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²⁷Al NMR STUDY OF THE EFFECT OF AQUEOUS AND METHANOLIC MEDIA ON DISTRIBUTION OF TETRAPHENYLAMMONIUM ALUMINOSILICATE SPECIES**N. Goudarzi**

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The effects of tetraphenylammonium (TPhA) on the equilibrium distribution of aluminosilicate oligomers in aqueous and methanolic alkaline aluminosilicate solutions were investigated using ²⁷Al NMR spectroscopy. Alkaline solutions containing both silicate and aluminate ions are of considerable research interest *inter alia* because of their involvement in the synthesis of zeolites. In the present work, we use ²⁷Al NMR to characterize alkaline aqueous and methanolic tetraphenylammonium (TPhA) aluminosilicate solutions with different Al/Si ratios. Tetraphenylammonium (TPhA) used as a cation template and no alkaline metals are used for preparation of aluminosilicate solutions. The distribution of aluminosilicate species was affected by the presence of the alcohol such as methanol and the method of mixing the silicate and aluminosilicate solutions. To understand the reaction between silicate and aluminate ions in this system, the evolutions of ²⁷Al NMR spectra with time are investigated.

Keywords: ²⁷Al NMR spectroscopy, tetraphenylammonium hydroxide, evolution with time, methanolic aluminosilicate solutions.

INTRODUCTION

The cation of the organic or inorganic base is considered to play a structure directing role in the synthesis of zeolites, an interesting but as yet poorly understood phenomenon. This role is commonly discussed in terms of the cation having a templating function during the formation of the aluminosilicate framework from mixing of silicate and aluminate solutions. However, the importance of the initial solution chemistry for the preparation of a specific zeolite structure has long been recognized [1, 2]. It is clear 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 [3—7]. In principle, NMR spectroscopy is powerful tool for detecting and characterizing aluminum 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, aluminate and aluminosilicate solutions [8—27]. Kinrade and Swaddle identified ²⁹Si-NMR peaks due to low molecular weight aluminosilicate anions of sodium aluminate solutions by ²⁹Si NMR spectroscopy [18]. Using similar methods, Mortlock *et al.*, investigated tetrapropylammonium (TPA) aluminosilicate solutions [17, 21]. They also reported the correlation between the partial charge on Si atoms and chemical shift was used to confirm the assignment of ²⁹Si-NMR peaks due to cage species containing double-rings, such as prismatic hexamer and cubic octamer, with some replacement by aluminum [28].

Evidence of dissolved aluminosilicate anions has come from both ^{29}Si and ^{27}Al NMR spectroscopies [29—35]. The notation Q^n for silicate solutions, where n refers to the number of siloxane bridges, is well established [10—15]. In the case of individual aluminum sites in aluminosilicate anions there is a special notation that is similar. An aluminum site is presented as " q " with the number of oxygen bridges to silicon indicated by a superscript. Thus, if aluminum has no siloxane bridges, as for the aluminate anion AlO_4^{5-} (or its protonated congeners up to $\text{Al}(\text{OH})^-$), it is represented as q^0 , where q^1 , q^2 , q^3 and q^4 indicate $\text{Al}(\text{OSi})$, $\text{Al}(\text{2OSi})$, $\text{Al}(\text{3OSi})$ and $\text{Al}(\text{4OSi})$, respectively. It is generally assumed that Loewenstein's [36] rule is obeyed, i.e., there are no $\text{Al}-\text{O}-\text{Al}$ bridges. Muller *et al.* assigned chemical shifts (from the signal for $\text{Al}[\text{H}_2\text{O}]_6^{3+}$) of 79.5, 74.3, 68.5 and 64.2 ppm to q^0 , q^1 , q^2 and q^3 , respectively, using TBMA aluminosilicate solutions [34]. Dent Glasser and Harvey, 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 and q^3 , respectively [35].

Interest in the physical-chemical processes occurring during zeolite synthesis has stimulated the study of dissolved silicate oligomers in aqueous alkaline solutions and their possible link to zeolite nucleation and crystal growth. Although laboratory and industrial syntheses typically involve only aqueous precursor solutions, several authors have noted the effects of adding organic solvents to silicate solutions [36, 37]. This work represents some insight into interactions between the aluminate and silicate species in aqueous and methanolic tetraphenylammonium (TPhA) aluminosilicate solutions and compares and contrasts the interaction between aluminate and silicate species after mixing of these solutions with and without an alcohol. Also, in the present work, we have used ^{27}Al NMR to characterize aluminosilicate solutions with different Al/Si mole ratios using tetraphenylammonium as a template. No alkaline metals such as sodium or potassium were used for the preparation of silicate or aluminate solutions. For more information and understanding of the reaction between aluminate and silicate ions, the evolution of ^{27}Al NMR spectra with time was also investigated.

