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Aluminium-27 NMR Investigation of the 2-Hydroxyethyl(trimethyl)ammonium Aluminosilicate Solution

Abdolraouf Samadi-Maybodi,*[1] **Nasser Goudarzi,**[1] **and Hossein Naderi-Manesh**[2]

[1]Department of Chemistry, Faculty of Basic Sciences, Mazandaran University,
P. O. Box 47416-1467, Babolsar, Iran

[2]Tarbiet Modarress University, P. O. Box 14115-111, Tehran, Iran

Received August 4, 2005; E-mail: samadi@umz.ac.ir

Alkaline solutions containing both silicate and aluminate ions are of considerable research interest *inter alia* because of their involvement in the synthesis of zeolites. ^{27}Al NMR spectra of alkaline aluminosilicate solutions generally show a maximum of five broad bands. In the present work, we use ^{27}Al NMR to characterize aluminosilicate solutions with different Al/Si ratios using 2-hydroxyethyl(trimethyl)ammonium as a cation template, no alkaline metals are used for preparation of aluminosilicate solutions. To understand the reaction between silicate and aluminate ions in this system, the evolutions of ^{27}Al NMR spectra with time are investigated.

It is proposed that nucleation for zeolite formation and crystal growth occurs through the co-polymerization of aluminate and silicate ions in a solution mixture. The question of whether dissolved aluminosilicate species are involved as precursors in the hydrothermal formation of natural or synthetic zeolites has been investigated by a number of authors for some years.[1–5] In principle, NMR spectroscopy is uniquely capable of detecting and characterizing aluminium and silicon containing species in aqueous solution. Accordingly, a number of investigations have been carried out to address the structure of ions present in silicate[6–13] and aluminosilicate solutions.[14–19]

Kinrade and Swaddle[15] identified ^{29}Si NMR peaks due to low molecular weight aluminosilicate anions of sodium aluminate solutions by ^{29}Si NMR spectroscopy. Using similar methods, Mortlock et al.[14,18] investigated tetrapropylammonium (TPA) aluminosilicate solutions. They also reported the correlation between the partial charge on Si atoms and chemical shift was used to confirm the assignment of ^{29}Si NMR peaks due to cage species containing double-rings, such as prismatic hexamer and cubic octamer, with some replacement by aluminium.[19] Recently, Samadi-Maybodi and co-workers,[20] investigated aqueous and methanolic TMA aluminosilicate solutions by ^{27}Al NMR spectroscopy.

Evidence of dissolved aluminosilicate anions has come from both ^{29}Si and ^{27}Al NMR spectroscopies.[21–27] The notation Q^n for silicate solutions, where n refers to the number of siloxane bridges, is well established.[6–13] In the case of individual aluminium sites in aluminosilicates anions, there is a special notation that is similar. An aluminium site is presented as "q" with the number of oxygen bridges to silicon indicated by a superscript. Thus, if aluminium has no silioxane bridges, as for the aluminate anion AlO_4^{5-} (or its protonated congeners up to $Al(OH)^-$), it is represented as q^0, where q^1, q^2, q^3, and q^4 indicate Al(1OSi), Al(2OSi), Al(3OSi), and Al(4OSi), respectively. It is generally assumed that Loewenstein's[28] rule is obeyed, i.e., there are no Al–O–Al bridges.

Muller et al.[26] assigned chemical shifts (from the signal for $Al[H_2O]_6^{3+}$) of 79.5, 74.3, 68.5, and 64.2 ppm to q^0, q^1, q^2, and q^3, respectively, using TMA aluminosilicate solutions. Dent Glasser and Harvey,[17,27] using potassium aluminosilicate solutions, found several bonds in the ^{27}Al NMR spectra lying at shifts of 80, 70–72, 66, 61, and 58 ppm and assigned them to q^0, q^1, q^2, q^3, and q^4, respectively.

