Studies on the Hydrolysis of Metal Ions

XI. The Aluminium Ion, Al^{3+}

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In 1952, one of us (Brosset [1]) published the results of extensive studies on the behavior of the aluminium ion in perchlorate solutions of varying acidity at 40° C. The ionic medium was kept constant by means of 2 C $NaClO_4$, and the concentration of free H^+ (or OH^-) was measured by means of a hydrogen electrode.

Considerable difficulties were met with because equilibrium was attained rather slowly, especially in the region where precipitation occurred. It is however thought that the values finally given were not far from those at real equilibrium.

From the data it was obvious — contrary to what had been stated by many authors — that the main products of Al^{3+} hydrolysis are *polynuclear* complexes, and not mononuclear ones, even at rather low degrees of hydrolysis. To explain the data, the formation of an infinite series of complexes was assumed: $Al((OH)_3Al)_n^{3+}$ in the acid range, and $(Al(OH)_3)_nOH^-$ in the alkaline range. A satisfactory fit with the data was then obtained in a considerable part of the experimental range.

In the meantime, general methods for dealing with polynuclear complex equilibria have been given [2,3,4]. We have now applied these methods to the same data [1] in order to find out whether an equally good or perhaps better agreement could be obtained with some other polynuclear mechanism than those mechanisms originally proposed.

We shall use the same notation as in other papers of this series [4,5,6]: M = total Al concentration, h = hydrogen ion concentration, Z = average number of H^+ split off (OH^- bound) per Al. In the original paper [1], M and h were denoted by $[Al_t]$ and $[H^+]$, and Z by $\bar{n}$. In the original tables and figures, pOH was given as a measure of the acidity; it is easily recalculated to h using the pK_w value measured by Brosset [1] for the temperature and ion medium in question:
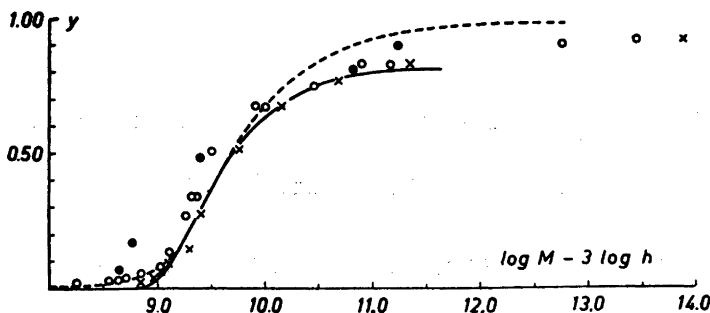
$$\log h = \text{pOH} - 13.52 \qquad (1)$$

*Fig 1. Acid range $y(x)$ for reactants $-H^+$ and Al^{3+} with $t = 3.0$. Experimental data:
$\times$ 2.209 mC, $\circ$ 11.07 mC, $\bullet$ 55.41 mC. Full-drawn curve: hypothesis II, $N = 5$. Dotted
curve: hypothesis IIIa, $\log k = -9.4$, $k_0 = 0.1$.*

The data were plotted (Fig. 7[1]) in the form $Z(pOH)_M$ which is equivalent
to $Z(\log h)_M$ because of (1). Three values for M were used: 55.41, 11.07, and
2.209 mC. In the alkaline range only the two lower concentrations were stu-
died. As seen from Fig. 7 in the original paper[1], Z changes rapidly with $\log h$
in two ranges: in an *acid range*, $- \log h \approx 3$—5, with positive Al complexes
(Z from 0 to about 2.5), and in an *alkaline range*, $- \log h \approx 9$—11, with nega-
tive Al complexes (Z from 3 to 4). The intermediate range, $Z = 2.5$—3, is
characterized by very slow attainment of equilibrium.

We shall now discuss the acid and alkaline ranges separately.

