Aluminium-27 Nuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 2.[1] Gel-permeation Chromatography

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The gel-permeation chromatography of two different types of hydrolysed aluminium(III) solution are described, the separations being monitored by conductivity, pH, pCl, and ^{27}Al n.m.r. measurements. Solutions hydrolysed by dissolution of aluminium metal in $AlCl_3$ solution contain at least four components including $[Al(OH_2)_6]^{3+}$ and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ whereas hydrolysis with $Na_2[CO_3]$ produces only a high-molecular-weight polymeric ionic material and the $Al_{13}{}^{7+}$ cation. A fraction was obtained which contained only the latter ion and was more stable than the original solution.

We have shown that the ^{27}Al n.m.r. spectra of hydrolysed aluminium(III) solutions, and therefore the species present in them, depend markedly on the way in which the hydrolysis is carried out.[1] Not all the aluminium present need give rise to an observable ^{27}Al n.m.r. resonance,[1,2] the inference being that the nuclei concerned are present in highly distorted environments and/or large polymeric ions. The form of the spectra arising from each type of preparation is very variable so that several species must be formed in varying proportions. In order to know more about such a system it is desirable to be able to study its individual components and this may best be achieved by some form of chromatography. Gel-permeation chromatography (g.p.c.) has been used successfully by Spiro [3] to separate a polymeric ion from hydrolysed iron solutions, and the same technique has recently been applied to hydrolysed aluminium salt solutions by Schönherr and Frey.[4] The method depends for its success upon the physical separation of molecules according to size because of their different retention times in the pores of the gel.[5-7] In addition the gels are practically inert and this is essential if any change in the hydrolysis status of the solutions is to be avoided. Schönherr and Frey [4] used a conductivity cell to monitor changes in their column effluent and then determined the degree of hydrolysis, m, of interesting fractions using a method based on the Ferron assay.[8] They found two well defined conductivity peaks but the m values indicated overlap of the polymeric, oligomeric, and monomeric species which they proposed were present.

We have now applied the method to two different classes of hydrolysed solutions, monitoring the column effluent using the pH and pCl as well as conductivity, and have examined appropriate fractions using ^{27}Al n.m.r. spectroscopy and chemical assay.

EXPERIMENTAL

Gel-permeation chromatography was carried out using a K16/100 column (Pharmacia) with an internal diameter of 1.6 cm and a gel length of 70 cm, which was the greatest length found to allow adequate flow rates of 0.2—0.9 cm^3 min^{-1}. Sephadex G25 chromatographic gel was used, which has an exclusion limit for globular proteins of the order of $M = 1\,000$. The cation $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ (abbreviated as $Al_{13}{}^{7+}$ below), which is known to be present in many hydrolysed aluminium(III) solutions,[1] is of similar weight but is much more compact than an organic molecule since the constituent Al^{3+} ions are very small, and for sizing purposes we can consider the ion to be an O_{40} unit corresponding to a molecular weight for globular proteins in the region of 640. Thus we would expect this ion to be appreciably retarded by the gel. Elution was carried out with 0.001 mol dm^{-3} $K[NO_3]$ to avoid instability of the conductivity meter. The sample was applied using a standard sample loop so that the flow was not perturbed, and the column effluent was examined continuously using cells designed to measure pH, pCl, and conductivity, in-line, the readings being plotted on a recording device. Fractions were collected and assayed for Al or subjected to ^{27}Al n.m.r. spectroscopy at appropriate points.

Hydrolysed solutions were prepared to a hydrolysis ratio of $m = 2.5$ where m = OH added/Al present. Type 1 was a solution hydrolysed rapidly by adding $Na_2[CO_3]$ over *ca.* 30 min to 1 mol dm^{-3} $AlCl_3$ solution at *ca.* 100 °C, as described in Part 4.[9] The ^{27}Al n.m.r. spectrum shows that in this solution 75% of the Al occurs as the $Al_{13}{}^{7+}$ cation, the remainder being an unobservable species. The solution was used immediately after preparation. Solution 2 was prepared by dissolving AR aluminium metal wire in boiling $AlCl_3$ solution over 48 h using a little mercury as catalyst as described in Part 5.[10] The ^{27}Al n.m.r. spectrum shows that this solution contains a little $Al_{13}{}^{7+}$, a little Al^{3+}, and several species which give rise to broad lines with both octahedral and tetrahedral components. A similar starting solution was used by Schönherr and Frey.[4]

The ^{27}Al n.m.r. spectra were obtained as described previously.[1]

