

820. *Hydrolysis of the Aluminium Ion: Ultracentrifugation and Acidity Measurements*

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Equilibrium ultracentrifugation and acidity measurements of hydrolysed aluminium perchlorate solutions in 1M-sodium perchlorate at 25° have been interpreted by assuming the species $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_{13}(\text{OH})_{32}^{7+}$. The least-squares refined formation-constants are

$$2\text{Al}^{3+} + 2\text{H}_2\text{O} = [\text{Al}_2(\text{OH})_2]^{4+} \log \beta_{2,2} = -7.07 \pm 0.06$$

$$13\text{Al}^{3+} + 32\text{H}_2\text{O} = [\text{Al}_{13}(\text{OH})_{32}]^{7+} \log \beta_{32,13} = -104.5 \pm 0.06$$

ALTHOUGH the aluminium ion is perhaps the best known example of metal-ion hydrolysis, there is little agreement in the literature on the formulæ of the species that are formed; even the same workers have sometimes revised their hypothesis several times. For example, Brosset¹ first interpreted his potentiometric-titration data by assuming an infinite series of polynuclear complexes with the formula $[\text{Al}(\text{OH})_3]_n^{3+}$. In a subsequent reinterpretation of the same results² the single complex $[\text{Al}_6(\text{OH})_{15}]^{3+}$ was favoured, although the existence of an infinite series, this time with the revised formula $\text{Al}[\text{Al}_2(\text{OH})_5]_n^{(3+n)+}$, was not ruled out. In a later Review Article, Sillén³ mentions $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$, which has been shown to exist in some basic aluminium salt crystals,⁴ as a possibility and, still more recently,⁵ a mixture of $[\text{Al}_{13}(\text{OH})_{34}]^{5+}$ and $[\text{Al}_7(\text{OH})_{17}]^{4+}$. Likewise, on the evidence of colloid coagulation, Matijevic at first suggested a dimer,⁶ but later retracted this in favour of an octamer.⁷ On the other hand, several authors⁸⁻¹¹ consider the classical monomeric mechanism, first suggested by Brønsted,¹² is adequate to explain their results; others,^{13,14} realising that the concentration-dependence of their titration curves was incompatible with this simple scheme, have suggested a mixture of monomers and dimers.

These markedly divergent schemes, based mainly on titration data, may well stem from the slow equilibria that seem to exist, coupled to the fact that, unless accurate e.m.f. values are available (*i.e.*, within about a millivolt, corresponding to a change of 0.02 pH), it is difficult to distinguish between the extreme hypotheses of a single species and an

¹ C. Brosset, *Acta Chem. Scand.*, 1952, **6**, 910.

² C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, 1917.

³ L. G. Sillén, *Quart. Rev.*, 1959, **13**, 146.

⁴ G. Johansson, *Acta Chem. Scand.*, 1960, **14**, 771.

⁵ L. G. Sillén, "Hydrolytic Aqueous Species," Lecture, Houston, Texas, November 1962.

⁶ E. Matijevic and B. Tezak, *J. Phys. Chem.*, 1953, **57**, 951.

⁷ E. Matijevic, K. G. Mathoi, R. H. Ottewill, and M. Kerker, *J. Phys. Chem.*, 1961, **65**, 826.

⁸ R. K. Schofield and A. W. Taylor, *J.*, 1954, 4445.

⁹ W. H. Hartford, *Ind. Eng. Chem.*, 1942, **34**, 920.

¹⁰ T. Ito and N. Yui, *Sci. Reports Tôhoku Univ.*, 1953, **37**, 185 (*Chem. Abs.*, 1954, **48**, 5613).

¹¹ C. R. Frink and M. Peech, *Inorg. Chem.*, 1963, **2**, 473.

¹² J. N. Brønsted and K. Z. Volquartz, *Z. phys. Chem.*, 1928, **134**, 97.

¹³ J. Faucherre, *Bull. Soc. chim. France*, 1954, **21**, 253.