ACID RANGE

General formula of the complexes

In the acid range, the $Z(\log h)_M$ curves for the three M values are approxi-
mately parallel, which would indicate that the complexes can be written in
a "core + links" form

$$Al((OH)_t Al)_n \tag{2}$$

where t is a constant whereas n may assume several values. From the distance
between the curves we obtain values for the derivative

$$\left(\frac{\partial \log M}{\partial \log h}\right)_Z \tag{3}$$

between 2.5 and 3, which should be equal to t, the number of OH groups in the
"link" of the complexes (part VIII[4], 14, 15).

To check the value for t, we plotted the function $y(x)$ where

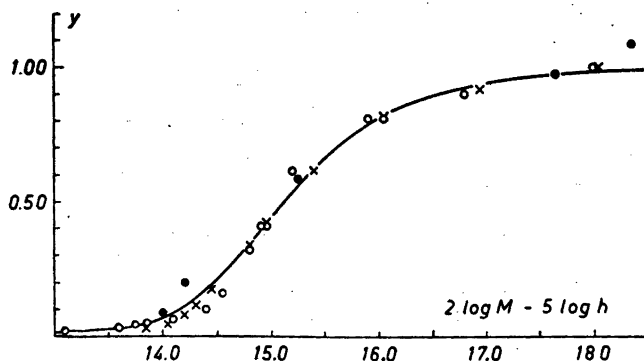$$y = \frac{Z}{t} \tag{4}$$

$$x = \log M - t \log h \tag{5}$$

Fig 2. Acid range y(x) for t = 2.5. Experimental data: × 2.2 mC, ○ 11.07 mC, ● 55.41 mC. Curve calculated for IIIa, $k_0 = 0.5$, log $k = -14.8$.

assuming t to be 3.0 (Fig. 1), 2.75, or 2.5 (Fig. 2). For the correct t value the points should be on the same curve. This is approximately so in both Fig. 1 and Fig. 2. Considering the general spread of the data, we thought it safe not to exclude any part of the range $t = 2.5 \rightarrow 3$. With $t > 3$, the spread becomes too great — mechanisms with $t < 2.5$ could not explain that the Z curves bend off close to $Z = 2.5$.

We shall thus assume that all complexes formed in appreciable amounts can be written in the form (2). However, we shall for the present leave the question open whether t is 2.5 or 3.0, or has some intermediate value.

Comparison with simple mechanisms

In the previous papers [5],[6] on Th^{4+} and UO_2^{2+} a "direct analysis" of the $y(x)$ curve was made. Integrating $y(x)$ and applying equations (ABII[3], 14, 15, 73) a function $g(u)$ could be calculated which should be a polynomial with coefficients equal to the equilibrium constants for the formation of the various complexes. By differentiation of g one could moreover obtain the average number of "links" in the complexes at any value for x. Unfortunately, the spread of the data for Al^{3+} is too great to allow this procedure to be carried out with any accuracy.

We must then restrict ourselves to studying certain simple mechanisms, I—III, described in ABII [3] and involving only one or two parameters to be determined. Following ABII we compared the experimental $y(x)$ data for the tentative t values with families of curves $y(x)$, calculated for the simple mechanisms I—III.

Mechanisms with a single complex

With hypothesis I (no soluble complex, precipitate formed), no satisfactory agreement was found.

With hypothésis II (only one complex formed, with $n = N$) an acceptable agreement was found

for $t = 3.0$ with $N = 5$ $Al_6(OH)_{15}^{3+}$, $Z_{max} = 2.50$
for $t = 2.75$ with $N = 8$ $Al_9(OH)_{22}^{5+}$, $Z_{max} = 2.44$
for $t = 2.75$ with $N = 12$ $Al_{13}(OH)_{33}^{6+}$, $Z_{max} = 2.54$
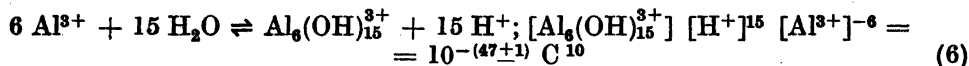for $t = 2.5$ with no value for N.