RESULTS

Solution Type 1.—The readings of the various detectors are shown in Figure 1 together with the total aluminium assays. Two peaks are visible in the aluminium assay, one where the effluent volume equals the void volume of the column and a larger peak due to the $Al_{13}{}^{7+}$. The ^{27}Al n.m.r. spectrum only gave a response for the first region at 350 K and this was then weak and broad. This is consistent with the presence of a large polymeric ion. The $Al_{13}{}^{7+}$ ion gave the usual sharp line at 62.5 p.p.m. A trace of Al^{3+} was also detected in the tail of the effluent. The conductivity trace is dominated by the NaCl which elutes later in the run, and only shows the aluminium peaks very weakly. The pCl trace is similar, although it rises significantly at the same time as the first component appears and so confirms that this is probably cationic. The pH rose markedly in this region also and then fell to the pH of the original solution as the run progressed. After the run appeared to be complete it was found that *ca.* 25% of the aluminium remained on the column and could only be removed by extended elution. It is not known whether this indicates that the gel is reactive towards aluminium or whether some decomposition to Al^{3+} occurs which then becomes deeply absorbed by the gel particles.

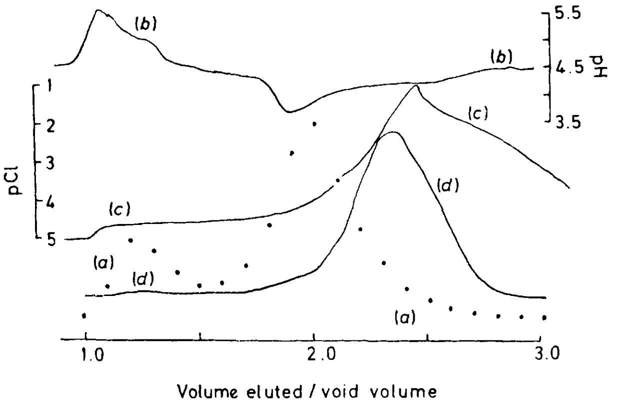

FIGURE 1 Gel-permeation chromatography of a solution of $AlCl_3$ after fast hydrolysis with sodium carbonate. (*a*) (●) Aluminium assays of fractions; (*b*) pH, (*c*) pCl, and (*d*) conductivity of the eluent. The elution volume is expressed as the number of void volumes passed

Confirmation that the main fraction of the effluent was unusually pure was obtained by studying its reaction to the addition of $Na_2[SO_4]$ solution. Customarily, crystals of the sulphate salt of the $Al_{13}{}^{7+}$ cation are prepared by adding $Na_2[SO_4]$ solution to a diluted, freshly prepared type 1 solution. If a solution is used which is more than about 16 h old then an amorphous precipitate is obtained. The properties of the solution thus alter in some way with time, although the ^{27}Al n.m.r. spectrum remains unchanged. We examined the effect of adding $Na_2[SO_4]$ solution to the two principal fractions obtained from g.p.c. and found that the first gave a gel whereas the second gave good clean crystals, even after the solution had been standing for 1 week. The change which occurs in the original solution thus seems to be related to the first fraction which presumably alters its structure or composition on standing. The $Al_{13}{}^{7+}$ cation is obviously reasonably stable in solution when it is pure.

Solution Type 2.—Figure 2 shows the ^{27}Al n.m.r. spectrum of the original solution which obviously contains several components. The majority of the Al present is visible in the spectrum, some 10—20% being unobserved. The changes registered in the column effluent are shown in Figure 3 which also contains the ^{27}Al n.m.r. spectra of the various fractions. The conductivity and pCl of these solutions are both much lower than in the previous run since no NaCl is produced by the method of hydrolysis. The conductivity, pCl, and pH all show a sharp increase when one void volume of effluent is reached indicating the emergence of high-molecular-weight material. Interestingly, the pH rises to the high value of 6.5 which is normally only obtained in these solutions at the expense of much precipitation of solid. This indicates that this material may be hydrolysed to the point where it can no longer give up H^+ without a major structural change occurring. The ^{27}Al n.m.r. spectrum shows a broad featureless resonance overlayed with some of the broad doublet feature of the later fractions and this is consistent with a large species. Assay showed this fraction to contain 20% of the Al although the division is rather arbitrary. The next three spectra contain a broad doublet showing both octahedral and tetrahedral Al to be present. We shall present evidence in Part 5 [10] that this doublet arises from more than one species, which since they have not been separated by g.p.c. are presumably of similar molecular weight. The emergence of this species is accompanied by a fall in pH but very little change in the other traces. All of this species is eluted across these fractions and is accompanied by an increasing proportion of the $Al_{13}{}^{7+}$ cation, whose sharp AlO_4 resonance at 62.5 p.p.m. is very obvious. Its maximum concentration is reached at a later point than that of the species giving the broad doublet, and so it is likely to be of lower molecular weight. This maximum is accompanied by a distinct hump on the high-molecular-weight sides of the main peaks of the conductivity

