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Highly resolved ^{27}Al NMR spectra of aluminosilicate solutions

Abdolraouf Samadi-Maybodi,[a] S. Naser Azizi,[ab] Hossein Naderi-Manesh,[c]
Hamidreza Bijanzadeh,[c] Ian H. McKeag[b] and Robin K. Harris *[b]

[a] *Department of Chemistry, Faculty of Basic Sciences, Mazandaran University, PO Box 311, Babolsar, Iran*
[b] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: r.k.harris@durham.ac.uk; Fax: +44-(0)191-386-1127*
[c] *Tarbiet Modarress University, PO Box 14115-111, Tehran, Iran*

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The first highly resolved ^{27}Al NMR spectra of alkaline aluminosilicate solutions have been recorded and are discussed. The linewidths and number of resolved lines are shown to depend critically on several factors, especially the pH and Si : Al ratio. At least thirteen separate peaks or bands are observed at pH ≈ 10.35 and Si : Al = 1 : 1. A substantial range of anionic species, comparable to those found for alkaline silicate solutions, is thus shown to exist in dynamic equilibrium. Tentative assignments of some bands are presented, based on ^{27}Al and ^{29}Si shift comparability, ^{27}Al linewidths and ^{27}Al spin–lattice relaxation measurements. Relative intensities of the various ^{27}Al signals are given for the pH ≈ 10.35 solution.

Introduction

Alkaline solutions containing both silicate and aluminate ions are of considerable research interest, *inter alia* because of their involvement in the synthesis of zeolites. Silicate solutions themselves are well known to contain a range of anionic species in rapid equilibrium (so that isolation of individual species is not feasible). However, the exchange is sufficiently slow relative to the NMR timescale under most conditions that separate signals can be seen in ^{29}Si NMR spectra, and assignments to individual chemical structures obtained with the aid of enrichment in the ^{29}Si isotope. It is supposed that a similar situation exists in alkaline aluminosilicate solutions, but in this case remarkably little is known in detail about the species present, in spite of the existence of a number of publications on the topic.[1–8] The apparent reason for the sparse information is that ^{27}Al, being quadrupolar, gives relatively broad NMR resonances, obscuring small chemical shifts and any spin–spin coupling effects. Thus, ^{27}Al spectra of alkaline aluminosilicate solutions generally show a maximum of five broad bands, which have been assigned[7,8] (following some controversy)[1–6] to environments denoted as q^0, q^1, q^2, q^3 and q^4, where q refers[7,8] to four oxygen atoms bonded to Al and the superscripts indicate the number of bridges to Si (the remaining positions being occupied by OH or O^-, with no distinction between these various possibilities). This notation parallels that used (Q^n) for purely silicate species. The implicit assumption is that replacement of AlOH or AlO^- groups by AlOSi results in a substantial change of the ^{27}Al chemical shift to low frequency just as replacement of SiOH or SiO^- groups by SiOSi causes a well known decrease in ^{29}Si chemical shift. However, the former effect appears to be significantly less (*ca.* 5 ppm) than the latter (*ca.* 10 ppm). Furthermore it has explicitly or implicitly been assumed that Al–O–Al bridges are not formed (Loewenstein's rule), though this is clearly not true for, say, solid alumina or for species such as the Keggin ion.[9,10] We have shown[7,8] that in many circumstances fewer than five ^{27}Al bands are observed because of chemical exchange, and that the most labile environments are q^0 and q^1. However, most if not all of the published work has used solutions with high Si : Al molar ratios, although we have indicated[8] that lower ratios may inhibit the exchange.

The objective of the present work was to exploit the relative stability of species to exchange in order to ascertain if more detailed structural information could be obtained. As part of this work we carried out a careful study of the effect of lowering the pH, and were rewarded by the appearance of the highly resolved spectra which are the subject of this article. In order further to understand the nature of the solutions, we have measured spin–lattice relaxation times, linewidths and relative intensities of the highly resolved ^{27}Al spectrum for a pH ≈ 10.35 solution.

For practical expediency, the solutions investigated contain both sodium and tetramethylammonium counter ions, since the method of preparation was to mix aqueous tetraalkylammonium silicate solutions with aqueous sodium aluminate solutions. Further work is in progress on varying the counter ion.

