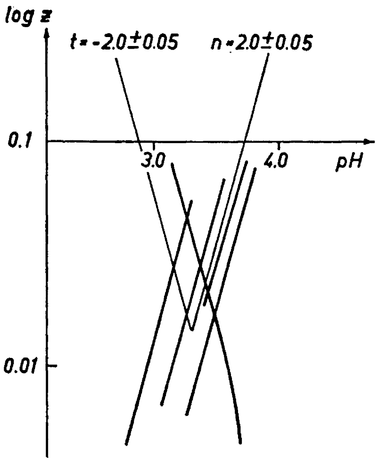

Fig. 1. A plot of log Z *versus* pH for the hydrolysis of the VO^{2+} ion. Data, Ref.[10]

and approximately

$$x' = \frac{t'}{t'-n'}(y'-n')\left(1 \pm \sqrt{\left(\frac{n'\Delta t'}{t'(t'-n')}\right)^2 + \left(\frac{\Delta n'}{t'-n'}\right)^2}\right) \tag{41}$$

The uncertainty of $\beta^{q'/r'}_{r',x'}/\beta_{q',y'}$ can be found from an equation similar to eqn. 38.

APPLICATION OF THE FORMULAS

The following hydrolysis equilibria will be discussed.

Species	Ref.
VO^{2+} ion	Rosotti and Rosotti[10]
VO_2^+ ion	Rosotti and Rosotti[11]
Al^{3+} ion	Brosset[12]

The vanadyl ion

In this case the function

$$Z = \frac{\Sigma\Sigma u[B_iA_u]}{C_B} = \frac{\Sigma\Sigma u[(VO^{2+})_i(OH^-)_n]}{C_{VO^{2+}}}$$

is being studied.

The data of Rosotti and Rosotti[10] are shown in Fig. 1 in a log$Z$ *versus* pH plot. In the range $0.005 < Z < 0.1$ the curves are parallel. The values for n and t in this range are

$$n = 2.0 \pm 0.05 \qquad t = -2.0 \pm 0.05$$

For low concentrations $t \rightarrow \infty$, and monomeric hydrolysis products may be assumed, as this means $r = q$. The data do not go to low enough concentrations to permit any conclusions about the monomeric hydrolysis.

The insertion of the values for n and t into eqn. 16 gives

$$x = (2.0 \pm 0.07)\ y + 2.0\ (\pm 0.05)$$

As $y = 0$ is the only value compatible with the low value of Z we immediately get

$$x = 2.0 \pm 0.05$$

From eqn. 15 is obtained

$$r = 2.0\ (\pm 0.07)q$$

Literature indicates a value for q equal to unity. We therefore obtain

$$r = 2.0 \pm 0.07$$

The linear curves can therefore be taken as representing the equilibrium

$$2\ VO^{2+} + 2\ OH^- \rightarrow (VO)_2(OH)_2^{2+}$$

as also proposed by Rosotti and Rosotti [10].

At $Z \simeq 0.1$ the curves bend slightly wherefore additional complexes are being formed, the exact nature of which cannot be ascertained.

For $C_B = 0.0207$ M and $C_B = 0.0515$ M the determination of $\beta_{2,2}$ gives

$$\beta_{2,2} = 10^{21.5 \pm 0.3}$$

and $$\varkappa_{2,2} = 10^{-6.9 \pm 0.3} \text{ with } K_w = 10^{-14.22} \text{ Refs.}^{11,12}.$$

From Ref.[10], $\varkappa_{2,2}$ was found to be

$$\varkappa_{2,2} = 10^{-6.88 \pm 0.05}$$

There is seen to be fair agreement between the two methods of analysis of the data in this case.

Rosotti and Rosotti were also able to determine the primary hydrolysis product at low concentrations as $(VO)OH^+$. An analogous determination cannot be made here with reasonable certainty as the true monomeric curve is not contained in the data.

The VO_2^+ ion in acid medium

In this case the function

$$Z = \frac{\Sigma\Sigma u[B_iA_n]}{C_B} = \frac{\Sigma\Sigma u[(VO_2^+)_i(OH^-)_u]}{C_{VO_2^+}}$$

is being studied.

The data from the publication of Rosotti and Rosotti [11] are shown in Fig. 2 in a $\log Z$ *versus* pH plot. The data for $Z < 0.08$ are rather irregular and will not be considered in the analysis. The curves are linear for $0.08 < Z < 0.4$.