In the present work, we have used ^{27}Al NMR to characterize aluminosilicate solutions with different Al/Si mole ratios using 2-hydroxyethyl(trimethyl)ammonium as a template. No alkaline metals such as sodium or potassium were used for the preparation of silicate or aluminate solutions. For more understanding of the reaction between aluminate and silicate ions, the evolution of ^{27}Al NMR spectra with time was also investigated.

Experimental

2-Hydroxyethyl(trimethyl)ammonium (2-HETMA), was used as a template. 2-Hydroxyethyl(trimethyl)ammonium chloride was converted to hydroxide by dissolving it in a minimum of water and passing it down a column of Aldrich amberlite resin IRA-400(OH). Elution with double distilled water was carried out until the solution was at pH 7. The water was then removed under reduced pressure.

A clear solution with a molar ratio of 2-HETMA:SiO_2 of 1:1 was prepared in a polyethylene bottle from 2-HETMA hydroxide, silica (made by the hydrolysis of $SiCl_4$), and double distilled water. Dissolution of silica required ca. one week at a temperature of 70 °C, yielding a clear solution. Aluminate solutions were made by dissolving a suitable amount of aluminium powder in 0.6 molar of 2-HETMAOH solutions. The concentration aluminate ion in solution was 0.1 molar.

Fresh aluminate solution was added to the silicate solution at ambient temperature (ca. 25 °C) to achieve the desired Si/Al molar ratios. After mixing, the solutions were allowed to equilibrate for one week at room temperature. All solutions contained ca. %5 v/v D_2O (Aldrich chemical company) to provide field/

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frequency lock for the NMR spectroscopy.

Spectra were measured using a Bruker AMX 500 spectrometer, operating at 130.3 MHz for ^{27}Al NMR. Aluminium-27 NMR spectra were obtained by applying 90° pulses (14 µs pulse duration), a recycle delay of 0.2 s was sufficient to allow a complete return of the magnetization to equilibrium.

The ^{27}Al chemical shifts were measured by substitution with a 1.0 molar aqueous sample of $AlCl_3$ and are thus considered to be referenced with respect to the octahedral $[Al(H_2O)_6]^{3+}$ cation. All solutions were clear to the eye at the time of recording the spectra (i.e. no gel had been formed).

Results and Discussion

The Effect of Al/Si Mole Ratio on 2-HETMA Aluminosilicate Solution. To investigate the effect of the Al/Si molar ratio on the distribution of aluminosilicate species, a series of aluminosilicate solutions with Al/Si mole ratios of 1.0, 5.0, 8.0, 10.0, and 12.0 were prepared by mixing aqueous 2-HETMA aluminate and aqueous 2-HETMA silicate solutions with a constant silicon concentration (0.15 M Si for all of solutions), with various aluminium concentrations; no alkaline metals such Na or K were used in these solutions. Data related to chemical composition for this experiment are listed in Table 1 and the corresponding ^{27}Al NMR spectra of the solutions are shown in Figs. 1a–1e. All solutions were allowed to reach steady state for one week before spectra were obtained.

It was reported[29,30] that aluminosilicate solutions with high concentrations of Si show improved signal-to-noise ratios as the mole percent of Al increases, but the features of the spectra do not change substantially. However, results obtained from our work indicate that with low concentrations of Si and high Al/Si mole ratios, the mole percent of Al increases as the intensity of some species such as q^0 and q^1 are increased, but some of them, like q^3, decrease; it should be mentioned that the pH of the solutions were the same (i.e. ca. pH = 13).

