# The Hydrolysis of Metal Ions. Part 8.[1] Aluminium(III)

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An automated potentiometric titration technique has been used to study the hydrolytic behaviour of the aluminium(III) ion in 0.10 mol dm$^{-3}$ sodium nitrate at 25 °C. Low aluminium(III) concentrations (up to 0.1 mol dm$^{-3}$) were used so that the monomeric species, $[Al(OH)]^{2+}$ and $[Al(OH)_2]^+$, could be identified. The data treatment indicates the presence of the species $[Al(OH)]^{2+}$, $[Al(OH)_2]^+$, $[Al_3(OH)_4]^{5+}$, and a high-molecular-weight polymer with a $q/p$ ratio (OH/Al) of *ca.* 2.46 and a $p$ value between 6 and 14. The $-\log \beta_{pq}$ values for these species $\{\beta_{pq} = [Al_p(OH)_q^{(3p-q)+}][H^+]^q/[Al^{3+}]^p\}$ are estimated to be 5.33 (0.009), 10.91 (0.04), 13.13 (0.005), and $5.73-3.6p+4.64q$ (0.04) respectively, the estimated standard deviations being given in parentheses.

The hydrolysis of aluminium(III) has been investigated extensively over the last 50 years.[2–8] In these studies, polymerisation reactions predominate, but the equilibria have been found to be difficult to quantify because of the presence of slow reactions in the composition regions of major interest. The work of Aveston[3] (at 25 °C) and Mesmer and Baes[2] (at 62.5, 99.6, 124.8, and 149.8 °C) indicates that the most important (polynuclear) species under their experimental conditions are $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, and $[Al_{13}(OH)_{32}]^{7+}$; the studies at the elevated temperatures partly avoided some of the experimental difficulties caused by the slow reactions.

Kubota[4] carried out measurements with solutions of low aluminium(III) concentrations and was able to characterise $[Al(OH)]^{2+}$ as the only hydrolysis product. Numerous other investigations have been reported[9–13] but these have been of limited value in identifying the products formed; in particular, the species $[Al(OH)_2]^+$ has not been adequately documented.

The present work was carried out in such a way that *both* monomeric and polymeric species might be investigated simultaneously, thus allowing better elucidation of the aluminium(III) hydrolysis equilibria. Measurements were made at 25 °C with 0.10 mol dm$^{-3}$ sodium nitrate as ionic medium.

## Experimental

*Reagents.*—The source of aluminium was aluminium(III) nitrate 9-hydrate (Merck G. R.). Potassium hydrogencarbonate (Fluka Guarantie) was used as titrant, rather than hydroxide, in order to avoid localised concentration effects; complex formation by, or protonation of, carbonate, at least in the pH range of the measurements, is negligible. This approach was first used by Hedström[14] in his study of the hydrolysis of iron(III). Sodium nitrate and nitric acid were Merck Suprapur grade. The aluminium(III) nitrate stock and test solutions were analysed using ethylenediaminetetra-acetic acid.[15]

*Procedure.*—The general procedure used has been previously described.[1] The stock aluminium(III) nitrate solution (nominally $10^{-2}$ mol dm$^{-3}$) was prepared at pH 2 and allowed to stand at 25.0 ± 0.5 °C for 3 months. The test solutions were then prepared at pH 2.5—3.5 [depending on the aluminium(III) concentration] and allowed to stand a further week. All titrations were commenced at pH *ca.* 4 where it was estimated that about 5% hydrolysis had occurred. Under these conditions only monomeric species were present and hence kinetic effects were absent. The titrations were carried out by adding titrant (nominally 0.10 mol dm$^{-3}$ potassium hydrogencarbonate) every 5 min, the pH value being recorded every minute. The titrations were continued to pH values higher than where equilibrium could otherwise be obtained almost immediately (less than 1 min). For the purposes of data analysis, the pH values employed were well before this region in order to be certain that non-equilibrium effects could be excluded.