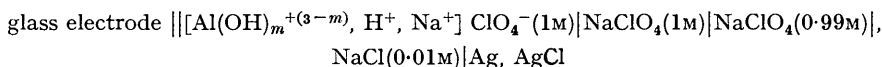
¹⁴ H. Kubota, *Diss. Abs.*, 1956, **16**, 864.

infinite series.¹⁵ The aim of the present investigation was therefore to establish, at least approximately, the degree of aggregation of the aluminium species by equilibrium ultra-centrifugation, and thus to reduce the range of species available for interpretation of the acidity measurements.

EXPERIMENTAL

Centrifugation, Refractive-index Increments, and Volumes.—Centrifugations were carried out with a Spinco model E ultracentrifuge at 25°. Densities were measured with a *ca.* 24-ml. pycnometer and refractive-index increments at 546 μ with a Brice-Phoenix differential refractometer. The centrifugation and computational procedures described by Johnson, Scatchard, and Kraus¹⁶ were used. Computations were carried out on an IBM 7090 computer.

Acidity Measurements.—The e.m.f. of the cell



was measured with an Electronic Instruments Ltd. (E.I.L.) model 33B Vibron electrometer in conjunction with a vernier potentiometer. A screened E.I.L. glass electrode, type G.H.S. 33, and R.A.G. 23 silver-silver chloride reference electrode assembly were used. The electrode system was standardised every hour with a solution of 0.001M-perchloric acid in 0.999M-sodium perchlorate. If the e.m.f. of the standard differed by more than 0.2 mv from the previous value, the acidities of the aluminium solutions measured between these standardisations were repeated. The response of the glass electrode was checked at the start of the measurements by using a series of perchloric acid-sodium perchlorate mixtures 1M in total perchlorate and was found to approach closely the theoretical value at low acidities. The acidity of the aluminium solutions was taken as

$$\log C_H = \log(C_H)_{\text{std}} + (E_{Al \text{ soln}} - E_{\text{std}}) / 59.16$$

where E is the potential in millivolts. The average number of OH^- ions bound per Al ion, m is equal to the amount of base added plus the free acid, divided by the aluminium concentration. The whole electrode system was immersed in a thermostat at $25^\circ \pm 0.01^\circ$.

Materials.—All reagents were AnalaR grade. A stock solution of aluminium perchlorate was prepared by dissolving a known weight of aluminium wire in hydrochloric acid followed by repeated evaporation with perchloric acid. The perchlorate concentration was determined by passing an aliquot portion of the stock solution through a cation-exchange resin saturated with hydrogen, and titrating the effluent with standard base. The concentration of free acid, obtained from the difference of the total perchlorate and aluminium concentration (equivs. per kg.), was checked by the potentiometric procedure described by Brosset.¹ Sodium perchlorate was prepared by neutralising sodium hydroxide with perchloric acid to pH 4, removing carbon dioxide with a stream of nitrogen, and then neutralising further to pH 7. The slight precipitate which formed on standing was filtered off, the solution re-acidified to pH 4 under nitrogen, brought back to pH 7 with carbon dioxide-free sodium hydroxide, evaporated, and allowed to crystallise. The crystals were redissolved in water and the stock solution analysed by evaporating samples to dryness at 110° and weighing as $NaClO_4$.

Preparation of Solutions.—Preliminary experiments indicated that, although clear solutions containing up to 2.5 equivalents of base (sodium hydrogen carbonate solution) per mole of aluminium could be initially obtained, these solutions became cloudy after a few weeks at 25°. If the amount of base were reduced to 2.43 equivalents, the solutions remained clear indefinitely, but when examined in the ultracentrifuge (by using short columns of solution) were found to be far removed from equilibrium. The initial degree of polymerisation, which was not measured but from the number of fringes was estimated to be of the order of several hundred, decreased to about twice the equilibrium value after 5 days, when the experiment was stopped. However, if the neutralisation was carried out at 50° and the solution kept at this temperature for a further 15 min. while the carbon dioxide was removed with a stream of nitrogen and then cooled to 25°, a stable solution was obtained in the following 4—5 days needed to reach equilibrium

¹⁵ L. G. Sillén, *Quart. Rev.*, 1959, **13**, 159.