The values for n and t are estimated to

$$n = 7.0 \pm 0.6 \quad \text{and} \quad t = -1.4 \pm 0.05$$

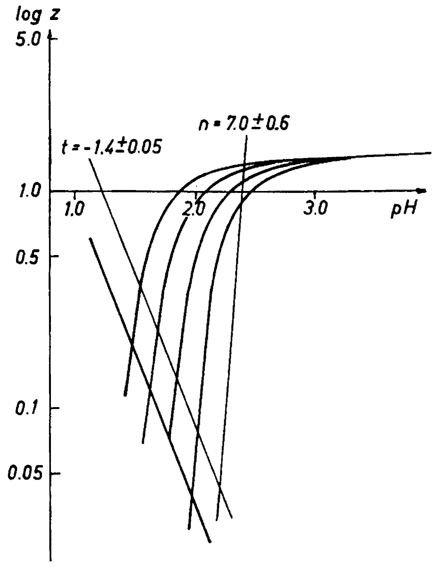

Fig. 2. A plot of log Z *versus* pH for the hydrolysis of the VO_2^+ ion. Data, Ref.[11]

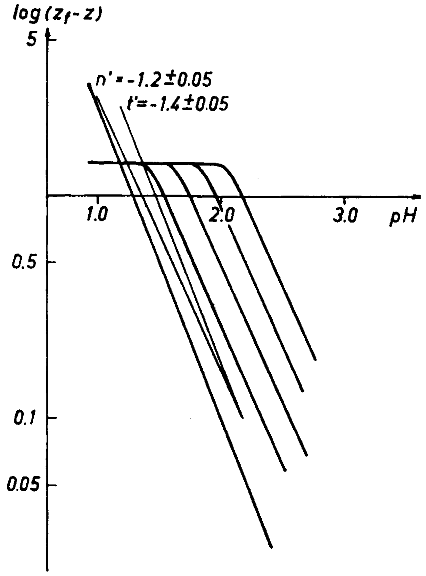

Fig. 3. A plot of log (1.41 − Z) *versus* pH for the hydrolysis of the VO_2^+ ion. Data, Ref.[11]

From these values we find

$$r = 6.0 \pm 0.6 \qquad \text{and} \qquad x = 5\ (\pm\ 0.5)\ y + 7\ (\pm\ 0.6)$$

The insertion of the values $y = 0$, which is reasonable for low values of Z, and $q = 1$ according to Ref.[11] leads to

$$r = 6.0 \pm 0.6 \qquad \text{and} \qquad x = 7.0 \pm 0.6$$

The following equilibrium can therefore be assumed to be responsible for the linear parts of the curves.

$$6\ VO_2^+ + 7\ OH^- = (VO_2)_6(OH)_7^-$$

The corresponding formation constant $\beta_{6,7}$ has been determined by means of eqn. 33 for $C_{VO_2^+} = 0.0025$ M and 0.02 M.

$$\beta_{6,7} = 10^{94.6 \pm 0.5}$$

$$\varkappa_{6,7} = 10^{-2.0 \pm 0.5} \text{ with } K_w = 10^{-13.8} \text{ (Ref.}^{11}\text{)}$$

The value of (x/r) does not satisfy the Z_f value of 1.40 ± 0.05 measured on the curves, for which reason further polymerisation must be supposed to occur.

In Fig. 3 the data are shown in a plot of $\log(Z_f - Z)$ *versus* pH.

From the curves we determine the best values of n' and t' as

$$n' = -1.2 \pm 0.05 \qquad \text{and} \qquad t' = -1.4 \pm 0.05$$

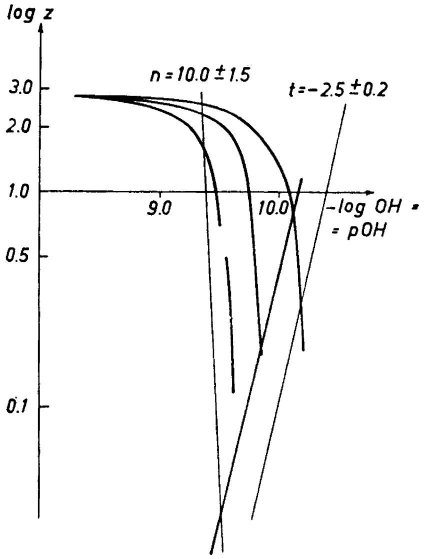

Fig. 4. A plot of log Z *versus* pOH (= $-\log[\mathrm{OH}]$) for the hydrolysis of the Al^{3+} ion. Data, Ref.[12]