*Computational Procedure and Selection of* pH *Range.*—In our previous work we have equated the hydrogen-ion concentration and the pH value according to equation (1) where λ (when both

$$[H^+] = 10^{-pH}/\lambda \qquad (1)$$

mass-balance equations are of equal importance) is an unknown, and hence a refinable parameter. The presence of λ in the mass-balance equations results in the refinable formation constants being a function of λ. This means that the equilibrium constant for the ionisation of water cannot be simultaneously included in a set of hydrolysis constants being refined together with λ.[16] However, below pH values of about 5 the effect of the inclusion of the water ionisation reaction had a negligible effect on the values of the formation constants (although having a significant influence on the estimated standard deviations of the hydrolysis constants). This allowed the value of λ to be numerically refined together with the equilibrium constants initially, in the absence of the water reaction, and then held constant (at this refined value) while the equilibrium constants were further refined with the presence of a constant (not refined) water reaction.

All unknowns (stability constants, analytical proton-excess values, and the λ parameter) were refined simultaneously using our version[17,18] of the MINIQUAD program.[19,20]

The pH range used for data analysis was chosen so that the change in pH measured over the length of time between titrant additions (as determined from the pH recorded at 1-min intervals) was not more than 0.002 units. A summary of the titrations is given in Table 1; full details are available on request.

**Table 1.** Summary of potentiometric titration data for aluminium(III) hydrolysis at 25 °C and in 0.10 mol dm$^{-3}$ sodium nitrate

| Total initial aluminium(III) concentration ($10^{-3}$ mol dm$^{-3}$) | pH Range | Number of points |
|---|---|---|
| 0.992 | 3.990—4.463 | 110 |
| 0.496 | 3.997—4.679 | 98 |
| 0.198 | 3.974—4.796 | 90 |
| 0.099 | 3.984—4.905 | 75 |

## Results

The (hypothetical) hydrolysis reactions (2) lead to the stoicheiometric equilibrium constants being defined as in (3).

$$p\mathrm{Al}^{3+} + q\mathrm{H_2O} \rightleftharpoons [\mathrm{Al}_p(\mathrm{OH})_q]^{(3p-q)+} + q\mathrm{H}^+ \quad (2)$$

$$\beta_{pq} = [\mathrm{Al}_p(\mathrm{OH})_q{}^{(3p-q)+}][\mathrm{H}^+]^q/[\mathrm{Al}^{3+}]^p \quad (3)$$

Hydrolytic species are represented by chemical formulae or as ($p$,$q$) pairs.

In the investigation of a hydrolysing metal ion system, the accessible pH range (and hence, the extent of hydrolysis) is usually limited by precipitation reactions. The onset of precipitation can be sharp and is indicated before the precipitate becomes visible by the pH values decreasing, despite the addition of base.[21] This apparently paradoxical result is readily explained in terms of the ligand number (average ratio of hydroxide/metal ion): a point of supersaturation is reached where the metal ion, though almost exclusively present as polymeric species, has a ligand number significantly less than that in the solid phase; once the latter begins to form, upon further addition of base the ligand number changes so rapidly that the hydrogen ions which result are not compensated for by the base. The change in pH (ΔpH) between titration additions, having earlier begun to decrease, actually becomes zero and then changes sign. This phenomenon has been observed in a number of systems,[16,21–23] including zinc(II), manganese(II), copper(II), and indium(III).

There are, however, other systems such as aluminium(III), where the onset of precipitation is preceded by the initiation of very slow reactions (further polymerisation or slow precipitation reactions, or both) and the ΔpH values obtained with the continued addition of base slowly decrease and become near zero, over a relatively large pH range, depending on the metal ion. This can be described as the 'disequilibrium region' and is best regarded as a slower version of the above rapid onset of precipitation. Stable pH values in this region may take considerable time to be reached (minutes to months). In such systems there is the conflicting problem of increasing the pH value high enough in order to detect all of the rapidly formed species without, at the same time, allowing the superimposed slow reactions to interfere to any significant extent. It is a somewhat arbitrary decision as to where such a titration is terminated. Since only the rapidly formed species were of interest in the present work, experimental points were taken at only 5-min intervals. In the higher pH regions, whilst the rapidly formed species would probably reach equilibrium within this interval, the overall equilibrium became increasingly less well established and the data increasingly influenced by the cumulative effects of these slow reactions. The only truly correct way of assessing the arbitrariness of the data selection in such systems must be provided by the data analysis. It is for this reason that the data were selected in the manner described above.