¹⁶ J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, 1959, **63**, 787. For details of the computational programme (Fortran) used see O. E. Esvál, Thesis, University of N. Carolina, 1962.

in the centrifuge. This was the procedure finally adopted, except that all solutions were stored at 25° for a further 2 weeks before the ultracentrifugation and acidity measurements were begun.

RESULTS

Ultracentrifugation.—The computed value of the degree of polymerisation, N_w of a charged monodisperse polymer sedimenting in the presence of a supporting electrolyte with a common ion depends on the charge per monomer unit, z' , and the concentration of the solute, c'_2 (monomoles/l.), relative to that of the supporting electrolyte, c_3 . As part of the variation of N_w with z' is concentration-dependent, centrifugation at different values of c'_2 will give concordant results at only a single value of z' , if the various assumptions of the treatment, such as the constancy of refractive-index increments, volumes, densities, and most important, activity coefficients, are valid. Additional approximations involved in treatment of data for a polydisperse solute have been discussed earlier.¹⁷

The apparent molal volumes, ϕ_v and refractive-index increments, $\Delta n/c'_2$ of the aluminium species $\text{Al}(\text{OH})_m(\text{ClO}_4)_{(3-m)}$ in 1M-sodium perchlorate given in the Table, showed no significant concentration-dependence. Average values were therefore used to compute dn/dc'_2 and the partial specific volume, \bar{V} , for each value of m . The experimental scatter about the mean of the volume and refractive-index values results in an uncertainty of about 1% in the degree of polymerisation in each case.

The results of the equilibrium ultracentrifugations were computed for a series of z' between the extreme assumptions of maximum charge (no counter-ion binding) and zero charge (complete counter-ion binding). The actual values of z' and the corresponding values of N_w should lie between these extreme values which are given in the Table. For solutions with $m = 2.42$ and 2.45, the logarithm of the difference in refractive index between the solution and back-ground was found to increase almost linearly with the square of the radius, which is indicative of a monodisperse solute. At lower values of m the solute became increasingly polydisperse

Apparent molal volumes, ϕ_v , refractive-index increments $\Delta n/c'_2$, and apparent degrees of polymerisation computed for zero and maximum charge of $\text{Al}(\text{OH})_m(\text{ClO}_4)_{3-m}$ in 1M- NaClO_4

n	c_2 (monomole l. ⁻¹)	ϕ_v (ml. monomole ⁻¹)	$\Delta n/c'_2$ (l. monomole ⁻¹)	Speed (r.p.m.)	N_w		
					$z' = 0$	$z' = 3 - m$	$m = z'_{\text{max}}$
1.51	0.05	63.9	0.0190	24,570	2.0	5.7	
	0.10	63.0	0.0192	21,698	1.8	6.2	
	0.20	66.6	0.0186	17,186	1.6	7.8	
2.02	0.30	64.3	0.0190	15,183	1.4	8.1	
	0.05	54.9	0.0149	24,570	3.8	9.1	
	0.10	54.6	0.0149	21,698	3.6	10.3	
	0.20	54.1	0.0149	17,186	3.3	13.4	
	0.30	54.6	0.0150	15,183	3.0	16.4	
2.19	0.05	52.3	0.0132	24,570	5.3	11.8	
	0.10	52.0	0.0131	21,698	5.1	13.5	
	0.20	53.2	0.0130	17,196	4.6	16.5	
	0.30	53.3	0.0132	15,183	4.2	20.3	
2.42	0.05	46.3	0.0118	24,570	7.2	13.2	
	0.10	45.2	0.0117	21,698	7.1	14.3	
	0.20	45.5	0.0116	17,186	6.4	15.4	
	0.30	45.8	0.0117	15,183	5.9	16.5	
2.45	0.05	43.7	0.0113	24,570	7.5	13.6	
	0.10	45.5	0.0112	21,698	7.4	14.6	
	0.20	45.7	0.0116	17,186	6.8	15.5	
	0.30	45.5	0.0115	15,183	6.7	16.8	