Experimental

Sample preparation

Pure silica was produced by hydrolysis of silicon tetrachloride (99.8% purity; Janssen Chemical Co.) using doubly distilled water. The precipitate was filtered off and washed many times with doubly distilled water to remove all acid. It was then dried at *ca.* 105 °C for 48 hours. Aqueous silicate solutions were prepared in a plastic bottle by dissolving an appropriate quantity of silica in doubly distilled water containing *ca.* 15% v/v of D_2O (Aldrich Chemical Co.) to provide a field/frequency lock for the NMR and made alkaline by the addition of tetramethylammonium hydroxide, TMAOH (97% purity; Aldrich Chemical Co.). The dissolution of the silica was very slow at room temperature, so it was assisted by heating the samples in an oven at *ca.* 70 °C until the solutions became clear. Plastic bottles were employed so as to avoid contamination by paramagnetic ions, which can arise from leaching of glass containers at high pH. The initial TMA silicate solution prepared in this way contained 0.7 molar SiO_2 and 1.4 molar amine hydroxide. Aqueous sodium aluminate solution was prepared by dissolving $NaAlO_2$ (Fisons plc) in doubly distilled water. An aluminosilicate solution was then obtained by mixing the freshly prepared

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sodium aluminate and TMA silicate solutions in the correct proportions for our investigations (see below). The molarities of SiO_2, AlO_2^- and Na^+ in the solutions are equal, with TMA^+ at twice this concentration.

Solutions with lowered pH were prepared by adding concentrated HCl solution dropwise down to pH 11.8, then with addition of 1 M HCl solution to reach lower pH values. The quantities used were such that there is only a small change in the concentrations of Si, Al, TMA and Na (estimated to be a decrease of *ca.* 1% between pH 12.78 and 10.35). Measurement of pH was carried out using a PHM92 LAB PHMETER (Radiometer, Copenhagen) and a PHC 2015 combined pH electrode, suitable for pH readings from 0 to 14. In fact the pH values reported are those measured within 5 minutes of sample preparation. Below pH ≈ 10.5, when significant coagulation may be occurring as a function of time,[3,11–13] with turbidity and even precipitation being seen, the pH will clearly change as the samples age. At very low pH (<4) the solutions again become clear to the eye, although the silica content is in excess of the solubility.[14]

Aluminium-27 NMR spectra at variable pH were obtained using a Varian Inova 500 spectrometer at 130.23 MHz and *ca.* 22 °C. Proton decoupling was employed, though this was not strictly necessary. Typically, 90° pulses of duration 10.7 μs were used, with acquisition times of 180 ms and recycle delays of 20 ms for the variable pH experiments. The probe used for these experiments involved components containing aluminium, so that a broad background signal centred at $\delta_{Al} \approx 60$ (the same region as the q^4 peak) could be observed. Several ways of compensating for this signal were tried. Eventually, backward linear prediction for the first 12 points of the FID (free induction decay) was used. Whereas this gave spectra of good apparent quality, making many aspects of interpretation easier, it did result in uncertainties regarding the extent of the true q^4 signal from the aluminosilicate solution. Moreover, phasing the spectra was not easy because the background signal invariably had a different phase from those of the peaks arising from the solutions. There are further complications affecting the q^4 region because of the presence in the sample (in increasing quantities as the pH is lowered to neutral values, but to unknown extents) of condensed particles, in extreme cases giving rise to gels or even precipitates. Such particles presumably give very broad signals which are difficult or impossible to detect in high-resolution spectra, giving rise to the phenomenon of "invisible aluminium". The signals actually observed at pH values in the range 9–5 represent only a very small fraction of the aluminium content of the samples.

Spin–lattice relaxation times for the pH 10.35 solution were measured by the inversion–recovery method, using a total of 11 delays for relaxation. However, because the q^0 peak dominates the spectrum (and has the longest relaxation time), it was not feasible to use the full number of points for most peaks. Moreover, peak overlap and signal-to-noise considerations, together with the requirement to compensate for the probe background, make determination of T_1 problematic. Three approaches were used: (a) baseline estimation by eye, followed by peak height measurements, (b) baseline estimation by eye, followed by measurement of both peak height and peak width, the product being used as a crude measure of total intensity, and (c) use of the standard software associated with the spectrometer. The values of T_1 reported here are best estimates from a combination of the three methods, mediated in some cases by observation of the times required to null signals.