The species selected for examination and analysis of the data consist of the monomers (1,1) and (1,2), and the polymers (2,2), (3,3), (3,4), (3,5), and (4,4), together with the 'high' polymers (5,12), (6,15), (7,17), (8,20), (9,23), (10,24), (13,32), and (14,34). All of these 'high' polymers have $q/p$ ratios in the range 2.400—2.556:1 (average 2.460:1). The rationale for model selection is based upon ($a$) previously published work,[2–13] ($b$) the need to include, at least, one 'high' polymer of $q/p$ ratio of about 2.46:1, as suggested previously,[2–13] and ($c$) the development of a base model consisting of monomers and 'low' polymers, the latter being of acceptable stoicheiometry based on considerations of the co-ordination number of the hydrolysing metal ion.[24]

The results of these calculations, performed with our version[17,18] of the computer program MINIQUAD,[19,20] led first to the choice of the species (1,1), (1,2), and (3,4) for use as a base model, and secondly to the data listed in Table 2 where a 'high' polymer has been added to this base model. The 'high' polymers listed in Table 2 are those that have been previously postulated.[2–13] All of the high polymers required initial estimates of the formation constants. In many instances, these can be of critical importance since too poor an estimate can cause numerical problems such as divergence. In all cases, the initial estimates used were obtained from the Sylva–Davidson equation[25] and these were found to be satisfactory. If necessary, better estimates could have been obtained from the Brown–Sylva–Ellis equation.[24]

The criteria used for the choice of a 'best' model are manifold and consist of the following: ($i$) the absence of a negative formation constant in any model; ($ii$) the presence of chemically 'sensible' values of parameters such as λ and the analytical proton-excess values at the commencement (zero addition of titrant) of a titration (the latter can assume negative values); ($iii$) the 'chemical sense' of the stoicheiometries of the species in the model, based on present knowledge;[24] ($iv$) the precision of the detection of the individual species in a model, as determined from the estimated standard deviations of the refined formation constants; ($v$) the correlation between the model and data, as measured by the $R$ factor. Our experience has shown that, in relation to ($iv$) and ($v$), the originally proposed acceptable values of the estimated standard deviations of all of the formation constants (<10%) and the $R$-factor (<0.002)[17,18] are still appropriate, though the precision in formation constants obtained can often be much better than 5%.[1] It should be stressed, however, that the choice of these two criteria requires judgement that is entirely subjective.

## Discussion

Previous work has shown[24] that aquated metal ions having a co-ordination number of six [as does the aluminium(III) ion[26,27]] form the (2,2) dimer, whereas those metal ions with a co-ordination number of four and eight or more do not. The present work demonstrates quite clearly the absence of this species whose formation constant becomes negative and remains so, even under conditions where larger polymers are appreciably formed (see Table 2 and Figures 1 and 2). If the (2,2) species were to exist, the Sylva–Davidson equation[25] would predict a value of 6.7 for $-\log \beta_{22}$ and, as such, the species should be detectable ($ca.$ 15% under optimum conditions). Furthermore, it can be shown by speciation calculations that the value of $-\log \beta_{22}$ of $ca.$ 8 suggested in earlier work[3,28] means that the (2,2) species postulated was, even under optimum conditions of metal-ion concentration and pH, only a minor species present to about 1% of the total metal-ion concentration. Further evidence of the absence of the (2,2) species comes from the work of Öhman and Forsling.[7] They found that the species gave an insignificant contribution to the data and its formation constant could not be adequately refined.

