Aluminium-27 Nuclear Magnetic Resonance Investigations of Highly Alkaline Aluminate Solutions

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The high-field ^{27}Al n.m.r. spectra are reported of three solutions from which solid materials can be crystallised containing either a dimeric anion with tetrahedrally co-ordinated aluminium or anions with octahedrally co-ordinated aluminium. In two cases the principal ionic species present in solution is $[Al(OH)_4]^-$ and only in the case of a sodium aluminate solution is evidence obtained that significant concentrations of species exist in solution prior to crystallisation which may be related in composition to that of the crystalline products.

Previous work has shown that monomeric $[Al(OH)_4]^-$ anions are the dominant species present in solutions of alkaline aluminates. Only in highly concentrated solutions is there i.r. spectroscopic evidence that a small amount of a dimeric species may form.[1] The compounds which crystallise from these solutions, however, do not contain such monomeric anions. In this work we consider three examples. (A) Potassium aluminate solutions, 2.3 mol dm^{-3} in Al with $K_2O : Al_2O_3$ = 5.5 : 1, give the compound $K_2O{\cdot}Al_2O_3{\cdot}3H_2O$ at room temperature which contains dimeric $[(OH)_3AlOAl(OH)_3]^{2-}$ anions but where the aluminium is still tetrahedrally co-ordinated.[2] (B) Barium aluminate solutions, 0.1—0.4 mol dm^{-3} in Al with $BaO : Al_2O_3$ = 2 : 1, give $2BaO{\cdot}Al_2O_3{\cdot}5H_2O$ at 90 °C which contains dimeric $[Al_2(OH)_{10}]^{4-}$ with octahedrally co-ordinated aluminium,[3] which is thought also to exist in solution.[4] (C) Sodium aluminate solutions, 0.95 mol dm^{-3} in Al with $Na_2O : Al_2O_3$ = 24 : 1, give at 45 °C crystals of a highly alkaline sodium aluminate hydrate with the probable composition $[3Na_2O{\cdot}Al_2O_3{\cdot}6H_2O][4NaOH{\cdot}xH_2O]$ which solid-state ^{27}Al n.m.r. investigations show to contain octahedrally co-ordinated aluminium.[5,6] Aluminium-27 n.m.r. is known to differentiate between octahedral and tetrahedral co-ordination in hydrolysed salt solutions,[7,8] and high-field studies appear capable of differentiating very similar environments.[9,10] We have therefore extended such studies to the solutions described above with the object of trying to observe in solution species related to those which crystallise, at least immediately before or during crystallisation.

Experimental

Solutions were made up prior to examination according to the above specifications by dissolving Al wire in the corresponding hydroxide solution.[2,3,6] The resulting ^{27}Al n.m.r. spectra are shown in the Figure and were obtained at 104.2 MHz as detailed in ref. 9. The spectra were obtained under conditions where crystallisation could be expected to be imminent: room temperature for solution (A), 90 °C for (B), and 45 °C for (C).

Results and Discussion

The spectrum of solution (A) shows only the signal typical of monomeric $[Al(OH)_4]^-$ anions with a chemical shift of 80 p.p.m. from aqueous $[Al(H_2O)_6]Cl_3$, though with a broadened resonance due to the viscous nature of the solution and possibly due also to other interactions.[1] Increased temperature causes the resonance to narrow and no further resonances appear. However, even with the high chemical shift dispersion of the instrument used, it is unlikely that it would be possible to see a separate signal from the tetrahedral dimer, since the aluminium environment is very little changed. We therefore cannot rule out its existence in these solutions prior to crystallisation. Exchange between monomer and dimer forms would of course make a decision impossible at any field. The 80 p.p.m. resonance was the only one obtained for solution (B) also, and the octahedral precursors of the solid products [4] cannot be observed. For both solutions then we have to suggest that the tetrahydroxoaluminate anions are transformed into the product species at the point of crystallisation.