Centrifugation of $\text{Al}(\text{OH})_m(\text{ClO}_4)_{(3-m)}$ in 1M- NaClO_4

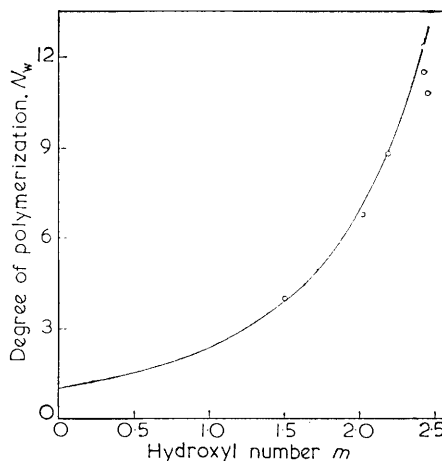
although for all values of m essentially coincident values of N_w , independent of concentration, were obtained when the results were plotted as N_w vs. z' . These values of N_w which correspond to $z' = ca. 0.7 z'_{\text{max}}$, are given by the points in Figure 1. They are considered to be less accurate at low values of m where N_w may in fact be concentration-dependent, although computations based on the hydrolysis scheme finally adopted indicated that, at constant m , this variation is negligible over the concentration range used in the centrifugation.

¹⁷ R. M. Bush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, 1962, **1**, 378.

The ultracentrifuge results are clearly inconsistent with published schemes of hydrolysis involving only monomers and dimers. It is also difficult to reconcile the near-monodispersity observed at high values of m with the existence of any of the various infinite series of polynuclear complexes that have been suggested. The results are also considered to be sufficiently accurate to rule out the possibility of $[\text{Al}_6(\text{OH})_{15}]^{3+}$ being the predominant species at high values of m . The species $[\text{Al}_8(\text{OH})_{20}]^{4+}$ also seems unlikely, especially as the published evidence for it rests on the assumption that the aluminium species can be written as $[\text{Al}_2(\text{OH})_6]_n^{n+}$ and also on the absence of counter-ion binding, neither of which seem valid in the light of the present work.

There remains the species $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$ which has been shown to exist in some crystals. Values of N_w as a function of m , computed from the formation constants found from the acidity

FIGURE 1. Weight-average degree of polymerisation of hydrolysed aluminium perchlorate as a function of the average number of hydroxyl ions bound per aluminium atom. The line represents the computed value of N_w , assuming the species $[\text{Al}_2(\text{OH})_2]^{4+}$ and $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$ with formation constants $\log \beta_{2,2} = -7.07$ and $\log \beta_{32,13} = -104.5$.



data for a scheme involving this ion together with $[\text{Al}_2(\text{OH})_2]^{4+}$ are shown in Figure 1. The agreement with the experimental points is as good as can be expected at high values of m , and rather better at the lower values.

When the present study was begun 3 years ago, some centrifugations were carried out in a supporting electrolyte of 2.5M-sodium perchlorate. As with the more dilute medium, solutions with $m > 2.4$ appeared to be essentially monodisperse, but some indication of non-ideal behaviour was given by the fact that the computed values of N_w increased with decreasing c_2' for all values of z' ; at the maximum value of z' the average value of N_w was about 70% of the values obtained in 1M-sodium perchlorate. When this work was resumed some 18 months later, it had been learnt¹⁸ that low results are often obtained with known solutes at very high ionic strength. However, numerous tests at more moderate concentrations of supporting electrolyte (1M- NaClO_4 ,¹⁸ 1M- NaCl ,¹⁷ 1M- HCl ¹⁶) leave little doubt as to the validity of the method under these conditions. One of the original aluminium solutions, with $m = 2.33$, was recently re-examined in the ultracentrifuge after it had stood at room temperature for 2 years; virtually the same (although erroneous) value of N_w was obtained, which is a good indication that this solution, and others prepared in a similar manner, were at equilibrium.