The deconvolution of a spectrum for pH 10.35 acquired over a long period (*ca.* 15 hours and plotted with no line broadening) was undertaken in four sections (76.7–72.7, 72.8–68.5 and 68.8–62.0, plus the q^0 peak separately), with normalisation of intensities to a common scale. Deconvolution proceeded by initial choice of observed frequencies for 3, 4 and 5 peaks in the three complex sections respectively.

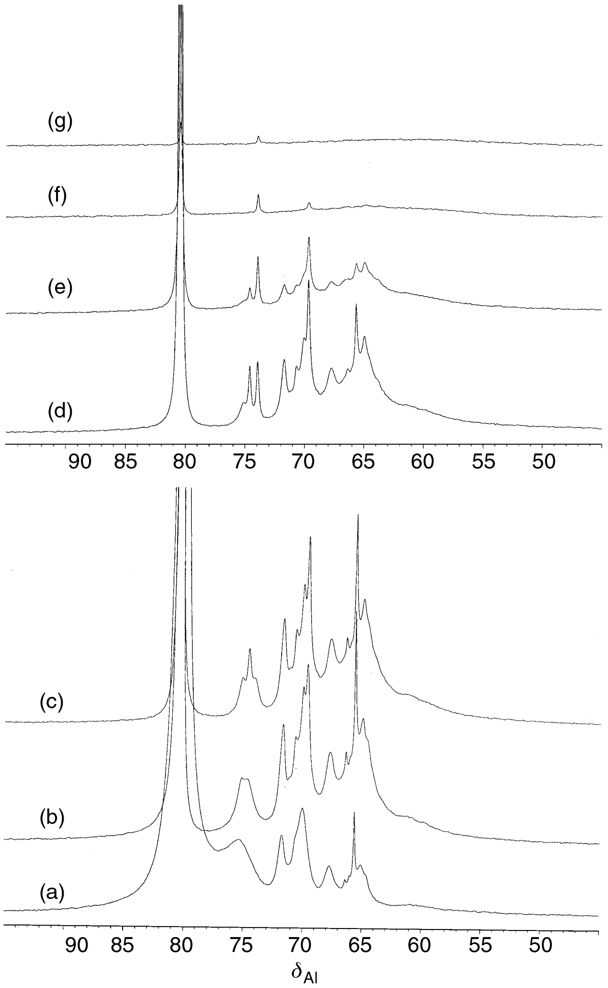


Fig. 1 Aluminium-27 NMR spectra at 130.23 MHz and ambient probe temperature of an aluminosilicate solution (see the text) as a function of pH: (a) pH 12.78, (b) 11.80, (c) 10.88, (d) 9.9, (e) 9.5, (f) 8.9, (g) 8.15.

The ^{27}Al chemical shifts are quoted with respect to the signal for 1 M aqueous $AlCl_3$ (implying the $Al(H_2O)_6^{3+}$ ion), and were obtained by the replacement technique, with D_2O field/frequency locking. It did not prove feasible to record ^{29}Si spectra at natural isotopic abundance of the solutions because of the low concentrations and the low natural abundance of ^{29}Si. However, a few spectra were obtained with samples enriched in ^{29}Si, the Varian Inova 500 spectrometer again being used (at a ^{29}Si frequency of 99.29 MHz). These samples were prepared using silica enriched to 99.35%, obtained from Cambridge Isotope Laboratories, Inc.

Results and discussion

A typical ^{27}Al spectrum of an as-prepared solution with Si : Al ratio of 1 : 1 is shown in Fig. 1(a). The solution contains total silicon and aluminium concentrations equivalent to 0.028 M, with a TMAOH concentration of 0.056 M. The sodium content equals that of Al. The pH was measured as 12.78. The spectrum is not dissimilar to that illustrated in Fig. 2 of ref. 8, except that it has been cosmetically improved (*e.g.* by backward linear prediction). Several features are immediately apparent: (1) The majority of the Al gives rise to the peak at a chemical shift δ_{Al} 80.3, which may confidently be assigned to the isolated aluminate species $[Al(OH)_4]^-$ (I) or one of its more highly ionised forms, *i.e.* to q^0. (2) The peak at δ_{Al} 75.4, assigned to "end-groups" (q^1), is relatively broad, which we attribute to incipient exchange with q^0 (see ref. 8). The exchange effect has been confirmed by a spectrum run at lowered temperature