EXPERIMENTAL

Tetraphenylammonium (TPhA) was used as a template. Firstly, tetraphenylammonium bromide (TPhABr) 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. Pure silica was produced by hydrolysis of silicon tetrachloride (99.8 % purity) using doubly distilled water. The precipitate was filtered off and washed many times with doubly distilled water to remove all the acid. It was then dried at *ca.* 105 °C for 48 h. Aqueous silicate solutions were prepared in polyethylene bottles by dissolving SiO_2 in appropriate amounts of tetraphenylammonium hydroxide. 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 aluminum powder in 0.6 molar of TPhAOH solutions. The concentration of aluminate ion in solution was 0.1 molar. The same procedure was performed for the preparation of methanolic silicate solutions, except methanol was used instead of water. For preparation of methanolic aluminate solutions, an appropriate amount of aluminum powder was dissolved in an alcoholic TPhAOH solution. 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 reach steady state for at least one week at room temperature (*ca.* 22 °C), except when the temporal evolution of the spectra was being studied. Data on the composition of aluminosilicate solutions are listed in Table 1. All solutions contained *ca.* %5 *v/v* D2O (Aldrich chemical company) to provide field/frequency lock for the NMR spectroscopy.

To investigate the degree of solute-solvent interaction, the aluminosilicate solution was modified by addition of an alcohol such as methanol. To understand the distribution of aluminosilicate species in methanolic media, four possible ways of mixing silicate and aluminate solutions with and without alcohol have been investigated. ^{27}Al NMR spectroscopy was therefore used to investigate the difference between these aluminosilicate solutions. We found that although the final concentrations of Si,

Table 1

Data on the composition of aluminosilicate solutions

| Sample No. | Al/Si mole ratio | Si, %w/w | Al, %w/w | MeOH, %w/w | H ₂ O, %w/w |
|------------|------------------|----------|----------|------------|------------------------|
| 1 | 7.5 | 0.301 | 0.125 | 0.0 | 91.90 |
| 2 | 7.5 | 0.341 | 0.137 | 38.12 | 51.09 |
| 3 | 7.5 | 0.344 | 0.136 | 39.31 | 51.02 |
| 4 | 7.5 | 0.391 | 0.154 | 88.27 | 2.78 |

Al, OH and TPhA in the methanolic aluminosilicate solutions were the same, nevertheless, the distribution of aluminosilicate species, which were prepared by mixing methanolic silicate and aqueous aluminate, is significantly different from aluminosilicate solutions prepared by mixing aqueous silicate and alcoholic aluminate solutions. In addition, the influence of alcohol (methanol) on the distribution of aluminosilicate anions was investigated at different Si:Al ratios. Furthermore, variation of different aluminosilicate species during evolution with time was monitored by ²⁷Al NMR spectroscopy.

Spectra were measured using a Bruker AMX 500 spectrometer, operating at 130.3 MHz for ²⁷Al NMR. Aluminum-27 NMR spectra were obtained by applying 90° pulses (14 ms pulse duration), a recycle delay of 0.2 s was sufficient to allow a complete return of the magnetization to equilibrium. The ²⁷Al chemical shifts were measured by substitution with a 1.0 molar aqueous sample of AlCl₃ and are thus considered to be referenced with respect to the octahedral [Al(H₂O)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 TPhA aluminosilicate solution. To study 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, 7.5, 10.0, and 12.5 were prepared by mixing aqueous TPhA aluminate and aqueous TPhA silicate solutions with a constant silicon concentration (0.12M Si for all of solutions), with various aluminium concentrations. All solutions were allowed to reach steady state for one week before spectra were obtained. It was reported [35, 36] 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).