**Table 2.** Comparison of some models of aluminium(III) hydrolysis containing a 'high' polymer and the (1,1), (1,2), and (3,4) species

| Species | | $-\log \beta_{pq}$* | | | | |
|---|---|---|---|---|---|---|
| (*p*,*q*) | *q*/*p* | (*p*,*q*) | (1,1) | (1,2) | (3,4) | *R* factor |
| None | | | 5.41 | 10.67 | 13.13 | 0.002 095 |
| | | | (0.01) | (0.02) | (0.006) | |
| (5,12)[10] | 2.400 | 43.41 | 5.30 | 11.10 | 13.16 | 0.001 567 |
| | | (0.03) | (0.009) | (0.06) | (0.006) | |
| (6,15)[6] | 2.500 | 53.78 | 5.31 | 11.00 | 13.14 | 0.001 563 |
| | | (0.03) | (0.009) | (0.04) | (0.005) | |
| (7,17)[13] | 2.429 | 59.48 | 5.32 | 10.95 | 13.14 | 0.001 563 |
| | | (0.03) | (0.009) | (0.04) | (0.005) | |
| (8,20)[6,13] | 2.500 | 69.82 | 5.33 | 10.91 | 13.13 | 0.001 603 |
| | | (0.03) | (0.009) | (0.03) | (0.005) | |
| (9,23)[6] | 2.556 | 80.14 | 5.34 | 10.88 | 13.13 | 0.001 630 |
| | | (0.03) | (0.009) | (0.03) | (0.005) | |
| (10,24)[8] | 2.400 | 81.18 | 5.34 | 10.86 | 13.13 | 0.001 580 |
| | | (0.03) | (0.009) | (0.03) | (0.005) | |
| (13,32)[3,7] | 2.462 | 107.47 | 5.35 | 10.82 | 13.13 | 0.001 637 |
| | | (0.04) | (0.009) | (0.02) | (0.005) | |
| (14,34)[2] | 2.429 | 113.14 | 5.36 | 10.81 | 13.13 | 0.001 639 |
| | | (0.04) | (0.009) | (0.02) | (0.005) | |

* Estimated standard deviations given in parentheses.

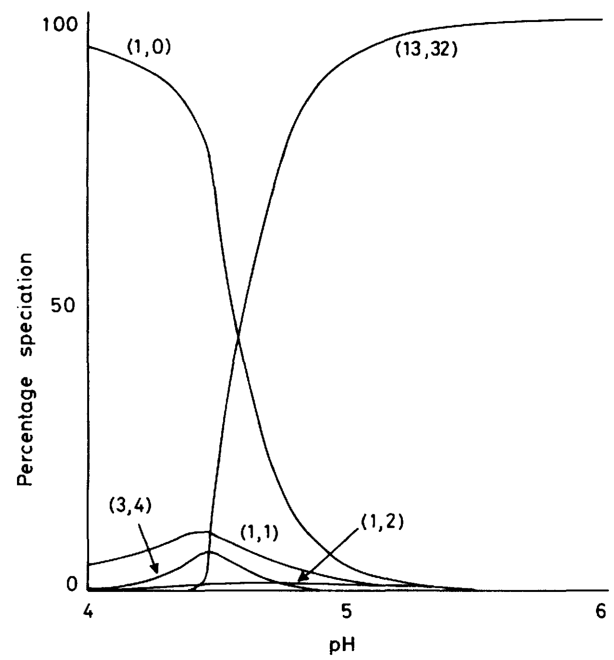

**Figure 1.** Percentage speciation of aluminium(III) hydrolysis products at a total (initial) aluminium(III) concentration of 0.992 mmol dm$^{-3}$ at 25 °C