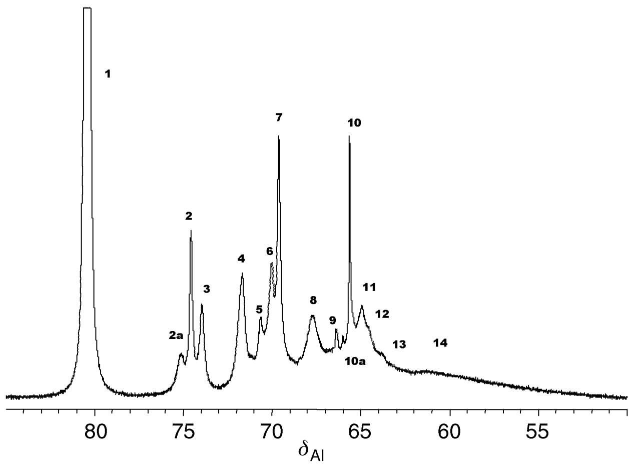


Fig. 2 Aluminium-27 NMR spectra of an aluminosilicate solution (as in Fig. 1) at pH 10.35, accumulated over 14.8 hours. The peak numbers used in the text are marked.

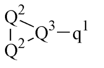
(*ca.* 0 °C), which showed no such broadening. (3) There are a number of peaks at lower frequency, which cannot simply be related to q^2, q^3 and q^4 in the manner assumed for solutions with higher Si : Al ratios (see below). Signals at δ_{Al} 71.7 and 67.7 occur between the values expected for q^1 and q^2 and q^2 and q^3 respectively. (4) Moreover, there is a surprisingly sharp signal at δ_{Al} 65.6. In fact this can be seen in Fig. 2 of ref. 8, but was not commented on at the time.

Fig. 1(b)–1(e) show what happens to the spectra as the pH is lowered. The first effect is that the q^0 and q^1 peaks become sharper, and the latter splits into two and then into three. We attribute this change to slowing of chemical exchange in the system, thus further confirming the origin of some line broadening at pH 12.78, as well as to a redistribution among the species present. At the same time further peaks appear in the lower frequency range, perhaps partly because of the slowing of exchange, but also arising from variations in the range and intensity of species present. The optimum resolution and number of peaks are observed at a pH of approximately 10.3. In fact, in addition to the intense q^0 peak and a broad signal at δ_{Al} *ca.* 60 (attributed to various q^4 environments, possibly including some coagulated material, but difficult to distinguish from the probe background), at least 12 peaks can clearly be seen. For the purposes of discussion, the peak numbers shown on Fig. 2 for a pH 10.35 solution will be used. This is the first time such high-resolution ^{27}Al spectra have been published in detail for aluminosilicate solutions. The three q^1 peaks change their relative intensities as the pH is lowered further. Moreover the total intensity in the spectrum decreases markedly as the pH is lowered below 9.5. It is obvious that the spectrum is not properly reflecting the presence of larger oligomers, condensed species and even insoluble material. At pH ≈ 8.6 only three relatively sharp signals can be seen (in the q^0, q^1 and q^2 regions), plus a broad intense band centred at δ_{Al} *ca.* 64. Presumably this is because the majority of the aluminium is in relatively large particles; the sample is very turbid. In view of this fact and because of the backward linear prediction which was applied, quantitative conclusions regarding q^4 species cannot be made for any of the spectra. As the pH is lowered still further the three sharp peaks decrease in intensity. The q^2 peak is not observed below pH ≈ 8.4 and the other two signals are lost below pH ≈ 7.4, only the broad band at $\delta_{Al} \approx 57$ remaining. Aluminosilicate hydrosol precipitates give rise[12] to a broad ^{27}Al band under magic-angle spinning conditions at slightly lower chemical shifts (δ_{Al} 53.0), but the additional shielding may arise from second-order quadrupolar effects. Of course, the existence of q^4 sites implies the presence of cations (or hydrogen) in the structure. At pH ≈ 5 a signal appears at $\delta_{Al} \approx 1$, which sharpens and strengthens as the pH is lowered further. This may confidently be assigned to the $[Al(H_2O)_6]^{3+}$ species, resulting from the amphoteric nature of aluminium oxide. At this pH silica is almost insoluble (≈150 ppm), and it may be assumed that the medium contains relatively large particles of silica, though it is clear to the eye. In the alkaline range, as the pH is reduced from 12.78, the solutions remain clear to the eye only down to pH *ca.* 10.4 whereas light-scattering measurements indicate some condensation. The sample chosen for further detailed study, at pH 10.35, was on the verge of showing turbidity.

