Characterization by Nuclear Magnetic Resonance Spectroscopy, Ferron Assay, and Acidification of Partially Neutralized Aluminium Solutions

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Aluminium solutions (0.1 mol dm^{-3}) were hydrolysed at 25 °C by a mild slow procedure involving the addition of NaOH to an aluminium salt. The amount of monomeric and polymeric species deduced from an ^{27}Al n.m.r. analysis of the solutions are in good accordance with results obtained by a spectrophotometric technique using ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid). It is shown that a minimal number of aluminium species are present, the dominant polymer being of the 'Al_{13}' form. A small amount of polymeric species remains unidentified although limited results obtained when solutions are heated above 70 °C seem to indicate that these species contain tetrahedral aluminium. It is also shown that the 'Al_{13}' form can be converted into monomeric species by addition of strong acid to the solution. This transformation however follows a complex path.

Because of their importance in many fields of application, hydroxyaluminium solutions have been the subject of numerous studies. The exact nature of the hydroxyaluminium polymers which are found in partially neutralized solutions is still however a matter of debate. Broadly speaking, two main proposals have been put forward concerning the hydrolysis–polymerization mechanism. The first is related to the final structure of the aluminium hydroxide solid phase and to the core–links theory of Sillen.[1,2] Based mainly on titration techniques, this hexameric model can accommodate a host of possible species having a general formula $Al[Al_2(OH)_5]_n^{(3+n)+}$. These hexameric rings are supposed to coalesce with ageing until they finally precipitate. Some authors[3–5] however, concluded that among all the possible polymers only a few seemed to be actually present. Another minimalistic model suggests that apart from monomers and a small amount of light oligomers, only one predominant polymeric species of formula $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ is present. This 'Al_{13}' polymer consists of a central tetrahedral aluminium symmetrically surrounded by 12 octahedral aluminium ions disposed in groups of three at each apex of the tetrahedron. The existence in solution of this polymer was first favoured because it was found to be present in basic aluminium sulphates and selenates.[6] More recently it has received support in solution from ^{27}Al n.m.r. studies,[7–14] and small angle *X*-ray scattering data.[15,16]

It is quite clear from the literature that the way the hydrolysis is conducted deeply affects the final product. By changing the hydrolysis agent, the temperature, and total time of reaction, it is possible not only to modify the relative concentration but also the intrinsic nature of the various species present in solution. We have adopted a mild slow type of formation involving the addition of NaOH to an aluminium salt; this method provides extremely reproducible data. Our results can therefore only be compared with previous studies using the same type of preparation. The work presented here was conducted on solutions having a hydrolysis level *R* (the ratio [OH] added/total [Al]) between 0 and 2:1 at a concentration of 0.1 mol dm^{-3} Al.[17]

Experimental

Preparation of the Hydroxyaluminium Solutions.—The solutions were prepared at 25 °C in a thermostatted vessel by adding to a rapidly stirred solution of $Al(NO_3)_3 \cdot 9H_2O$ (Merck p.a.), freshly prepared NaOH (Titrisol, Merck). The concentration of the added NaOH was fixed according to each chosen *R* value. The final aluminium concentration was 0.1 mol dm^{-3}. The NaOH solution was injected by employing a peristaltic pump at a rate of 1 cm^3 min^{-1}. This procedure minimizes, to a large extent, the formation of localized high hydroxide concentrations within the solution. The solutions are then transferred to polyethylene flasks and kept at ambient temperature.

^{27}Al *N.M.R.*—The ^{27}Al n.m.r. spectra were obtained at 65.2 MHz by using a F.T. Bruker WM250 spectrometer. Samples were placed in 10 mm tubes containing at their centre a capillary tube with an $[Al(OH)_4]^-$ reference solution of appropriate known concentration. Peak integrated intensities were calibrated with $Al(NO_3)_3 \cdot 9H_2O$ standards.