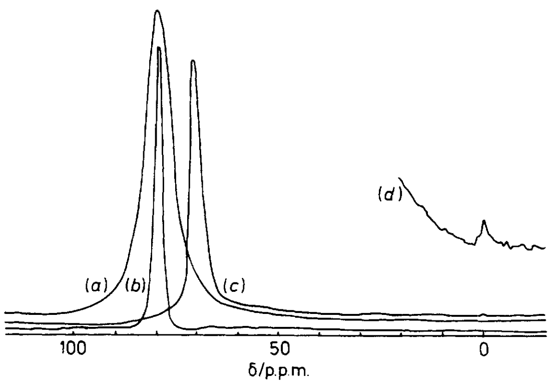

Figure. Aluminium-27 n.m.r. spectra of aluminate solutions: (*a*) potassium aluminate solution at room temperature; (*b*) barium aluminate solution at 90 °C; (*c*) sodium aluminate solution at 45 °C; (*d*) spectrum (*c*) × 16

Different results are obtained from the sodium aluminate solution (C). In this case the ^{27}Al spectrum obtained at 45 °C shows a strong signal at 70 p.p.m. with a very weak signal at 0 p.p.m. Comparison of intensities of the signals with that obtained from solution (A) shows furthermore that only one sixth of the aluminium present has been detected. Species are thus present which give rise to unobservably broad lines. We cannot know the aluminium environment but cannot exclude the presence of some proportion of octahedrally co-ordinated ions additional to that obvious from the spectrum.[5,7,9] The material giving the resonance at 0 p.p.m. is presumably in equilibrium with the non-visible species. Its position is characteristic of the hexa-aqua cation, and its breadth is indicative of a species with regular, undistorted co-ordination, so that we propose tentatively that we are observing $[Al(OH)_6]^{3-}$.

Table. Data for some tetrahedral aluminium environments

Compound	$\delta(^{27}Al)$/p.p.m.	*d*(Al–O)/pm
$[(HO)_3AlOAl(OH)_3]^{2-}$	80 [a]	176 (average) [b]
$\cdots AlO_4 \cdots$	—	175—180 [c]
Zunyite	69	179.8 [d]
$[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$	62.5 [e]	183.3 [f]
$[AlO_4W_{12}O_{36}]^{5-}$ [g]	71.7, 71.2 [h]	Similar to zunyite (?) [i]

[a] Estimated value; see text. [b] Ref. 2. [c] J. V. Smith and S. W. Bailey, *Acta Crystallogr.*, 1963, **16**, 801. [d] Refs. 11 and 14. [e] J. W. Akitt and A. Farthing, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1617. [f] G. Johannson, *Ark. Kemi.*, 1963, **20**, 305, 321. [g] The actual charge on this ion is not known, since it may be protonated. [h] Ref. 8. [i] Assumes that both have the Keggin structure.

Whatever the correct assignment may be, this is the first time that octahedrally co-ordinated aluminium has been detected experimentally in highly alkaline solution and suggests that the crystalline products form *via* solution species. The question remains as to what species the strong signal at 70 p.p.m. may be attributed. The chemical shift of $[Al(OH)_4]^-$ is always near 80 p.p.m. and is unaffected by the nature of the counter cation [*cf.* solutions (A) and (B) above] or by dilution, since the resonance still occurs at 80 p.p.m. in dilute sodium aluminate solutions of lower $Na_2O : Al_2O_3$ ratio.[1] The 70 p.p.m. signal thus cannot arise from the tetrahydroxo-anion.

The ^{27}Al chemical shifts of several AlO_4 fragments are now known and are summarised in the Table. In each case the environment is regular and the line is narrow, except for the solid-state spectrum of zunyite.[11] Broad resonances have, however, been observed at *ca.* 70 p.p.m. in certain hydrolysed solutions. Their origin is unknown but it is likely that it is some species derived from the decomposition of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.[12] One structural feature which varies with chemical shift is the length of the Al–O bond, also given in the Table. There is a clear, almost linear correlation between the two. In addition, the aluminotungstate $[AlO_4W_{12}O_{36}]^{5-}$, which has a chemical shift close to that of zunyite, has the Keggin structure which now also seems to be accepted for zunyite.[13,14] The inference is that the resonance at 70 p.p.m. is likely to arise from an AlO_4 moiety which is part of a polymeric structure with lengthened Al–O bonds.

Acknowledgements

We wish to thank the Royal Society for a study grant (to W. G.) and the S.E.R.C. for time on the Sheffield very high field n.m.r. facility.

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Received 12*th May* 1983; *Paper* 3/759