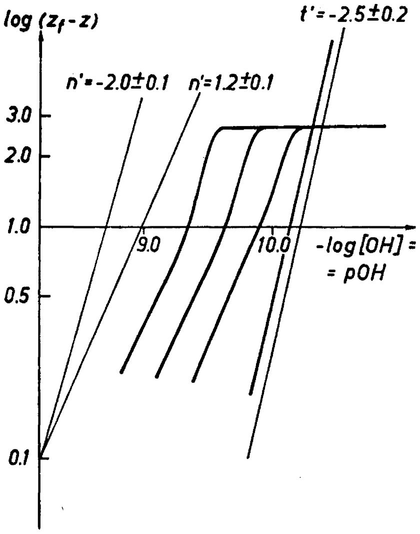

Fig. 5. A plot of log $(2.75 - Z)$ *versus* pOH ($= -\log[\mathrm{OH}]$) for the hydrolysis of the Al^{3+} ion. Data, Ref.[12]

From eqns. 20 and 21 is seen that the final product obviously is highly polymerised. Thus.

$$r' = \frac{-1.4}{-0.2} q' = 7q'(1 \pm 0.5)$$

$$x' = \frac{-1.4}{-0.2} (y' - n') = 7(y' - n')(1 \pm 0.5)$$

The substitution of (6,7) for (q',y') in eqn. 30

$$Z_t = 1.40 = \frac{7 + 1.4}{6} = 1.40$$

shows that the final reaction can be formulated as

$$N(\mathrm{VO_2})_6(\mathrm{OH})_7^- + N\ 1.4\ \mathrm{OH}^- = (\mathrm{VO_2})_{6N}(\mathrm{OH})_{8.4N}^{2.4N-}$$

where $N = 7 \pm 3$

The equilibrium constant for the final reaction has been determined by means of eqn. 35 in the case $N = 7$, for $C_{\mathrm{VO}_2^+} = 0.02$ M

$$\beta_{42,59}/(\beta_{6,7})^6 = 10^{100 \pm 2}$$

The above conclusions are well in accord with experimental data.

As depolymerisation of the polyvanadates is known to occur for Z values larger than Z_f ($= 1.4$) an isohydric point is defined at $Z = Z_f$. This is known to correspond to the state of maximum polymerisation which from the present analysis seems to correspond to polymers containing from 24 to 60 VO_2 units.

The Al^{3+} ion in acid medium.

In this case the function

$$Z = \frac{\Sigma\Sigma u[B_iA_u]}{C_B} = \frac{\Sigma\Sigma u[Al_i^{3+}(OH^-)_u]}{C_{Al^{3+}}}$$

is being studied.

The data from the publication of Brosset [12] are shown in Fig. 4 in a log Z *versus* pOH plot. His paper contains data measured ½ h and 10—20 h after the mixing of the reagents. Only the last data will be considered.

The data for $Z < 0.1$ are rather irregular and will not be used in the analysis. The curves show the slopes

$$n = 10 \pm 1.5 \quad \text{and} \quad t = -2.5 \pm 0.2$$

and $$Z_f = 2.75 \pm 0.03$$

For $(q,y) = (1,0)$, r and x are found to be

$$r = 5.0 \pm 0.7 \quad \text{and} \quad x = 10 \pm 1.4$$

The formation of the primary hydrolysis product of the Al^{3+} ion in a slow titration may therefore be formulated as

$$5\ Al^{3+} + 10\ OH^- \rightarrow Al_5(OH)_{10}^{5+}$$

The formation constant $\beta_{5,10}$ is found to be

$$\beta_{5,10} = 10^{107 \pm 1.5}$$

and $$\varkappa_{5,10} = 10^{-28 \pm 1.5} \text{ with } K_w = 10^{-13.5} \text{ (Ref.}^{12})$$

As the Z_f value is not satisfied with this product further polymerisation must be assumed.

From the log $(Z_f—Z)$ *versus* pOH plot (Fig. 5) two regions with linear curves are found.

For $(Z_f—Z) > 1.0$, n' and t' are found to be

$$n' = -2.0 \pm 0.1 \quad \text{and} \quad t' = -2.5 \pm 0.2$$

From eqns. 20 and 21 and $(q',y') = (1,0)$ are found

$$r' = 5.0 \pm 1 \quad \text{and} \quad x' = 10.0 \pm 2$$

in accord with the preceding analysis.