Figure 1, *a* shows the ²⁷Al NMR spectrum of aluminosilicate solution with an Al/Si molar ratio of 1.0. The spectrum illustrates four separated bands located at chemical shifts of ca. 80, 75.1, 69.9, and 65.1 ppm, which are associated with q^1 , q^2 , q^3 and q^4 , respectively. The ²⁷Al NMR peak assignments of TPhA aluminosilicate solution species are based on the assignment of similar peaks that appear in tetra-methylammonium (TMA) aluminosilicate by Muller *et al.* [30]. The following assignment for the ²⁷Al NMR spectrum of Fig. 1, *a* has been tentatively suggested in this work. The peak at the chemical shift of 65.1 ppm is possibly due to the Q₈³ (1Al) octameric species and signal at ca. 69.9 ppm might be assigned to the Q₆³ (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 regions. Figure 2 illustrates some proposed structures of aluminosilicate species. Also, the peaks located at ca. 80 and 75 ppm assigned to the q^0 and q^1 , respectively. Figures, 1*b*—1*e* reveals that by increasing the Al/Si mole ratio some new peaks can be observed from the corresponding spectra. Figure 1, *b* shows the ²⁷Al 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 $\delta_{Al} = 70.1$ and $\delta_{Al} = 71.6$ ppm are that associated to the aluminum 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,

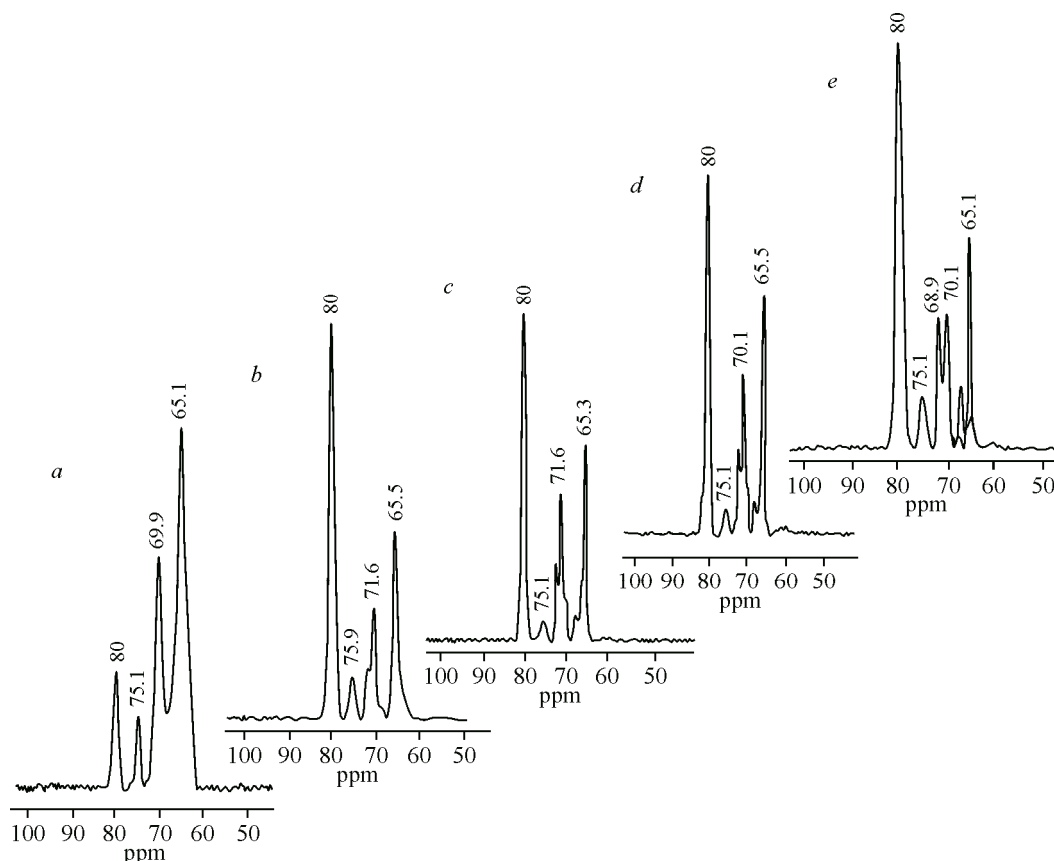


Fig. 1. ^{27}Al NMR spectra at 130.32 MHz of TPhA aluminosilicate solutions (aqueous TBMA silicate and ethanolic TBMA aluminate) with different Al/Si mole ratio: 1.0 (a), 5.0 (b), 7.5 (c), 10.0 (d) and 12.5 (e), and 0.12 molar silica concentration at 22 °C. Spectral width, 15576.3 Hz; acquisition time, 0.1 s; recycle delay, 0.20 s; pulse angle, 90° (14 μs); number of repetitions, 2048