Characterization by the Ferron Procedure.—The ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) reagent was prepared following the procedure proposed by Bersillon *et al.*[18] It was prepared by mixing a saturated ferron solution (500 cm^3), 4.3 mol dm^{-3} sodium acetate (200 cm^3), and acidified hydroxylamine hydrochloride solution (200 cm^3) (containing 100 g of hydroxylamine hydrochloride and 40 cm^3 of concentrated HCl). The mixture was then brought to 1 l with distilled water and left to stand for at least 5 d before use. To a beaker (50 cm^3) were added 10 cm^3 of this ferron solution, distilled water (15 cm^3) and a 0.02-cm^3 aliquot of the hydroxyaluminium solution. The mixture was vigorously

Table. Aluminium species, as determined by n.m.r. spectroscopy, for different degrees of neutralization R = OH/Al of 0.1 mol dm^{-3} aluminium solutions aged for 24 h

R	pH	Al monomer (%)	'Al_{13}' (%)
0	3.1	100	0
0.5	3.9	68.4	10.6
0.75	3.9	61.4	18.4
1.0	4.0	50.7	30.4
1.5	4.1	31.5	45.6
2.0	4.2	15.7	74.7
2.25	4.4	11.5	74.2

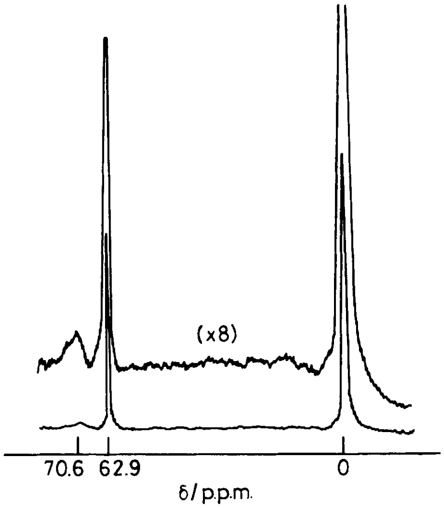

Figure 1. ^{27}Al N.m.r. spectrum of an R = 2 hydroxyaluminium solution heated to 87 °C within the magnet

agitated and the absorbance read at 370 nm at various time intervals (time zero corresponding to the addition of the aluminium aliquot) until no variation in absorbance was detected. The first reading was taken at 30 s.

Acidification of the Hydroxyaluminium Solutions.—The hydroxyaluminium solutions were characterized by adding known amounts of nitric acid to 10 cm^3 of the hydroxyaluminium solution. The variation of pH of the mixture was monitored as a function of time with a Consort 914 pH-meter equipped with a recorder. At regular time intervals (time zero corresponds to the addition of the acid) aliquots were taken and analysed for monomeric aluminium content by the ferron procedure. The evolution after acidification was also followed by n.m.r. spectroscopy. In this case, the acid was added directly to the n.m.r. tube: 0.1 cm^3 of a given concentration of HNO_3 was added to the hydroxyaluminium solution (1.3 cm^3); various [H^+] added/total [Al] ratios were examined by choosing the appropriate HNO_3 concentration. After addition of the acid, the n.m.r. tube was placed within the superconducting magnet. The minimum time required before obtaining n.m.r. data was 50 s.

Results and Discussion

^{27}Al *N.M.R.*—At room temperature, the ^{27}Al n.m.r. spectra of our partially neutralized hydroxyaluminium solutions on ageing for 24 h show, as observed by numerous other authors,[7,10,19,20] two distinct peaks: the first peak, set arbitrarily at 0 p.p.m., corresponds to aluminium monomers in octahedral co-ordination (as R goes from 0 to 2, width at half-height varies from 12 to 35 Hz); the second, at 62.9 p.p.m., has a chemical shift which corresponds to aluminium in tetrahedral co-ordination and which is assigned to the central aluminium ion of the 'Al_{13}' polymeric species (width at half-height, 12.5 Hz). The line corresponding to the $[Al(OH)_4]^-$ standard solution introduced for quantitative determinations lies at 80 p.p.m. From these measurements, the amounts of aluminium in octahedral and tetrahedral co-ordination can be deduced (see Table). If one considers that the peak at 62.9 p.p.m. corresponds to the central aluminium of the 'Al_{13}' polymer then the amount of this polymer present in our solutions can be obtained by multiplying the integral of this by 13. As is evident from the Table, a definite amount (between 10 and 20% of the total aluminium) of polymeric material cannot be detected given the high-resolution conditions under which these n.m.r. spectra are recorded.[20,21] Starting with either Cl^- or NO_3^- anion has no effect on our final results. Finally, when an R = 2 solution is heated *in situ*, *i.e.* in the spectrometer, a third low-intensity peak appears above 70 °C, in the tetrahedral region at 70.6 p.p.m. (see Figure 1). In order to obtain a sufficiently high signal-to-noise ratio, this signal has to be scanned a large number of times (≈5 000 scans). It was checked that under similar conditions this signal is not present at room temperature in the initial solution; it is also absent in a solution heated to 55 °C. Three higher temperatures were investigated: 72, 76, and 87 °C respectively. As the temperature increases in this range the small signal (70.6 p.p.m.) narrows and becomes more distinct. Within experimental errors, the integral line ratio between the two main lines at 0 and 62.9 p.p.m. remains equal to the one observed for the initial room-temperature spectrum. When the heated solutions are brought back to 25 °C, the line at 70.6 p.p.m. is no longer visible. To our knowledge, a line located in this region has only been reported once by Akitt and Farthing[22] but for a hydroxyaluminium solution prepared under completely different conditions: hydrolysis of aluminium metal (preparation time, 48 h at 100 °C) with R = 2.5 and final aluminium concentration of 1 mol dm^{-3}. In that particular case, the line at 71 p.p.m. is observed at 27 °C as a large, broad line which sharpens as the temperature is raised to 77 °C. It is suggested that this line originates from an 'Al_{13}'-like polymer with a more open and relaxed structure retaining octahedral-protected tetrahedral aluminium and which is part of the pool of unidentified aluminium complexes formed during our preparation procedure. The intrinsic correlation time of this species is sufficiently reduced by heating the solution so as to render it visible in the spectrum.