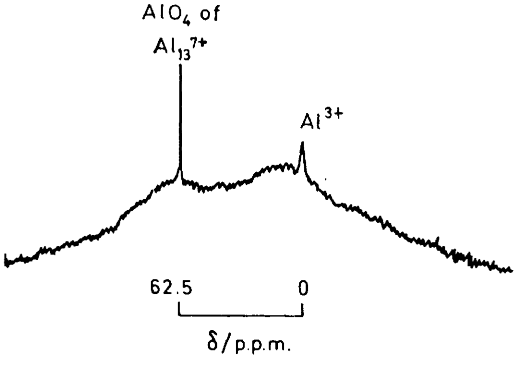

FIGURE 2 The ^{27}Al n.m.r. spectrum at 27 °C of a solution of $AlCl_3$ after slow hydrolysis by dissolution of aluminium metal. This is the material used to obtain Figure 3

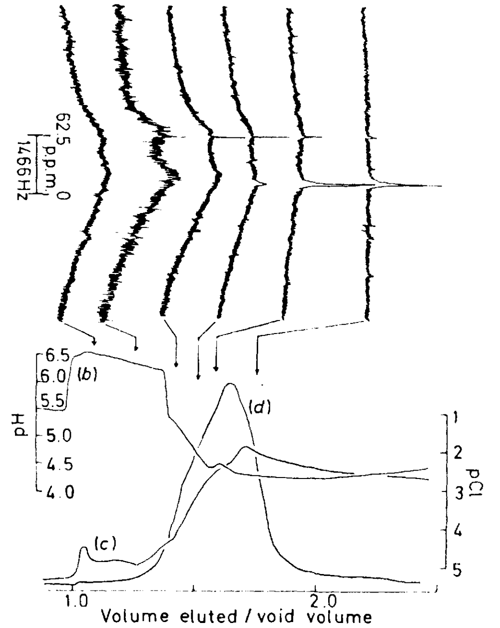

FIGURE 3 Gel-permeation chromatography of a metal-hydrolysed solution (*cf.* Figure 2). Curves (b)—(d) are as in Figure 1. The ^{27}Al n.m.r. spectra of various fractions at 27 °C are also shown and indexed to these curves

and pCl traces. From this point Al^{3+} is increasingly eluted and, since it is accompanied by the greatest concentration of Cl^-, gives a strong maximum in the conductivity peak.

DISCUSSION

The results reported here for solution 2 are in satisfactory agreement with those of Schönherr and Frey[4] although our techniques have not shown up the highly polymerised fraction as well as theirs did. This may be because they used the C10 gel which has a higher exclusion limit and so would be expected to separate the high-molecular-weight fraction more effectively from the remainder. The simultaneous use of several types of detector (Λ, pH, pCl) and ^{27}Al n.m.r. spectroscopy has however allowed us to discover much more detail. The Ferron method used by the previous workers to estimate the value of *m* for each fraction showed that there was considerable overlap of the different species in the eluant and that the conductivity trace gives only a very rough indication of the effluent composition. This perhaps should not surprise us since the sample contains small anions as well as the large cations and the former obscure the latter. The overlap of components is shown strikingly by the n.m.r. spectra. Nevertheless, relative movement of the components has been achieved sufficient to allow some general conclusions to be made about the composition of solution 2. The first material to emerge is a high-molecular-weight ionic material which has a different spectrum to the same fraction in the type 1 sample. The high pH is interpreted as indicating a high degree of hydrolysis, although there is no guarantee that this may not arise because of some interaction with the gel. The remaining unknown polymeric ions seem to be somewhat larger than Al_{13}^{7+} although by what factor is not known. The gel properties would be consistent with a factor of less than 1.5 although the overlap between Al_{13}^{7+} and Al^{3+} indicates the hazard involved in such an estimate.

There seem to be two problems relating to the use of g.p.c. in the way described here. Very little work has been published on ionic solutes and the response of the gels to such systems is unknown. The first point of concern, which is specific to the solutions studied here, is that for a system whose components are in quasi-equilibrium there is of course no guarantee that changes may not occur as the material is passing through the column, where the equilibria are disturbed by the separation of the components or because the gel catalyses a change. The absorption of material by the gel and the appearance of Al^{3+} in the type 1 run are worrying in this respect. Fortunately we have found that the equilibrium only changes after some months at room temperature and this, together with the fact that all the components in the spectrum of the input solution seem to be visible in that of the effluent, suggests that the separation reflects the composition of the input.

The second point, which is general to ionic solutions, is that each ionic component must be associated with oppositely charged ions that will be of different, often widely different, size. In the present case the small anions (Cl^-) will tend to have long retention times in the gel and so be held back behind the large cations. This will lead to charge separation which will be immediately opposed by the attractive forces between the ions. Thus ions of opposite charge and different size will tend to influence one another, the smaller slowing down the larger and *vice versa*, and this will inhibit separation. It may be that the performance of g.p.c. for ionic systems could be improved by adding, in this case, anions of greater size so that the larger ones would move more naturally with the larger cationic species. Certainly this differential size effect could explain why very similar results have been obtained in this work with a long 70-cm) column and previously with a short (20-cm) column.[4]

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