Assignment of the peaks in the spectra is difficult, in spite of the high natural abundance of ^{27}Al since no coupling information is available. Hydroxyl protons on aluminosilicate species are in rapid exchange with water and it is not feasible to observe splittings arising from ^{29}Si, ^{27}Al coupling, both because of the low natural abundance of ^{29}Si and (more particularly, since ^{29}Si could be isotopically enriched) because the ^{27}Al linewidths would obscure the relatively small splittings expected. We have examined ^{29}Si spectra for aluminosilicate solutions, but even for higher concentrations and Si : Al ratios we have been unable to observe peaks which could confidently be assigned to aluminosilicate species, presumably because these are in relatively low concentration and the resonances would be broadened[5] by the influence of neighbouring ^{27}Al. For the present solution conditions we were unable to detect any ^{29}Si signals at all for samples with ^{29}Si in natural abundance (see also refs. 15 and 16). However, a ^{29}Si spectrum was obtained for a 0.028 M silicate solution with Si : TMAOH = 1 : 2 and isotopic enrichment of ^{29}Si to 99.35%. The pH was *ca.* 12.8. Three sharp peaks corresponding[17] to species Q^0, Q_2^1 (the "dimer") and Q_3^2 (the "cyclic trimer") were observed, with decreasing intensity in that order, confirming earlier work. The Q_3^2 signal disappeared when the pH was lowered to ≈10.4. When sodium aluminate was added the Q^0 and Q_2^1 signals broadened substantially ($\Delta\nu_{\frac{1}{2}}$ for Q^0 becoming *ca.* 0.8 ppm), so that the signal-to-noise ratio after 10 h accumulation was only *ca.* 2 : 1 for the latter. No new signals were seen. Finally, ^{27}Al,^{27}Al coupling is unlikely to be observable, both because of the linewidths in the spectra and because the coupling constants are probably small. It is expected that Loewenstein's rule will be obeyed, so that no Al–O–Al bridges will be present. Certainly pure aqueous sodium aluminate solutions show ^{27}Al spectra indicating that nothing other than simple mononuclear anions $(Al(OH)_4^-$ or its deprotonated forms at high pH and $[Al(H_2O)_6]^{3+}$ at low pH) is present at any pH. However, the existence of species with Al–O–Al bridges cannot be ruled out. Under certain conditions polymeric aluminate species exist as gels, but the broad ^{27}Al signal in the region for four-co-ordinate environments is[9,10] at δ_{Al} *ca.* 71 (a substantially higher chemical shift than that of our "q^4" band), although the sharp central tetrahedral signal for the Keggin ions is[9] at δ_{Al} 62.6.

Some hints for assignments can come by analogy with ^{29}Si spectra of aqueous alkaline silicate solutions, which have been studied under a variety of conditions (including ^{29}Si enrichment). Indeed, this link has already been assumed in the literature starting with the original article by Mueller *et al.*[1] in designating broad bands as arising from q^0, q^1, q^2, q^3 and q^4 environments. In the case of ^{29}Si spectra, signals at unusual positions, between either the ranges for Q^1 and Q^2 signals or the regions for Q^2 and Q^3, may arise from two causes:[17] (a) the existence of "three-membered" $(SiO)_3$ rings, a decrease in the SiOSi or OSiO bond angles producing a well attested shift to high frequency, or (b) the presence of unusual specific cage structures, also giving rise to deshielding, but to a smaller extent than (a). Whereas the positions of peaks 4 (δ_{Al} 71.7) and 8 (δ_{Al} 67.7) in our ^{27}Al spectra would appear to be more in tune with (b) than (a), the intensities seem rather high for this origin, and we believe, for other reasons as well (see below), that these signals probably arise from q^2 and q^3 sites in species with "three-membered" rings.