The agreement was better for $t = 3$ than for 2.75. With $t = 3$, $N = 4$ or 6 might also be possible.

With intermediate values for t one may expect that an acceptable agreement with the data would be obtained assuming complexes like tne following

$Al_6(OH)_{14}^{4+}$ $(t = 2.8,$ $N = 5,$ $Z_{max} = 2.33)$
$Al_8(OH)_{20}^{4+}$ $(t = 2.86,$ $N = 7,$ $Z_{max} = 2.50)$
$Al_9(OH)_{23}^{4+}$ $(t = 2.88,$ $N = 8,$ $Z_{max} = 2.55)$

From the equilibrium data alone it is not possible to decide between these complexes and a few other similar ones. On the other hand, the data allow one to conclude that, if a single complex is formed in the acid range, it cannot be $Al_2(OH)_2^{4+}$, nor $Al_3(OH)_6^{3+}$, which have previously been proposed [7,8,9].

Assuming that the main product is the complex $Al_6(OH)_{15}^{3+}$, we may read off the x value where $y = \frac{1}{2}$, $x_{\frac{1}{2}} = 9.7 \pm 0.1$, and apply (ABII, 24), which gives log $k = -9.4 \pm 0.2$ and the equilibrium constant (k^5)

$$6 Al^{3+} + 15 H_2O \rightleftharpoons Al_6(OH)_{15}^{3+} + 15 H^+; [Al_6(OH)_{15}^{3+}] [H^+]^{15} [Al^{3+}]^{-6} =$$
$$= 10^{-(47\pm1)} C^{10} \qquad (6)$$

Repeated mechanisms

The hypotheses IIIa-c, involving the formation of complexes with all integral values for n, would have a physical meaning only for $t = 3$. For $t = 2.5$, complexes are possible only for even values of n $(n = 2 n *)$: $Al((OH)_{2.5}Al)_{2n*}$ or $Al((OH)_5Al_2)_{n*}$. Since the link would be $Al_2(OH)_5$, it is easily seen that one can use the same arguments as in ABII after a few simple transformations. The expression for the concentration of the $n*$:th complex, c_{n*}, in (VIII, 30) will then always contain a power of $u* = m^2h^{-5} = u^2$, and one may use the equations given in ABII (8, 8a, 9, 9a etc.), with the only difference that x is replaced by $x* = 2 \log M - 5 \log h = 2 x$.

Likewise, to compare the data recalculated for $t = 2.75$ with infinite mechanisms, one should plot y as a function of $x* = 4 \log M - 11 \log h = 4 x$.
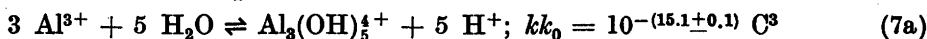
For $t = 3$, the lower part of the experimental curve could be made to agree with the calculated curve for IIIa with $k_0 = 0.1$ if placed at $x_{\frac{1}{2}} = 9.7$, which gives $\log k = -9.4$ (Fig. 1). (The mechanism proposed in the earlier paper [1] was IIIa with $k_0 = 0.08$, and $\log k = -9.22$.) However, for $y > 0.5$ the experimental values were systematically lower than those calculated. A similar partial agreement could be obtained with IIIb $(k_0 \approx 0.1)$ and IIIc $(k_0 \approx 0.01)$.