For very small values of $(Z_f—Z)$ are found

$$n' = —1.2 \pm 0.1 \qquad \text{and} \qquad t' = —2.5 \pm 0.2$$

The insertion of $n' = —1.2$ and the replacement of q' and y' with r and x (5,10) into eqn. 22 leads to

$$Z_f = 2.75 = \frac{y'—n'}{q'} \neq \frac{10 + 1.2}{5} = 2.24$$

which show that the final product cannot be formulated as a direct polymerisation product of $Al_5(OH)_{10}^{5+}$.

From eqns. 20 and 21 are found

$$r' = 1.9q(1 \pm 0.2) \qquad \text{and} \qquad x' = 1.9(y' + 1.2)(1 \pm 0.2)$$

which indicates that the last reaction is a dimerisation.

Recently Johansson[13] has investigated the crystalline basic sulphates and selenates of composition Na_2O:13 Al_2O_3:8 SO_3:x H_2O and Na_2O:13 Al_2O_3:- SeO_3:x H_2O and has identified a chemical entity of composition $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ ($= Al_{13}(OH)_{32}^{7+}$) in the crystals. The entity has a structure reminiscent of that of the heteropolyacids.

It seems reasonable to assume that the final product in the present analysis contains this Al_{13}-unit. A final product of structure

$$(Al_{13}(OH)_{36}^{3+})N \qquad x'/r' = 36/13 = 2.77$$

where N is unknown will therefore be proposed.

GENERAL DISCUSSION

The method presented seems well suited to treat titration data involving the formation of polynuclear complexes.

Because of the nature of the problem the principle of the method is somewhat similar to previously applied methods; however, it often leads to different results as shown in the examples.

It is obvious that a mathematical approach to the problem of polymer formation in itself offers no solution to the chemistry involved, but only the consequent use of the mass-action relationship connects the analysis to chemistry. Accordingly only data where this law is valid can be treated by the method, *i.e.* data involving real equilibria or apparent equilibria where the chemical reactions following the main reactions are very slow.

The present method is one by means of which the dominating terms in an unknown polynomium Z are identified and their coefficients determined. This is possible only under certain circumstances by the present method, but will almost always be the case for low values of the function Z.

Owing to experimental errors one can never be sure that the true term (or equivalent chemical entity) is identified with certainty, but within experimental error the term proposed by the present analysis will be as well suited to represent the experimental data as will results found by other methods of analysis.

A fit between curves calculated by means of constants found by the mathematical analysis with the experimental curves will eliminate large errors in the analysis but it will seldom allow a decision between two alternative polymerisation products proposed.

In principle any experimental curve can be approximated very closely by a polynomium when minor terms are included in the analysis. However, the magnitude of the experimental error often makes the inclusion of such minor terms of rather doubtful value.

The dominating term can, however, be identified with some certainty.

Other terms useful for the fitting of theoretical curves with experimental ones are preferably determined by identification of the corresponding chemical species if possible.

Alternatively one can propose a sort of mechanism for polymerformation as, *e.g.*, the "core-link" hypothesis where polymers are thought of as formed by the addition of links of constant composition one by one to a core usually being a single atom of B. Only terms corresponding to polymers of "core-link" composition are then taken into account when the theoretical curves are approximated to the experimental ones.

The success of this method in describing experimental data, however, does not prove that this is the actual mechanism of polymerformation.

An equally acceptable mechanism of polymer formation could be chemical reactions of polymers with each other to still larger aggregates — a sort of sequential dimerisations.

The actual mechanism of polymerformation might well be a "mixture" of those proposed above.

Which species actually are stable must depend very much on the geometrical pattern of the polymers and therefore on which atoms are involved, their radii, charge, electronegativity, *etc.* It seems reasonable to assume that the most stable ionic polymers (*i.e.* hydrolysis products of metal salts, *etc.*) in their structure should follow the rules set forth by Pauling [14] for the structure of ionic crystals.

As is seen, the analysis of the complex data obtained in the study of polymerisation reactions leaves much to chemical intuition. The present method cannot claim to be more exact or accurate than previous ones but has the advantage that it is more easy to apply. A distinct advantage is that the primary polymerisation product often can be determined with certainty.

The data [A] and A_b necessary for an analysis are usually (especially in the case of metal complexes) found by titrations where [A] is measured directly and A_b calculated.

Formally the equations 1, 2, 3... are symmetrical in A and B. The result of an analysis is therefore independent of which atom is considered central atom or ligand.

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