Table 1. Data Composition of 2-HETMA Aluminosilicate Solutions with the Constant Silicate Concentration (0.15 M)

Al/Si mole ratio	C_{Al}/M
1.0	0.15
5.0	0.75
8.0	1.20
10.0	1.50
12.0	1.80

Figure 1a illustrates the ^{27}Al NMR for an aluminosilicate solution with an Al/Si molar ratio of 1. The spectrum shows four separated bands located at chemical shifts of ca. 80, 75.3, 70.1, and 65.1 ppm, which are associated with q^0, q^1, q^2, and q^3, respectively. The ^{27}Al NMR peak assignments of 2-HETMA aluminosilicate solution species are based on the assignment of similar peaks that appear in TMA aluminosilicate by Muller et al.[26]

The following assignment for the ^{27}Al NMR spectrum of Fig. 1a, has been tentatively suggested in this work: The peak at the chemical shift of 65.1 ppm is possibly due to the $Q^3{}_8$ (1Al) octameric species and signal at ca. 70.1 ppm might be assigned to the $Q^3{}_6$ (1Al), prismatic species. However, it should be noted that some other aluminosilicates species which are created through replacing Si with Al in the related prismatic and cubic octamer silicate species can be present in these

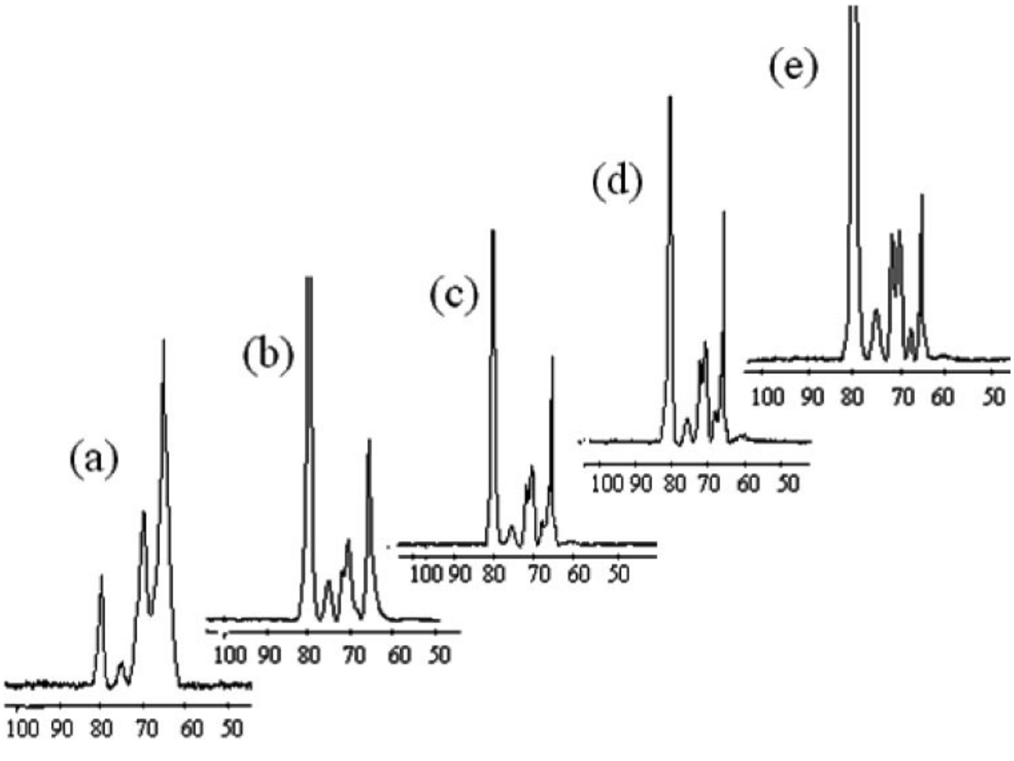
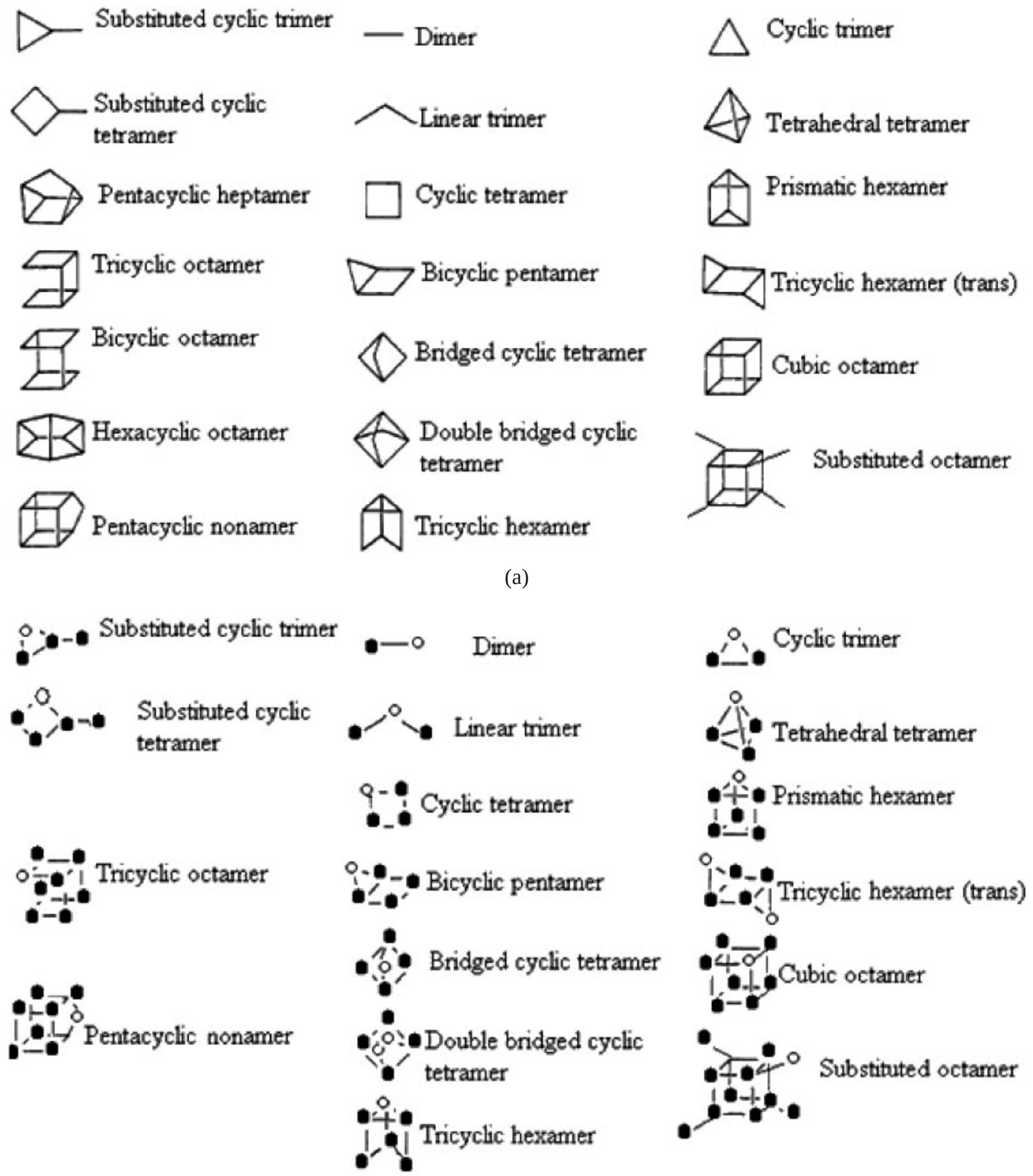


Fig. 1. ^{27}Al NMR spectra at 130.32 MHz of 2-HETMA aluminosilicate solutions with different Al/Si mole ratio, (a) Al/Si = 1, (b) Al/Si = 5, (c) Al/Si = 8, (d) Al/Si = 10, and (e) Al/Si = 12, and 0.15 molar silica concentration at 22 °C. Spectral width, 15576.3 Hz; acquisition time, 0.1 s; recycle delay, 0.20 s; pulse angle, 90° (14 µs); number of repetitions, 2048.