For $t = 2.75$, IIIa ($k_0 = 5 \rightarrow 10$) was acceptable for the lowest y, but not for the high y values. Both IIIb ($k_0 \approx 10$) and IIIc ($k_0 \approx 2$) were acceptable in a somewhat wider range. We have $x_{\frac{1}{2}}^{*} = 34.5$.
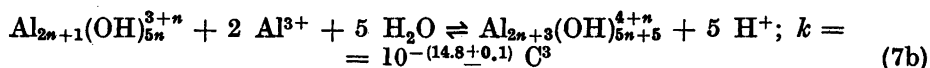
For $t = 2.5$, an acceptable agreement was found with both IIIa ($k_0 \approx 0.5$) and IIIb ($k_0 \approx 0.1 \rightarrow 0.5$) in both cases with $x_{\frac{1}{2}}^{*} = 15.1 \pm 0.1$, whereas IIIc gave no good fit.

We conclude that an unlimited mechanism with $t = 3$ (complexes $Al((OH)_3Al)_n^{3+}$) is not likely but that, with the present data, one cannot exclude unlimited mechanisms with the formation of $Al((OH)_5Al_2)_n^{3+n}$ ($t = 2.5$) or $Al((OH)_{11}Al_4)_n^{3+n}$ ($t = 2.75$). With intermediate values for t one might get agreement with, e. g., $Al((OH)_8Al_3)_n^{3+n}$ ($t = 2.67$).

If we assume the main product to be a series of complexes $Al((OH)_5Al_2)_n^{3+n}$, we would have the equilibrium constant for the initial reaction

$$3 \ Al^{3+} + 5 \ H_2O \rightleftharpoons Al_3(OH)_5^{4+} + 5 \ H^+; \ kk_0 = 10^{-(15.1\pm0.1)} \ C^3 \tag{7a}$$

and for all following n

$$Al_{2n+1}(OH)_{5n}^{3+n} + 2 \ Al^{3+} + 5 \ H_2O \rightleftharpoons Al_{2n+3}(OH)_{5n+5}^{4+n} + 5 \ H^+; \ k = $$
$$= 10^{-(14.8\pm0.1)} \ C^3 \tag{7b}$$

The $y(x)$ curve so calculated is given in Fig. 2.

Discussion

The data [1] for Al^{3+} hydrolysis thus allow us to exclude a number of mechanisms that have been proposed or might otherwise be conceived. Even if we keep to the simple one- or two-parameter mechanisms there remain, however, a certain number of mechanisms which would all give an acceptable agreement within the accuracy of the data.

To decide among them, or to discuss more complicated mechanisms (say, the formation of several complexes) one must have equilibrium data of higher accuracy and perhaps in a wider range of concentrations. To get such data, however, would involve difficult experimental problems. There are, fortunately, other data which may have some value as evidence.

A number of authors have studied Al-OH solutions which have been obtained by mixing Al^{3+} and OH^- in various proportions and allowing the mixture to age for different times. Clear chloride or nitrate solutions can be obtained with a ratio of up to 2.5 OH/1 Al ($Z = 2.5$, "$\frac{5}{6}$ basic solution")[7,10,11,12,13]. The formation of the Al^{3+} —OH^- complexes takes considerable time — of the order of 10—30 hours at about 20° C — and an intermediate precipitate is often observed which dissolves gradually. On the other hand, if H^+ is added to an aged $Al(OH)_{2.5}$ solution, the H^+ ions react very slowly. On titration with OH^-, an aged Al—OH solution gives a distinct pH change at about $Z = 2.5$.

This behavior is consistent with the slow formation of either a series of complexes $Al((OH)_5Al_2)_n^{n+3}$ (limiting ratio $Z = 2.5$) or a single complex such as $Al_6(OH)_{15}^{3+}$ or $Al_8(OH)_{20}^{4+}$.

Now a series of salts are known which can be written as containing the group $Al_2O_3H^+aq$ or $Al_2(OH)_5^+aq$ (thus $Z = 2.5$) and some anion. The chloride and nitrate are very soluble and hard to crystallize but several other salts, such as the sulfate, chromate, phosphate, silicate and oxalate, are only sparingly soluble (order of magnitude 0.05 mC[15]). The sulfate is described as forming nice tetrahedral crystals [12].