The three signals in the q^1 range are almost certainly due to individual species. The relative intensities of the peaks at δ 74.6 and 74.0 change with pH, the former being the larger at pH ≥ 10.1 but the latter being the more important below this range. At pH < 9.0 only the line at δ 74.0 can be observed. One of these peaks presumably arises from q^1Q^1 (II), and the most likely assignment (by comparison with the corresponding ^{29}Si case) is that it is the one remaining at relatively low pH, *i.e.* δ_{Al} 74.0. The other probably arises from the linear trimer $q^1Q^2Q^1$ (III). As some confirmation of this possible assignment it may be noted that in ^{29}Si spectra for the corresponding purely silicate species the Q^1 peak for the linear trimer occurs[17] 0.44 ppm to high frequency of that for the dimer in aqueous KOH solution. However, it is not clear why linear trimeric aluminosilicate ions should be more abundant than dimers at pH ≈ 11. An alternative assignment for the peak at δ_{Al} 74.6 is to the substituted cyclic trimer IV, since the corresponding pure silicate species in aqueous KOH solution resonates 0.55 ppm to high frequency[17] of the dimer and this species might also account for the signals at δ_{Al} 71.7 and 67.7, which diminish along with the δ_{Al} 74.6 peak as the pH decreases. However, a high abundance for such a species is unexpected, and it seems more likely that it gives rise to the weak signal at δ_{Al} 75.1 at pH 10.35. One puzzle remains from this discussion, namely the assignment of the q^2 signal at δ_{Al} 69.6 at pH ≈ 9.0, which might be thought to be from the linear trimer but for the fact that the corresponding q^1 signal is scarcely present at so low a pH. Of course, it is possible (though unlikely) that the intrinsic probability of replacing Si by Al is greater for Q^2 than for Q^1 in the linear trimer in spite of the statistical factor of 2 : 1 in favour of Q^1 replacement.



IV

Some peaks are significantly sharper than others (see Table 1), which presumably indicates either that the broader signals are composites or that the electric field gradient at aluminium is significantly smaller for some environments (giving rise to the sharp peaks) than for others. Particularly mobile species may also have higher transverse relaxation times and therefore give sharper peaks. At the higher values of pH it is difficult to disentangle true peak widths from the effects of chemical exchange, but the signal at δ 65.6 always remains relatively sharp. This matter is explored in more detail below. Owing to both its position and the known stabilising effect of tetraalkylammonium ions on cage silicate species,[18] it is tempting to assign this signal to the substituted cubic octamer (V). Moreover, the corresponding purely silicate species has[19] a relatively long T_1 (^{29}Si), which might correlate with the narrow ^{27}Al linewidth for the δ 65.6 peak. A similar species involving germanium has been reported,[20] and even cubic octamers doubly substituted by germanium.[21] Indeed, Engelhardt and co-workers have obtained both trimethylsilylation[22] and ^{29}Si NMR[23] evidence for the existence of V and of cubic octamers multiply substituted by Al in crystalline tetramethylammonium aluminosilicates. They conclude that Loewenstein's rule is generally obeyed, and they speculated about linkages involving Si–O–Al bridges between the cubic octamers to create polymeric structures. However, any assignment of the relatively sharp peak 7 (δ_{Al} 69.6) to the prismatic hexamer would be contradictory to the suggestion above that peaks 4 and 8 arise from three-membered rings.

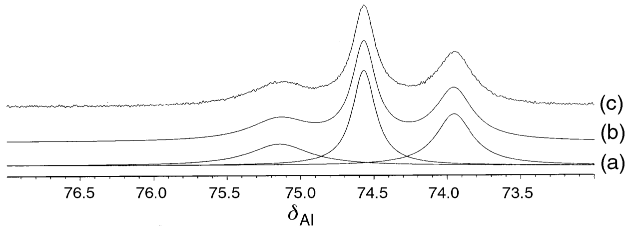


Fig. 3 Fitting by deconvolution of the three q^1 peaks observed at pH 10.35: (a) individual simulated peaks, (b) total simulated spectrum, (c) observed spectrum.