(a)

(b)

Fig. 2. Some proposed structures of silicate (a) and aluminosilicate (b) species.

regions. Figures 2a and 2b illustrate some proposed structures of silicate and aluminosilicate species, respectively. The peaks located at ca. 80 and 75 ppm assigned to the q^0 and q^1, respectively.

Figures 1b–1e reveal that by increasing the Al/Si mole ratio some new peaks can be observed from the corresponding spectra. Figure 1b shows the ^{27}Al NMR spectrum for an aluminosilicate solution with an Al/Si mole ratio of 5. The band located at the chemical shift of 68–73 ppm is well resolved in two peaks at $\delta_{Al} = 70.2$ and $\delta_{Al} = 71.7$ ppm are that associated to the aluminium with two siloxane bridges (i.e. q^2). The band positioned at ca. 63–68 ppm is resolved to at least four peaks at the chemical shifts of 64.4, 65.3, 65.9, and 66.1 ppm, where all peaks belong to aluminium with q^3 site. Figure 3 illustrates the horizontal expansion of the band in this region.

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. Thus, it is not easy to say exactly which kind of aluminosilicate species belongs to the observing signal. Nevertheless 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).[6–9] As a result, on the basis of shielding arguments and referring to the previous reports, we tentatively assigned the peaks at $\delta_{Al} = 70.2$ and $\delta_{Al} = 71.7$ ppm to cyclic tetramer (I) and doubly bridged cyclic tetramer (II), respectively (see

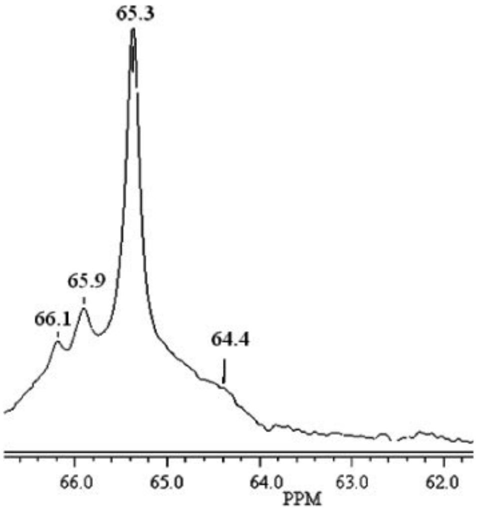


Fig. 3. The horizontal expansion of aluminium-27 NMR spectrum in the region of q^3.

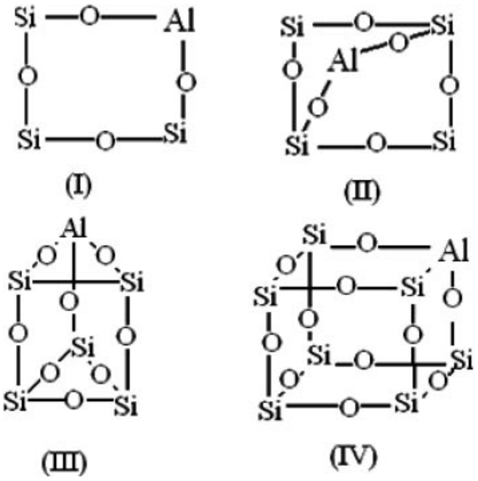


Fig. 4. Proposed some aluminosilicate species, cyclic tetramer (I), doubly bridged cyclic tetramer (II), prismatic hexamer (III), and cubic octamer aluminosilicate (IV).