It is remarkable that on addition of sulfate ions to solutions with Z between 1.7 and 2.5, the only salt precipitated is this well-crystallized sulfate of gross composition $(Al_2(OH)_5)_2SO_4aq$ [12]. Likewise, oxalate ions, on addition to solutions with $Z = 0.8$ to 2.5 always give the oxalate $(Al_2(OH)_5)_2C_2O_4$ [7].

Now if there were a series of complexes in the solution, say $Al((OH)_5Al_2)_n$, and the transformations between them were very slow reactions, it is hard to conceive that a well-crystallized compound of composition $(Al_2(OH)_5)_2SO_4$ could precipitate quickly out of such a solution.

If, on the other hand, only one single complex with 2.5 OH/Al is formed, then the formation of a crystalline precipitate is very natural, once the complex has had time to form in the solution.

So we are led, on the basis of the present evidence, to prefer mechanisms with a single complex of ratio OH/Al close to 2.50 — the analytical data on the solid salts may allow a small deviation, say to 2.44 or 2.54.

The equilibrium data allow no certain decision between the several conceivable formulas $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$ etc. However, it may be said that the agreement gradually gets worse when the number of Al per complex is increased beyond 6. We will not put undue stress on the fact that Kohlschütter and Hantelmann [7], by cryoscopic measurements on solutions with 2.5 OH/1 Al, have found a molecular size corresponding to 6 Al, thus $Al_6(OH)_{15}^{3+}$. However, the complex with 6 Al seems to be more likely because of the crystal structure of γ-$Al(OH)_3$, the stable form. It consists of sheets, in each of which the Al atoms form 6-membered rings (Fig. 3) [16], each Al being joined to the two neighbouring Al by double OH bridges. An ion $Al_6(OH)_{15}^{3+}$ may be pictured as such a ring where additional OH^- groups are attached to alternate Al in the ring, and the remaining coordination places are filled up with H_2O.

It would be interesting to study the crystal structure of one of the $Al(OH)_{2.5}$ salts, in order to find the size and structure of the complex ion. The chromate is perhaps the most promising salt to start with.

On the basis of the present evidence we thus consider ring-like complexes $Al_6(OH)_{15}^{3+}$ as the most probable main reaction product of the hydrolysis of Al^{3+} in the acid range.

ALKALINE RANGE

In the alkaline range, Brosset [1] observed a slow reaction which made the pOH of a mixture shift by as much as one unit during the measurements. Three series of data were given: 1) the "first values", for experimental reasons measured about half an hour after the solution was prepared, 2) the "final values" measured where the emf did not seem to change any more (often after 60—90 hours), 3) the "zero values" extrapolated to the time zero.
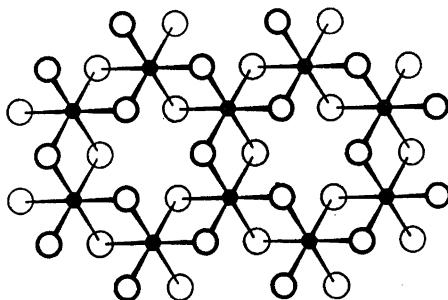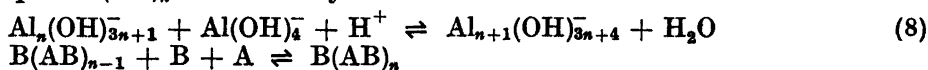
Fig 3. Part of the crystal structure of γ-Al(OH)$_3$ showing 6-membered Al rings. From A. F. Wells, Structural Inorganic Chemistry, second edition, Oxford University Press 1950, p. 417) by permission.

In Brosset's original Fig. 7, and in his calculations, only the zero values were considered. Clearly the "first values" represent a very arbitrary point in the slow process, and are not worth any special attention. Even the "final values" seem to spread strongly in a plot $Z(\log h)_M$, indicating that real equilibrium had perhaps not been reached.