Aluminium–Ferron Assay.—The characterization of hydroxyaluminium solutions by high resolution n.m.r. spectroscopy is limited to species in which the electric-field gradient experienced by the Al nucleus is close to zero.[23] It is therefore of interest to try and combine this technique with other wet methods such as the aluminium–ferron colourimetric method.[18–22,24–29] Ferron forms a coloured complex with aluminium which absorbs radiation most effectively at 370 nm. Since monomeric aluminium species react practically instantaneously with ferron, their concentration may be determined[18,19,24–26] by taking absorbance readings at a short fixed time (30 s) after mixing. These determinations can then be compared with the more direct n.m.r. technique of analysis. For low aluminium concentrations, it has been reported[29,30] that the arbitrary 30 s observation time is only adequate up to $R \sim 1.5$. We have found that for our 0.1 mol dm^{-3} aluminium solutions (aged 24 h) the comparison between n.m.r. and ferron analysis is quite good provided that the ferron : Al concentration is high ($\sim$25 : 1) and that the ferron solution has been aged for more than 5 d. This ferron technique was used to study the time evolution of the monomeric aluminium concentration of our solutions. It was found that, after preparation, the relative concentration of monomeric species with respect to the total aluminium content decreased

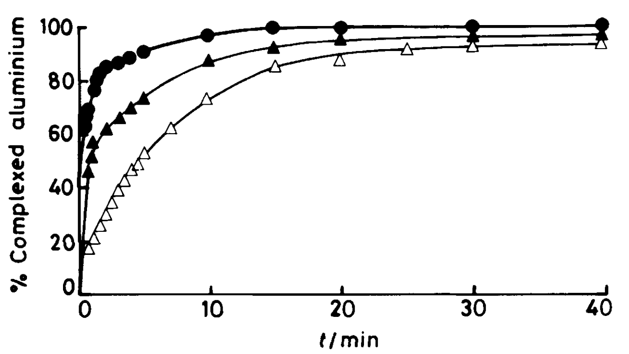

Figure 2. Variation with time of the fraction of aluminium complexed by ferron for different values of R:0.5 (●), 1.0 (▲), and 2.0 (△)

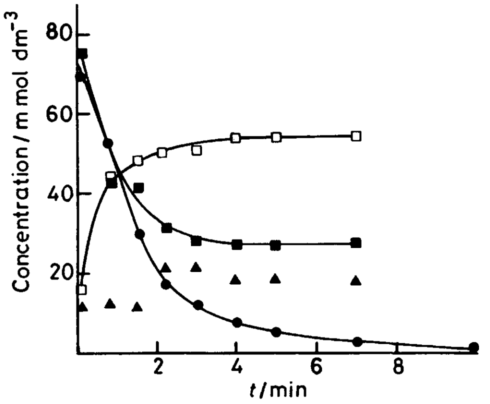

Figure 3. Variation with time, following acidification, of the concentrations (in mmol dm^{-3}) of monomers (□), 'Al_{13}' (■), unidentified Al (▲) and H^+ (●) when H/Al is equal to 1.4:1. The aluminium species were determined by n.m.r. spectroscopy

noticeably during the first few hours before stabilizing after approximately 24 h. During this period of time the decrease observed for $R = 0.5, 1$, and 2 was respectively 25, 20, and 10%.