Acidity Measurements.—As the slow equilibria encountered by Brosset and also indicated by the centrifugations precluded the usual type of e.m.f. titration at 25°, the method of "point titration" was employed. A series of hydrolysed 0.0992M-aluminium perchlorate solutions 1M in total (sodium) perchlorate was prepared as described previously and then diluted with 1M-sodium perchlorate to give 0.0298, 0.00893, and 0.00268M-solutions. The first series of measurements, made 2—3 weeks later was repeated for a few of the solutions after a further period of 3 weeks at 25° ± 0.01°.

The results are plotted in Figure 2 as m vs. $\log c_H$, where c_H is the hydrogen ion concentration. As the points for different concentrations fall on curves which are neither coincident nor parallel

¹⁸ J. S. Johnson, private communication.

over the whole range of m , it follows that two or more hydrolytic species are present, at least one of which must be polymeric. Three sets of formation quotients

$$\beta_{p,q} = \frac{[\text{Al}_q(\text{OH})_p^{(3q-p)+}][\text{H}^+]^p}{[\text{Al}^{3+}]^q}$$

assuming $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$ to be the predominant species, together with either $[\text{Al}_2\text{OH}]^{5+}$, $[\text{Al}_2(\text{OH})_2]^{4+}$, or $[\text{Al}_3(\text{OH})_3]^{6+}$ to account for the deviation of the points (from parallelism) at low values of m , were calculated and refined by using the O.R.G.L.S. Fortran least-squares programme¹⁹ to give the least-squares deviation in m from the experimental points. The corresponding standard deviation in m , σ_m for these three schemes was 0.062, 0.046, and 0.055.

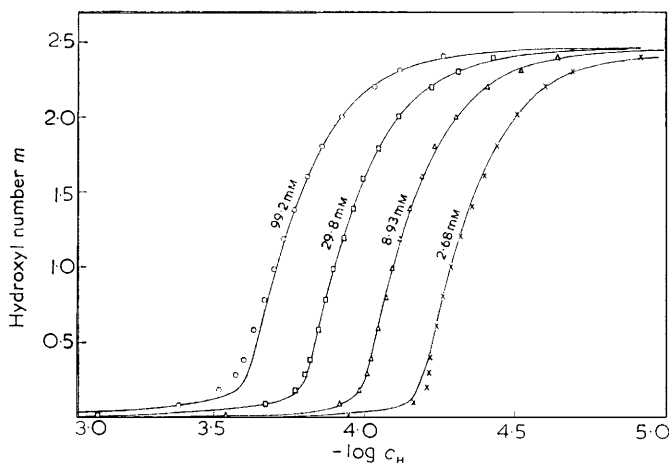
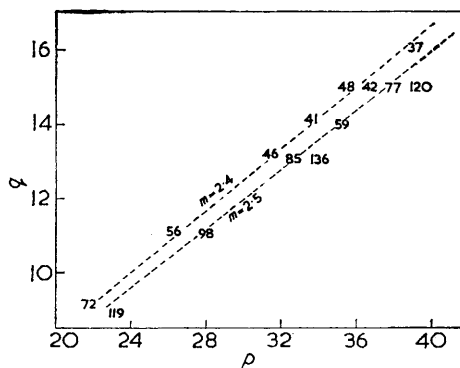


FIGURE 2. Hydrolysis of aluminium perchlorate: curves computed with the species and formation constants given in Figure 1