The "zero values", on the other hand, form two reasonably parallel curves. The distance between them gives us a value —1 for the derivative (3), so that the sign is reversed in comparison with the acid range.

Since the concentration of free Al^{3+} is negligible, the argument in (ABI[2], p. 308 and VIII[4], 19—21) can be applied. From ABI 20, or VIII 19, we conclude that the general formula of the complexes in this range may be written $OH(Al(OH)_t)_n$. Since the limiting values for Z are 3 and 4, we conclude that $t = 3$, and that the complexes may be written in the form $(Al(OH)_3)_nOH^-$ It is then convenient to proceed as outlined in (ABI, p. 311 and VIII 20—21), namely to consider the smallest complex, $Al(OH)_4^-$, as the core. The link, $Al(OH_3)$, is a complex of $Al(OH)_4^-$ and H^+. The reactants A and B in the equations of ABI and ABII thus correspond to H^+ and $Al(OH)_4^-$, and the general complex $B(AB)_n$ is formed by a reaction

$$Al_n(OH)_{3n+1}^- + Al(OH)_4^- + H^+ \rightleftharpoons Al_{n+1}(OH)_{3n+4}^- + H_2O \qquad (8)$$
$$B(AB)_{n-1} + B + A \rightleftharpoons B(AB)_n$$

The total concentration of B is M, and the average amount of A bound per B is Z', which is related to the Z defined with Al^{3+} and $—H^+$ as reactants by

$$Z' = 4—Z \qquad (9)$$

This follows from

$$Z = \frac{\Sigma(3n + 4)c_n}{\Sigma(n + 1)c_n} \; ; \; Z' = \frac{\Sigma n c_n}{\Sigma(n + 1)c_n} \qquad (9a)$$

The data can be reduced to the form $y(x)$ by the transformations

$$y = Z'/t' = 4—Z \qquad (10)$$
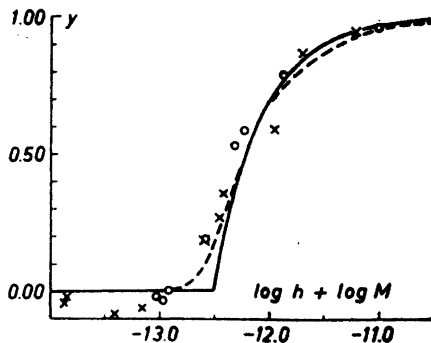$$x = \log B + \log a = \log M + \log h$$

Fig 4. Alkaline range, reactants H^+ and $Al(OH)_4^-$, $y(x)$ for $t = 1$. Experimental data, "zero values": $\times$ 2.209 mC, $\bigcirc$ 11.07 mC. Full-drawn curve calculated for mechanism I, broken curve for IIIa with $k_0 = 0.01$, log $k = 12.5$.

The "zero values" are given in the form $y(x)$ in Fig. 4, and are seen to lie roughly on the same curve. A certain spread in the experimental values makes it impractical to use the "direct analysis".

A comparison with the calculated $y(x)$ curves from ABII shows that the experimental points, within the limits of error, fall on the curve for the limiting hypothesis I: no soluble complex, precipitate formed (full-drawn curve in Fig. 4). One may also find a fair agreement with hypothesis IIIa using a very small value for k_0 (IIIa with $k_0 = 0.01$, log $k = 12.63$ was the hypothesis proposed in the original paper [1]; broken curve in Fig. 4). This is quite natural since I is the limiting case of IIIa for $k_0 \to 0$.