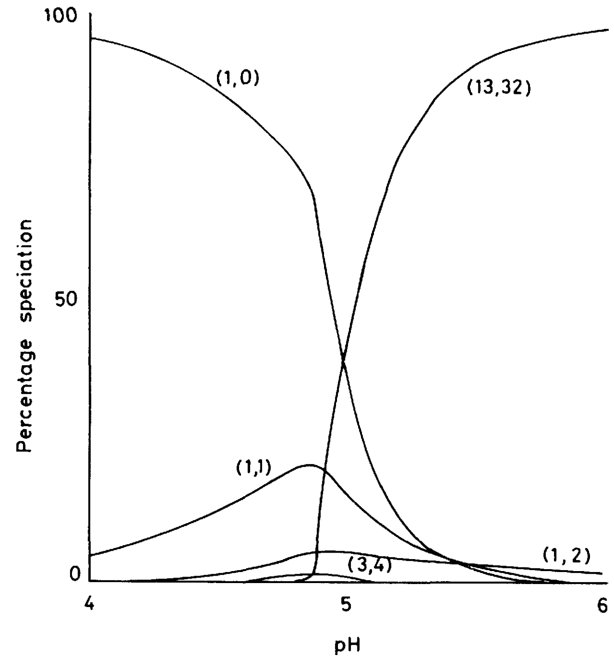

**Figure 2.** Percentage speciation of aluminium(III) hydrolysis products at a total (initial) aluminium(III) concentration of 0.099 mmol dm$^{-3}$ at 25 °C

On the other hand, Mesmer and Baes[2] in elevated-temperature measurements (62—150 °C) provided evidence for the formation of the (2,2) species. However, their data analysis confirms the inferiority of the ORGLS computer program[29] compared to MINIQUAD.[19,20] In the former work (*a*) no acceptance criteria are used, (*b*) the differences in a large number of models in explaining the data are small, and (*c*) in the model presented to explain the data, species have standard deviations as high as 34.5% [for the (2,2) species]. The postulation of the (2,2) species in this work is thus questionable.

The absence of the (2,2) species suggests that the aluminium(III) ion undergoes a reduction in co-ordination number from six to four during the formation of polynuclear species. Similar arguments can be applied to other metal ions[24] such as $Mg^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Cd^{2+}$.

The data from many of the studies of aluminium(III) hydrolysis are consistent with the formation of one high-molecular-weight polymeric species with a *q*/*p* ratio of *ca.* 2.46.[2,3,6—8,10,13,28] The stoicheiometry of this species is, however, still the subject of much conflict and species with the number of aluminium atoms ranging from five to fourteen have been postulated. Indeed, the ultracentrifugation experiments of Aveston[3] were consistent with a monodisperse solute (*q*/*p* from 2.42 to 2.45) which had between seven and seventeen aluminium(III) atoms per molecule. Aveston chose $[Al_{13}(OH)_{32}]^{7+}$, a species which was also consistent with the data from his potentiometric experiments. Recently, this species has been preferred[3,7,28] owing to its detection in the solid state.[29] However, the relationship between the species in solution and those in the solid state is tenuous. The fact that a species is present in the solid state does not necessarily mean that the same species will be present in solution. Indeed, the (2,2) dimer has also been detected in the solid state[30] and the present work shows quite clearly that this species is *not* detectable in solution.

The data given in Table 2 indicate, in regard to a high-molecular-weight polymer being added to the base model, (1,1), (1,2), and (3,4), that no unequivocal choice can be made. All of the previously postulated species, with the exception of (5,12) (whose estimated standard deviation is too large), meet the acceptance criteria. It is therefore apparent that a single technique such as potentiometry used alone cannot distinguish between a number of possible high-molecular-weight polynuclear species. Two or more methods would need to be used concurrently for there to be any likelihood of obtaining a definitive result. The present work does, however, allow a general equation (4) for the formation constant of this polymer to be derived. The formation constants predicted by the equation are within the range of the estimated standard deviation of each species.

$$-\log \beta_{pq} = 5.73 - 3.6p + 4.64q \qquad (4)$$

Nazarenko and Nevskaya[5] have studied the formation of the mononuclear species in dilute aluminium(III) solutions, using 0.1 mol $dm^{-3}$ sodium perchlorate to maintain ion strength. They used arsenazo I and pyrocatechol violet as competing ligands. This method has many complications[28] which have not been fully investigated, resulting in doubtful estimates of the species present. This is amply demonstrated by comparing the results from this method with those of Kubota[4] and the present work. Furthermore, our previous work[24] predicts the negative logarithm of the formation constant of the (1,2) species (at zero ionic strength) to be 11.12 which is consistent with the value of 10.91 estimated in this work.