Fig. 4). The peak at $\delta_{\mathrm{Al}} = 67.6$ ppm can be denoted as the prismatic hexamer (q^3) and $\delta_{\mathrm{Al}} = 65.3$ ppm ascribed to the substituted cubic octamer aluminosilicate species (IV) (Fig. 4), the latter suggested by Samadi-Maybodi et al.[31]

The results obtained from these experiments specify that by increasing the Al/Si mole ratio the intensity of peaks at $\delta_{\mathrm{Al}} = 70.2$ and $\delta_{\mathrm{Al}} = 71.7$ ppm are increased, while the intensity of the peak at $\delta_{\mathrm{Al}} = 65.3$ ppm is decreased. It is supposed that the silicate species, such as bridged cyclic tetramer and doubly bridged cyclic tetramer may act as precursors for the formation of the cubic octamer, $Q^3{}_8$. Since the aluminosilicate species can be more stable than the corresponding silicate species, once bridged cyclic tetramer (I) and doubly bridged cyclic tetramer (II) species are formed, the formation of the silicate species of the cubic octamer “$Q^3{}_8$.” is decreased, and as a result the concentration of the corresponding aluminosilicate (i.e. structure IV) is diminished.

By considering the above results, it can be concluded that the production and distribution of aluminosilicate species are influenced by the concentration of aluminium.

The Evolution of Aluminium-27 NMR Spectra with Time. The aim of this experiment was to provide some insight into the effects that aluminate/silicate replacement processes have on the appearance of ^{27}Al NMR spectra, and to show how these effects may be exploited in assigning structures and determining reaction mechanisms.

The aluminosilicate solution was made by adding 2-HETMA silicate solution to the 2-HETMA aluminate solution to achieve on Al/Si ratio of 10 without using alkaline metals. To study the evolution of the ^{27}Al NMR spectra with time, four different protocols were used at a temperature of 22 °C.

I) Recording ^{27}Al NMR spectrum soon after mixing the solution.

II) The first hour after mixing, recording a series of ^{27}Al NMR spectra for 10 min each without any interval of time between the spectra.

III) The second hour to the fifth hour after mixing, a series ^{27}Al NMR spectra were recorded for 30 min each.

IV) Then for ten hour, ^{27}Al NMR spectra of samples were recorded for one hour each.

Figure 5a represents the evolution of the ^{27}Al NMR spectra with time that were recorded for 10 min without interval time. Figures 5b and 5c show the evolutions with time of the ^{27}Al NMR that were recorded for 1 and 2 h each, respectively. The results specified that during the evolution time a growth in intensity occurred in the peaks located at the shifts ca. 75.2, 71.7, 70.2, 67.7, and 65.3 ppm, which completed after 15 h. A weak band at ca. 60 ppm assigned to “q^4” environments, which was scarcely visible immediately after mixing, did not improve significantly, i.e., this species is very small in this solution.

Figure 6a displays the ^{27}Al NMR spectrum immediately following mixing of aqueous 2-HETMA silicate and 2-HETMA aluminate solutions with an Al/Si ratio of 10 and 0.15 molar Si at 22 °C. The major peak, ca. 79.8 ppm, may be assigned primarily to free aluminate (q^0). However, peaks at ca. 75.2, 70.1, and 65.1 ppm represent q^1, q^2, and q^3 environments, respectively, which are clearly present very quickly after mixing.

Figures 6b–6d represent the ^{27}Al NMR spectra, the mixing of aluminate and silicate solutions after 1, 10, and 15 h, respectively.

The signal intensities corresponding to the different aluminosilicate environments vary with time, so that the signal at the highest frequency is highly dominant during the first hour after mixing, whereas the signals assigned to q^1, q^2, and q^3 are substantial at the end of the evolution time (i.e., after 15 h). This suggests that the aluminate anions react with the silicate anions in different ways depending on the individual silicate species involved. As explained elsewhere[20] formation of the aluminosilicate linkages is not necessarily step by step, i.e., building up the aluminium environments q^1, q^2, q^3, and q^4 might occur simultaneously. Indeed, this process can be expected because when the aluminate ions are introduced to the silicate solutions they are exposed to a number of preexisting silicate species,[6–9] e.g., monomer, dimer, cyclic trimer, linear trimer, prismatic hexamer, and cubic octamer, (Fig. 2a). The silicate solution used for this particular experiment was made one week before it was utilized. Therefore, it is likely