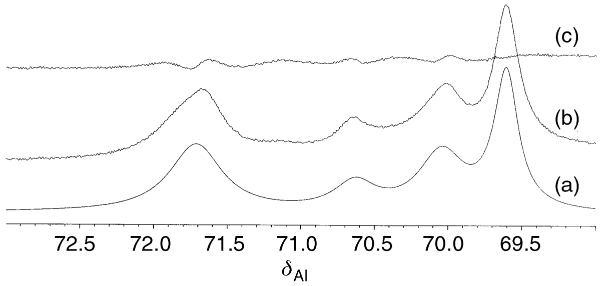
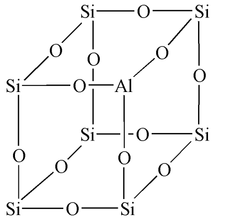


Fig. 4 Fitting of the q^2 region by deconvolution into four lines: (a) simulated spectrum, (b) experimental spectrum, (c) difference spectrum.



V

(exocyclic O^- or OH omitted)

A high-quality spectrum of a pH 10.35 solution, obtained by accumulation over 14.8 hours and plotted with no line broadening, was fitted by deconvolution to 13 lines. The quality of the fitting in the q^1 and q^2 regions is shown in Figs. 3 and 4. The intensities, normalised to that of the q^0 peak, the linewidths at half-height ($\Delta\nu_{\frac{1}{2}}$) and the implied value of the transverse relaxation times ($T_2 = 1/\pi\Delta\nu_{\frac{1}{2}}$) are given in Table 1. The background signal complicated this process, resulting in an obviously incorrect result for peak number 11. Indeed, the accuracy of the procedure is best at the high-frequency end of the spectrum. Integration of the spectrum is problematic in the low-frequency region, but better above δ_{Al} 73, showing that the total intensity of the three q^1 peaks is 6.6% of that of q^0, whilst deconvolution gives a value of 6.3%. The two independent measurements are thus in good agreement (especially since the background contributes a small amount to the q^1 intensities). The difference between the experimental spectrum and the one simulated by deconvolution shows clearly that peak 4 is asymmetric (see Fig. 4), and therefore consists of signals from at least two environments. Moreover, deconvolution reveals that there are additional (but unquantifiable) signals at least at the following positions: δ 71.2, 68.4, 64.5 and 63.7. We have designated the last two as peaks 12 and 13.

In order to obtain more information about the species present in aluminosilicate solutions, we have measured ^{27}Al spin–lattice relaxation times for the solution at pH 10.35, and the results are reported in Table 1. It can be seen that the values vary significantly for the different peaks, suggesting that either electric field gradients or mobility depend strongly on the species and site in question. The results may be compared with data on linewidths, $\Delta\nu_{\frac{1}{2}}$, also reported in Table 1. In the extreme narrowing approximation, with the quadrupolar interaction providing the dominant relaxation mechanism, values of T_2 ($=1/\pi\Delta\nu_{\frac{1}{2}}$) should equal T_1. The data in Table 1 show that in general T_1 and T_2 vary in parallel, with T_2 usually a little shorter than T_1. Of course, there are factors which affect $\Delta\nu_{\frac{1}{2}}$ other than the true T_2, so the latter situation is not unexpected. However, the parallelism of T_1 and T_2 suggests that a dispersion of chemical shifts does not give a strong contribution to line broadening

Table 1 Aluminium-27 NMR data for the aluminosilicate solution at pH 10.35 and ambient probe temperature

Peak no.	δ_{Al}	$\Delta\delta_{Al}$[a]/ppm	Intensity (%)[b]	$\Delta\nu_{1/2}$/Hz	T_2/ms	T_1[c]/ms
1	80.4	0	100.0	7	46	52
2a	75.1	−5.2	1.5	64	5	[d]
2	74.6	−5.8	2.6	25	13	22
3	74.0	−6.5	2.2	39	8	23
4	71.7	−8.7	4.2	56	6	8
5	70.6	−9.8	1.3	45	7	11
6	70.0	−10.4	2.9	47	7	9
7	69.6	−10.8	4.0	26	12	13
8	67.7	−12.9	3.5	97	3	2
9	66.4	−14.0	0.7	42	7	24
10a	66.0	−14.4	0.1	11	29	[d]
10	65.6	−14.8	1.5	11	29	36
11	65.0	−15.6	[d]	[d]	[d]	7
14[e]	*ca.* 60	*ca.* −20	[d]	[d]	[d]	[d]

[a] Separation from the q^0 peak. [b] By deconvolution; relative to the q^0 signal. [c] A considered average of the three methods mentioned in the Experimental section. [d] Not measured. [e] Difficult to distinguish from probe background.