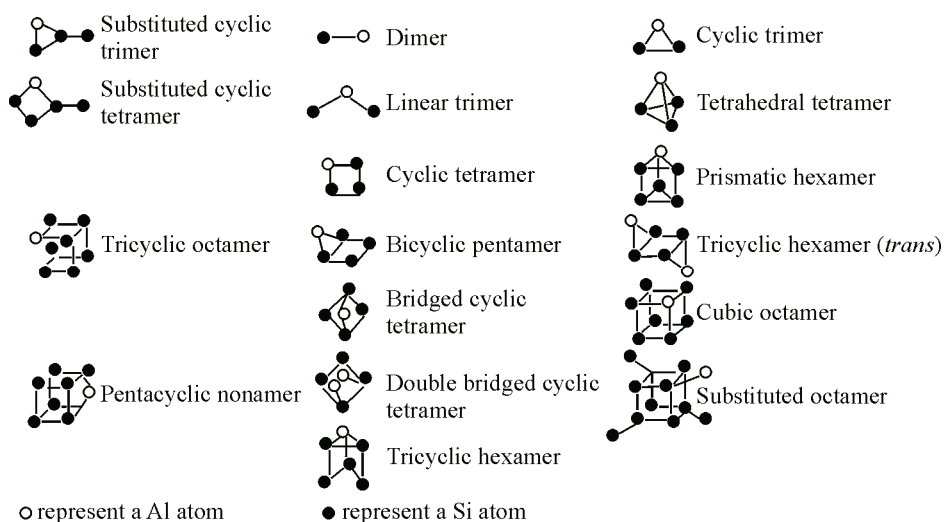


Fig. 2. Some proposed structures of silicate species

and 66.1 ppm, where all peaks belong to aluminum 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