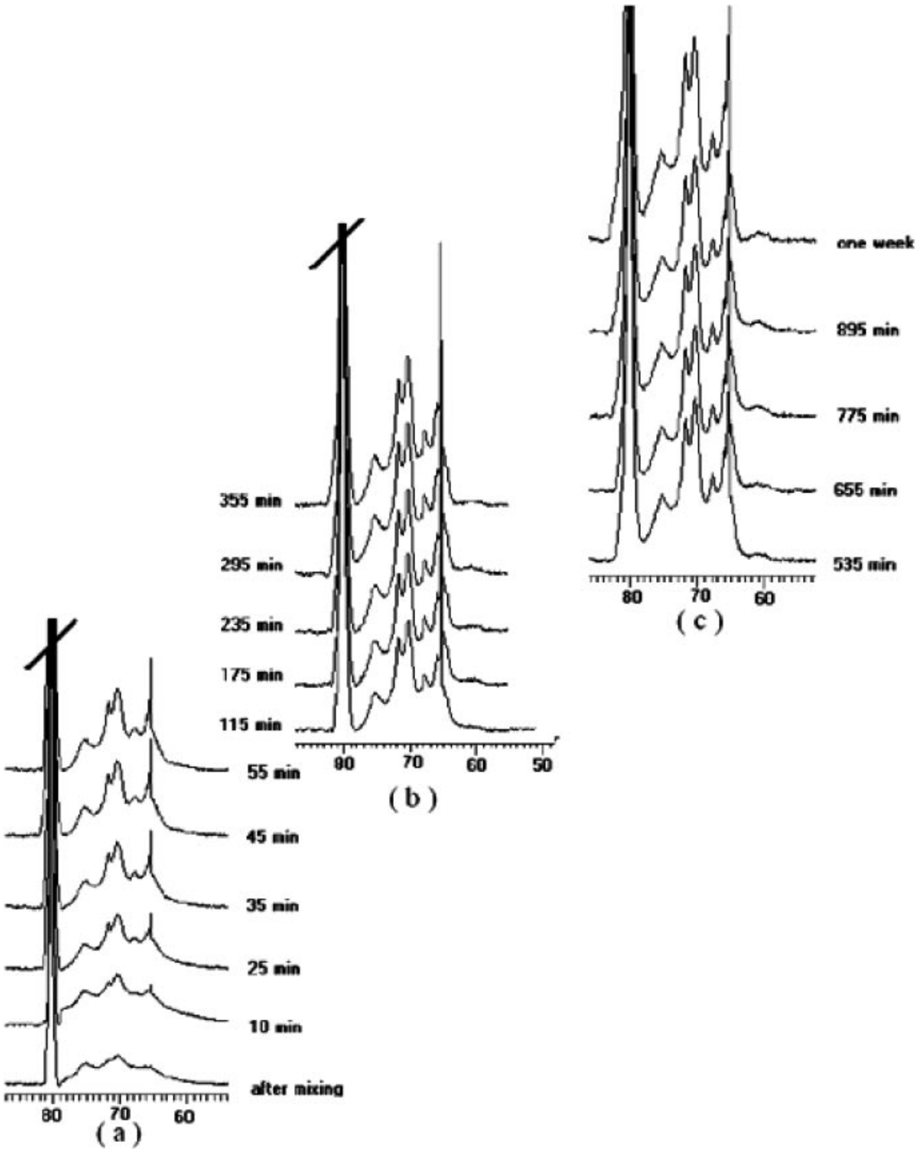


Fig. 5. ^{27}Al NMR spectra at 130.32 MHz of 2-HETMA aluminosilicate solution with Al/Si mole ratio of 10, taken at 22 °C, at the following times after mixing silicate and aluminate solutions with 0.15 molar SiO_2, (a) for 10 min times without interval time; (b) for 1 h interval time each; (c) for 2 h interval time each. Spectral conditions: Spectral width, 15576.3 Hz; acquisition time, 0.1 s; recycle delay, 0.20 s; pulse angle, 90° (14 µs).

that the aluminate ions could react with a number of silicate species at the same time, though the mode of reaction is a matter of speculation. Considering the results obtained from this experiment, it can be deduced that there are two different steps. At the first stage, the aluminate ions attack the silicate species simultaneously and the replacing of Si by Al occurs rather quickly. In the second step (i.e., 1–15 h), the reaction between silicate and aluminosilicate is slow and therefore the feature of the spectra do not vary with time quickly. It can be said that the system undergoes a re-equilibrium process; creation of aluminosilicate species are formed slowly in during this time.