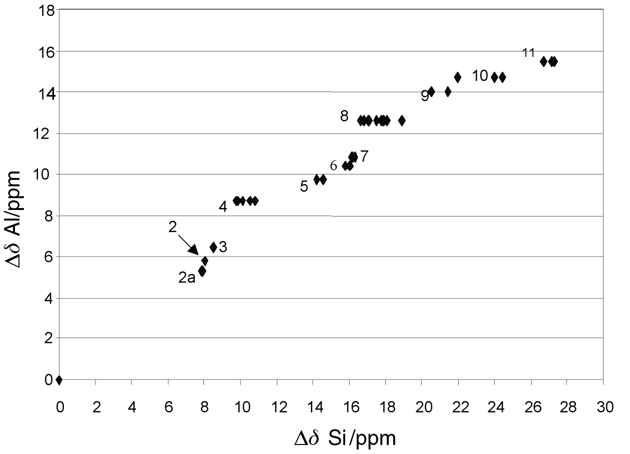


Fig. 5 Attempted correlation of ^{27}Al chemical shifts for alkaline aluminosilicate solutions with ^{29}Si chemical shifts for alkaline silicate solutions (relative to the signals for q^0 and Q^0 respectively). The ^{27}Al peak numbers, as given in Fig. 1 and Table 1, are indicated.

in many, if not most, cases. On the other hand, as noted above, the shape of signal 4 indicates that it consists of at least two peaks, in spite of the fact that the measured values of T_2 and T_1 do not differ very greatly. In fact, the largest deviations between T_1 and T_2 occur for peaks 3 and 9, which is particularly surprising in the former case. Of course peak 1 is assignable to a single type of site (q^0). This peak is by far the most intense and it is isolated from the rest of the spectrum, so the value of T_1, which is significantly higher than for any other signal, is accurate (within a few %). It arises from the smallest species, so the mobility is presumably the greatest of any aluminosilicate anion, which explains why it has the longest T_1. Moreover, when ionisation questions are ignored, q^0 should have a low electric field gradient because of symmetry, thus again leading to a relatively long T_1. It is not obvious why any other aluminium sites should have low electric field gradients or high mobility. The only species which might automatically fill these conditions is $q^4Q^1_4$, but this is not expected to appear in significant amounts, since the corresponding $Q_4Q^1_4$ is not normally seen in analogous silicate solutions.[24] The relatively sharp signal 10 at δ_{Al} 65.6 is therefore difficult to explain except by an "accidentally" small electric field gradient (*i.e.* electrical symmetry but not true structural symmetry around Al). Our best estimate is that this peak may arise from the cubic octamer V, as discussed above, the overall shape of this species perhaps giving it an enhanced mobility.

With all these considerations in mind, we have attempted to explore parallels between ^{27}Al and ^{29}Si shifts in corresponding aluminosilicate and silicate species. Fig. 5 shows the result. Of course, the ^{27}Al assignments are generally speculative. In some cases (for instance the Q^2 signals linked to ^{27}Al peaks 6 and 7) divisions are arbitrary. However, a general correlation can be observed. This suggests that the weak peaks 5 and 9 may perhaps arise from q^2 and q^3 sites in the unusual cage structures.[17] If the correlation is correct, the effect of incorporation into "three-membered" rings is significantly smaller for ^{27}Al than for ^{29}Si, giving rise to peaks 4 and 8 for the former. However, Fig. 5 deviates from our earlier discussion in suggesting the "cubic octamer" ^{27}Al signal corresponds to peak 11 rather than the sharp peak 10. If Loewenstein's rule is violated for any of the species, then further structural assignment possibilities arise.

Conclusion

We have shown that it is possible to obtain high-resolution ^{27}Al spectra of alkaline aluminosilicate solutions and that they contain at least 13 separate aluminium sites, corresponding to a range of anionic aluminium-containing species. Concentrations, and even relative intensities, vary significantly with the pH. Linewidths and spin–lattice relaxation times have been determined, and they also show a wide variation. Assignments of peaks to chemical structure are highly problematic in most cases, but some informed suggestions are made.

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