When partially neutralized aluminium solutions are treated with ferron it is observed (see Figure 2) that the absorbance increases steadily for a very long period of time. This has prompted many authors[21,27–30] to use a differential ferron complexation kinetics analysis in order to try and identify the various aluminium species present in solution. It is assumed that the large polynuclear aluminium species are responsible for the observed slower reaction process. The exact complexation mechanism is however still unknown and this explains why discordant results can be found in the literature. To this should be added the fact that the procedure and conditions under which the aluminium solutions are made influence the nature and amount of aluminium species present. When such an approach is used to analyze the data given in Figure 2 with the assumptions that (*i*) monomers react with ferron instantaneously, (*ii*) each aluminium species reacts with ferron in an independent manner, and (*iii*) the aluminium–ferron complexes obey a first-order reaction rate, it is quite remarkable how closely the experimental points are fit (in a graph, percentage of reacting Al *versus* time) by different sloped curves. If each segment is assumed to represent a different aluminium species then the proportion of these can be obtained (after correction for the contribution of an eventual slower reacting species) by extrapolation back to zero time. In our case, three different slopes can be identified and by taking, as usual,[29] the intermediate one as representing the 'Al_{13}' contribution then the extracted amount for this polymer can be compared with what is found by n.m.r. spectroscopy. For $R = 0.5$, 1.0, and 2.0, one finds for the percentage of 'Al_{13}' determined respectively by n.m.r. (see Table) and ferron analysis, values of 10.6, 21; 30.4, 29; and 74.7, 72%. Because this analysis oversimplifies the complexation mechanism, the excellent agreement found for $R = 1$ and 2 is probably fortuitous. Indeed, a recent study[31] carried out at $R = 2.25$, 6×10^{-2} mol dm^{-3} aluminium and at low ferron to aluminium molar ratios, highlights the complexity of the ferron–polynuclear aluminium species reaction and the difficulty of extracting reliable data from this indirect technique. In that work,[31] it was found that ferron interacts directly with the aluminium polymers. This differs from a previous view[25,29,32] which considered that all aluminium species were in relatively fast equilibrium with each other and that only monomers reacted with ferron. In that case, the slower rates reflected the decomposition of polymers into monomers which then reacted with ferron. We believe that this is not the case, as we have been able[33] to isolate, from normally hydrolysed solutions, fractions containing only polymeric species which after several days have still not switched back to the monomeric form.

Acidification of the formed Hydroxyaluminium Solutions.—In order to test the reversibility of the aluminium polymerization process, various amounts of acid were introduced into the formed hydroxyaluminium solutions aged for 24 h and the results analyzed as a function of time by n.m.r. and ferron assay. The amount of monomers appearing and 'Al_{13}' disappearing increases with the ratio of added H^+/total Al; when this ratio is equal or higher than 2:1, no 'Al_{13}' can be detected at our first observation time of 50 s. Limited acid additions were therefore conducted and an example is shown in Figure 3 for a solution reduced from $R = 2$ to $R = 0.6$. The addition of acid to the solution leads to an instant drop of the initial pH from 4.2 to 1.2; this is followed by a return to equilibrium at a rate which is much slower than the evolutions observed both for monomers and the 'Al_{13}' species. The concentrations of the two species reach plateau values after approximately 4 min. These two curves are however not symmetrical and, apart from the first 50-s point, the amount of 'Al_{13}' disappearing is not accounted for by an equal amount of monomers appearing. The polymerization process is therefore not completely reversible. The transformation leads to the appearance of an additional amount of undetected polymers which probably originate from loosely broken 'Al_{13}' species.[34] These forms together with partially deprotonated monomers continue pumping the available excess of protons as indicated by the slower variation of pH. These observations show not only the complexity of the reverse acid transformation but also the remarkable stability of the 'Al_{13}' structure under highly acidic conditions.

This work has shown how the joint study by n.m.r. and wet techniques can help characterize the products formed during the partial neutralization of aluminium solutions. It has confirmed that when a mild slow type procedure is used to prepare the solutions a minimal number of species is present, the dominant polymer being the 'Al_{13}' form. This species shows partial reversibility to monomeric species on the addition of strong acid. With our preparation procedure, only a relatively small amount of polymeric species remains unidentified. Some of this material has however been directly observed and limited evidence seems to show that it is constituted by tetrahedral aluminium probably protected from the acidic environment by an open, relaxed structure of octahedral aluminium.

Acknowledgements

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