Conclusion

The present work shows the formation of aluminosilicate anions through the reaction of aluminate and silicate anions using 2-hydroxyethyl(trimethyl)ammonium hydroxide (2-HETMAOH) as a base without any alkaline metal. The results obtained from this study specify that there are two stages for the formation of aluminosilicate. The results also indicate that in a constant concentration of silicate, the production and distribution of aluminosilicate species are influenced by the concentration of aluminum.

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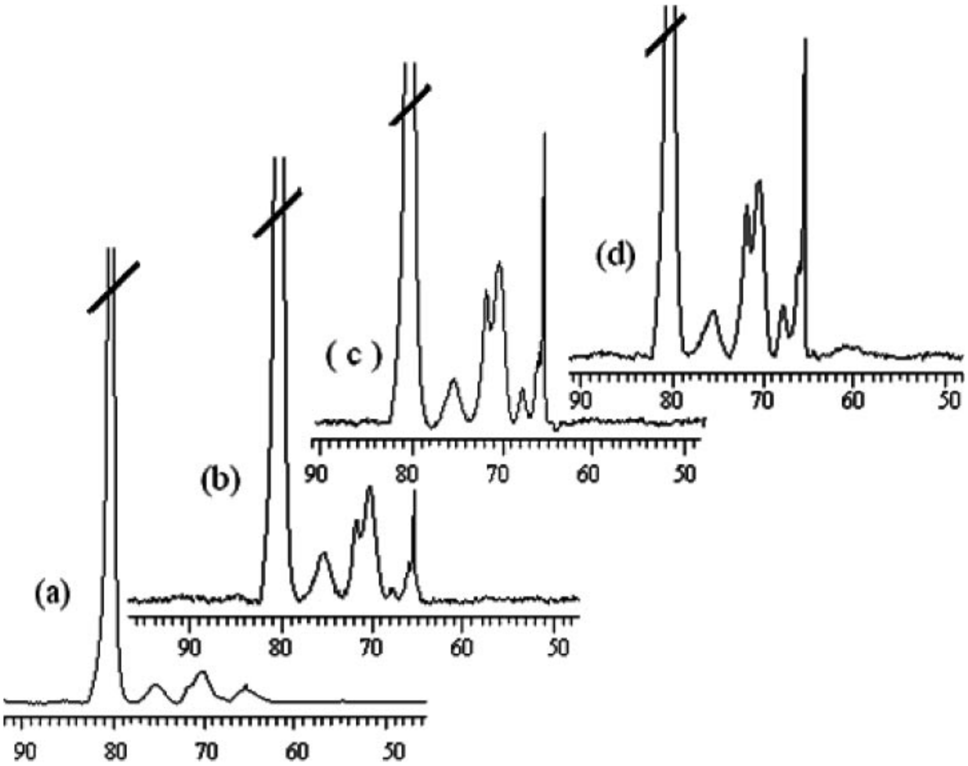

Fig. 6. ^{27}Al NMR spectra at 130.32 MHz of 2-HETMA aluminosilicate solution with Al/Si mole ratio of 10, taken at 22 °C, at the following times after mixing aqueous silicate and aluminate solution with 0.15 molar SiO_2, (a) after mixing; (b) 1 h; (c) 10 h; (d) 15 h, Spectral conditions: Spectral width, 15576.3 Hz; acquisition time, 0.1 s; recycle delay, 0.20 s; pulse angle, 9090° (14 μs).

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