In the concentration ranges studied, $[Al(OH)]^{2+}$ is the most important species. Only at high concentrations of both aluminium(III) and hydroxide ion does $[Al_3(OH)_4]^{5+}$ become of importance. The second monomer, $[Al(OH)_2]^+$, becomes significant only at high pH with lower aluminium(III) concentrations. The high-molecular-weight polymer becomes important only at very high pH and all aluminium(III) concentrations. The percentage speciations at the highest and lowest aluminium(III) concentrations are illustrated in Figures 1 and 2. For the purposes of illustration, the model containing the (13,32) species has been used in the Figures; the variation obtained with the other models listed in Table 2, in relation to the percentage speciation of each species, is small (*ca.* 2%).

In the present work a definitive description of the mononuclear and low-molecular-weight polymeric species has been obtained. A unique choice for a high-molecular-weight polymer could not be obtained because of inherent resolution problems, however, this is the first study which has simultaneously found evidence for all three types of species.

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## References

1 Part 7, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 2001.
2 R. E. Mesmer and C. F. Baes, *Inorg. Chem.*, 1971, **10**, 2290.
3 J. Aveston, *J. Chem. Soc.*, 1965, 4438.
4 H. Kubota, *Diss. Abstr.*, 1956, **16**, 864.
5 V. A. Nazarenko and E. M. Nevskaya, *Russ. J. Inorg. Chem.*, 1968, **13**, 825.
6 C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, 1917.
7 L. Öhman and W. Forsling, *Acta Chem. Scand., Ser. A*, 1981, **35**, 795.
8 K. Pulfer and J. R. Kramer, *Environ. Geochem. Rep.*, No. 1983/2, February, 1983 and refs. therein.
9 C. R. Frink and M. Peech, *Soil Sci.*, 1962, **20**, 346.
10 A. J. Rubin and P. L. Hayden, 'Aqueous-Environmental Chemistry of Metals,' ed. A. J. Rubin, Ann Arbor Science Publishers, Ann Arbor, 1974.
11 R. C. Turner, *Can. J. Chem.*, 1975, **53**, 2811.
12 R. M. Smith and A. E. Martell, 'Critical Stability Constants,' Plenum Press, New York, 1976, vol. 4 and refs. therein.
13 L. G. Sillén and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' Spec. Publ., The Chemical Society, London, 1964, no. 17; 1971, no. 25 and refs. therein.
14 B. O. A. Hedström, *Ark. Kemi*, 1953, **6**, 1.
15 'Complexometric Assay Methods with Titriplex,' E. Merck, Darmstadt, 1978.
16 Part 4, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1982, 1911.
17 Part 2, R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 1979, 465.
18 Part 5, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 31.
19 A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.
20 P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.
21 D. D. Perrin, *J. Chem. Soc.*, 1962, 2197.
22 R. N. Sylva, unpublished work.
23 D. D. Perrin, *J. Chem. Soc.*, 1962, 4500.
24 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1985, 723.
25 Part 3, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1980, 1577.
26 J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 2105.
27 J. C. Hindman and J. C. Sullivan, 'Coordination Chemistry,' ed. A. E. Martell, Van Nostrand Reinhold, New York, 1971, ch. 7.
28 C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley, New York, 1978.
29 G. Johansson, *Acta Chem. Scand.*, 1962, **16**, 403.
30 G. Johansson, *Acta Chem. Scand.*, 1960, **14**, 771.

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