Although the slightly better fit with the 2,2 species should not be construed as unambiguous evidence for its existence, such a complex ion has been shown to occur in crystalline basic aluminium sulphate.¹⁸ Moreover, by including it to improve the fit at low values of m , a more exact comparison can be made between various alternative schemes for the main hydrolytic species. Such a comparison is shown in Figure 3 where σ_m for fourteen schemes involving a

FIGURE 3. Standard deviations ($\sigma_m \times 10^3$) for various schemes involving $[\text{Al}(\text{OH})_2]^{4+}$ together with a second species, with values of q and p given by the ordinate and abscissa



single polymer, with q and p given by the ordinate and abscissa (together with the 2,2 species, which is important only at low values of m), are compared. Species with $p/q < 2.4$ were not tested, because the centrifugations showed that stable solutions could be obtained with m in excess of this value. Likewise a single species with p/q much greater than 2.5 is incompatible with the way the curves level off in this region. However, for intermediate values, the range of q which gives an acceptable fit to the data does not allow much confidence to be placed in

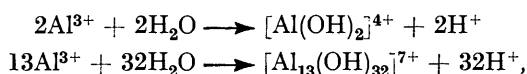
¹⁹ W. R. Busing and H. A. Levy, Oak Ridge National Report TM-271 (1962).

acidity values alone, especially when it is realised that an error of 0.2 mv in the e.m.f. of the solution and standard acid, which is about as good as can be obtained with the glass electrode, would cause a deviation in m of 0.02 over most of the range.

If it is assumed that the skeletal structure of the complex present in some basic aluminium salts is retained in solution, *i.e.*, $q = 13$, a conclusion which is fully consistent with the centrifuge results, then the acidity values clearly show that $p = 32$, giving the formula $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$, which is that found in the crystal. The titration curves shown in Figure 2 were computed with $\log \beta_{2,2} = -7.07$ and $\log \beta_{32,13} = -104.5$. The fit to the results is as good as can be expected, except perhaps for the most concentrated solution at low values of m . It is interesting to note that the addition of $[\text{AlOH}]^{2+}$, which has often been suggested to account for the hydrolysis, decreased σ_m by only 0.002, which is insignificant with the present figures. The fit at low values of m could no doubt be further improved by assuming the additional existence of other species with appropriate formation quotients but, as it is in just this region that the change in ionic strength is greatest, and thus where deviations stemming from variations in activity coefficient would be expected to reach a maximum, it is doubtful if such a procedure would be meaningful.

DISCUSSION

If evidence for a particular scheme of hydrolysis is to be entirely convincing, it is necessary to show that the results on which it is based are inconsistent with all other plausible schemes. It must be admitted that the acidity results, considered in the absence of other evidence fall short of this ideal. Although they may be interpreted quite well by assuming the reactions



there are several alternative schemes that would give an equally good fit. The ultracentrifugation results enabled the range to be much reduced but, because of their relatively low accuracy for such a light element, there still remained three or four plausible alternatives. The complex ions involved in one of these, *i.e.*, the scheme shown above, have been shown by X-ray evidence to be present in certain basic aluminium salts. Supporting evidence for this scheme is provided by the work of Rausch and Bale,²⁰ who measured the small-angle X-ray scattering from hydrolysed aluminium nitrate solutions and showed the radius of gyration of the species present at $m = 2.25$ to be in good agreement with the value for $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$ calculated from Johansson's data.⁴

Although there is no *a priori* reason for supposing that the structure of a complex ion in a crystal is necessarily retained in solution, recent work²¹⁻²³ has shown that this is frequently so; certainly in the present case, where nearly all the alternative schemes have been eliminated, and where the few remaining ones involve species closely similar to those existing in the solid, this assumption appears to be justified.

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²⁰ W. V. Rausch and H. D. Bale, *J. Chem. Phys.*, 1964, **40**, 3391.

²¹ J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.

²² J. Aveston, *Inorg. Chem.*, 1964, **3**, 981.

²³ J. Aveston and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 1051.