Since, with the present accuracy, we cannot definitely state that k_0 is different from 0, we shall assume the simplest hypothesis I ($k_0 = 0$) which implies that we have only the ion $B = Al(OH)_4^-$ and solid $AB = Al(OH)_3$ (or AlOOH; they cannot be distinguished by equilibrium measurements). The equilibrium constant comes out as

$$Al(OH)_3(s) + H_2O \rightleftharpoons Al(OH)_4^- + H^+; \quad K_s = k^{-1} = h\,[Al(OH)_4^-] =$$
$$= 10^{-12.5 \pm 0.2} \tag{11}$$
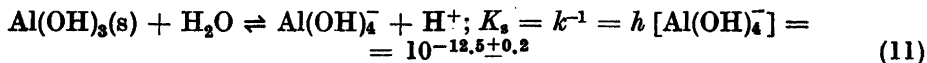
By using Brosset's value 13.52 for pK_w in this medium we find for the reaction

$$Al(OH)_3(s) + OH^- \rightleftharpoons Al(OH)_4^-; \quad K = [Al(OH)_4^-][OH^-]^{-1} = 10^{1.0 \pm 0.2}$$
$$= 10 \pm 6 \tag{11a}$$
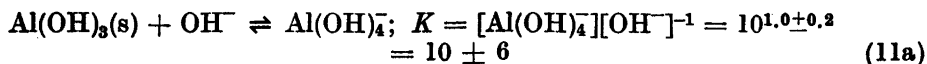
Of course, it is by no means proved that polynuclear anions are not formed in the solution but obviously the present data can, within the limits of accuracy, be explained by means of the simple reaction (11).

The "final values", if treated in the same way, give no smooth $y(x)$ curve (Fig. 5). Assuming that $Al(OH)_4^-$ and $Al(OH)_3$ (s), the latter in some other modification, are the only species present, one may draw a curve for hypothesis I
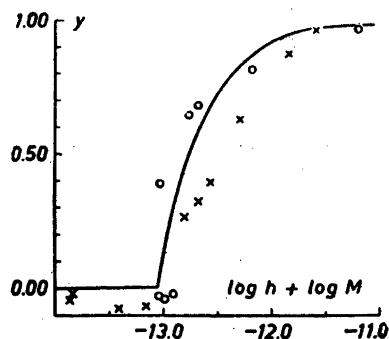
Fig 5. Alkaline range, "final values", $\times$ *2.209 mC,* $\bigcirc$ *11.07 mC. Curve calculated for I with log k = 13.0.*

through the points $y(x)$ and find a rough average value for log $k = 13.0 \pm 0.2$, and thus the constant in (11a) $K = 10^{0.5 \pm 0.2}$. The solid phase would then have been partly transformed into a less soluble modification. However, it is also conceivable that soluble complexes have been formed.

SUMMARY

Brosset's [1] data on the hydrolysis of Al^{3+} have been recalculated, using the general methods for treating polynuclear equilibria that have recently been published [2,3].

In the acid range ($Z = 0 \rightarrow 2.5$) Brosset's data can be explained assuming either a single and rather large complex, such as $Al_6(OH)_{15}^{3+}$, or an infinite series of complexes $Al((OH)_5Al_2)_n^{3+n}$. Mononuclear complexes ($AlOH^{2+}$, $Al(OH)_2^+$) and such polynuclear complexes as $Al_2(OH)_2^{4+}$ and $Al_3(OH)_6^{3+}$, if they exist, are certainly by no means the main product. The equilibrium data alone do not permit one to decide whether a single complex or a series of complexes is formed. However, judging from the behavior of aged solutions and crystallographic evidence, the complex $Al_6(OH)_{15}^{3+}$ is thought to be the most likely main product. The main reaction, and its equilibrium constant, are given in equation (6).

In the alkaline range ($Z = 3 \rightarrow 4$) Brosset's "zero values" can be explained assuming the existence of a single complex $Al(OH)_4^-$ and solid $Al(OH)_3$. For $Al(OH)_3(s) + OH^- \rightleftharpoons Al(OH)_4^-$, log $K = 1.0 \pm 0.2$. The aging process may be the transformation of the originally precipitated $Al(OH)_3$ to a more stable form for which log $K = 0.5 \pm 0.2$.

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