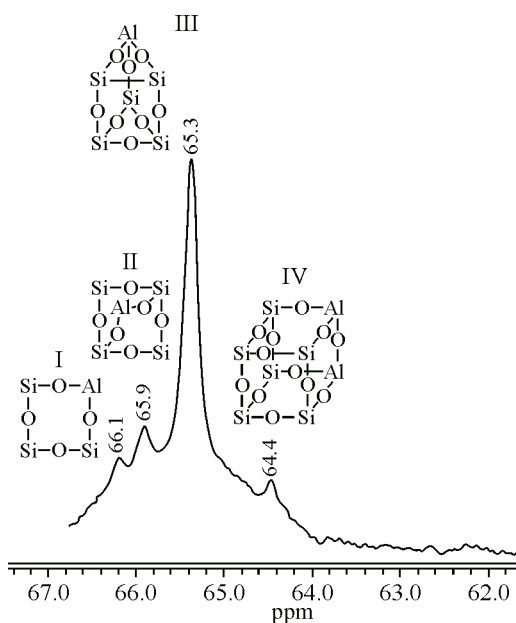


Fig. 3. The horizontal expansion of ^{27}Al NMR spectrum in the region of q^3

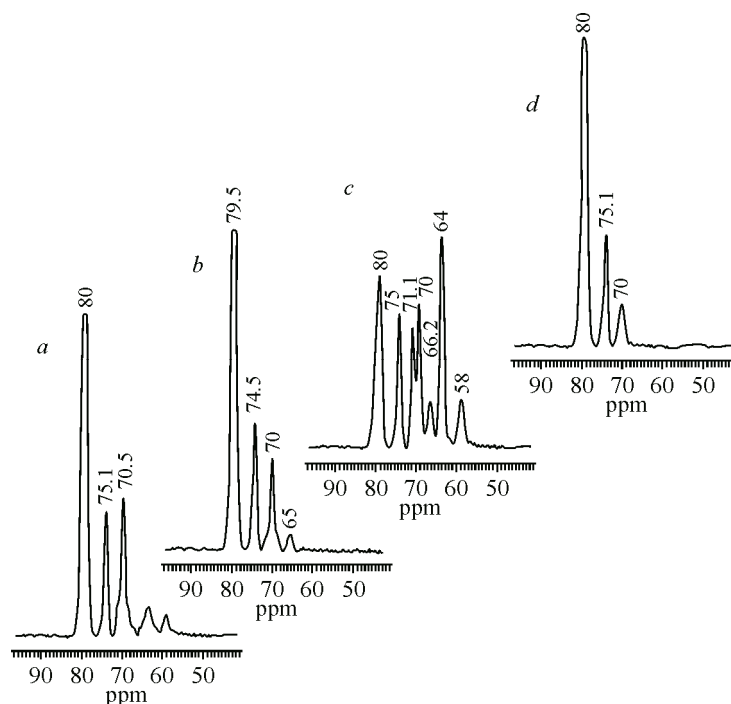
exactly which kind of aluminosilicate species belongs to the observing signal. Nevertheless assignments can come by analogy with ^{29}Si spectra of aqueous alkaline silicate solutions, which have been studied under a variety of conditions (including ^{29}Si enrichment) [11]. As a result, on the basis of shielding arguments and referring to the previous reports, we tentatively assigned the peaks at $\delta_{\text{Al}} = 70.2$ and $\delta_{\text{Al}} = 71.7$ ppm to cyclic tetramer (I) and doubly bridged cyclic tetramer (II), respectively (see and cubic octamer silicate species can be present in these Fig. 3). The peak at $\delta_{\text{Al}} = 67.6$ ppm can be denoted as the prismatic hexamer (q^3) and $\delta_{\text{Al}} = 65.3$ ppm ascribed to the substituted cubic octamer aluminosilicate species (IV) (Fig. 3), the latter suggested by Samadi-Maybodi et al. [22]. The results obtained from these experiments

specify that by increasing the Al/Si mole ratio the intensity of peaks at $\delta_{\text{Al}} = 70.1$ and $\delta_{\text{Al}} = 71.6$ ppm are increased, while the intensity of the peak at $\delta_{\text{Al}} = 65.3$ 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_8^3 . 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_8^3 " 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 aluminum.

The effect of methanol. In order to investigate the effect of an alcohol such as methanol on the reaction of aluminate anions with silicate species, the following aluminosilicate solutions have been prepared by mixing: (a) aqueous silicate solution with aqueous aluminate solution (Sample No. 1); (b) alcoholic silicate solution with aqueous aluminate solution (Sample No. 2); (c) aqueous silicate solution with alcoholic aluminate solution (Sample No. 3); and (d) alcoholic silicate solution and alcoholic aluminate solution (Sample No. 4). Data on the chemical composition of the solutions and their characterizations are shown in Table 1.

Aluminum-27 NMR spectra were recorded at ambient NMR probe temperature (*ca.* 22 °C) with the same spectral conditions and are shown in Figure 4, *a–d*. Figure 4, *a* represents a ^{27}Al NMR spectrum of sample No. 1 that shows five separate bands, indicating the existence at least five kinds of aluminosilicate species. In this figure, q^0 (AlO_4^{5-}) and q^1 (aluminosilicate species with one siloxane bridge) should be present at 80 and 75 ppm, respectively [38–40]. However, the first band at the highest frequency appears at 80 ppm that related to q^0 species and the second band in NMR spectrum illustrates the aluminosilicate species with one siloxane bridge (q^1). The other bands located at *ca.* 70.5, 64.2 and 59.5 ppm represent q^2 (Al_2OSi), q^3 (Al_3OSi) and q^4 (Al_4OSi), respectively. The intensity of peak at *ca.* 59.5 ppm is very small that means the probability of the formation of q^4 species in the aluminosilicate solution is weak. The ^{27}Al NMR spectrum indicates that the concentrations of these species are not equivalent, so that $q^0 \gg q^1 \sim q^2 > q^3 \gg q^4$. Indeed, there are different kinds of aluminosilicate species which contain aluminum with the same siloxane bridges, i.e., with the similar q^n sites, for instance, there are different aluminosilicate species, which all contain q^2 sites (Fig. 2). Such structures have been proposed by Engelhard *et al.* [41] for silicate anions and subsequently by other authors for silicate and aluminosilicate species [11–13]. ^{27}Al NMR spectra of these four solutions indicate when we mix of aqueous silicate solution with ethanolic aluminate solution (Sample No. 3),

Fig. 4. ^{27}Al NMR spectra at 130.32 MHz of TPhA aluminosilicate solutions contain: (a) aqueous silicate solution with aqueous aluminate solution (Sample No. 1); (b) methanolic silicate solution with aqueous aluminate solution (Sample No. 2); (c) aqueous silicate solution with methanolic aluminate solution (Sample No. 3); and (d) methanolic silicate solution and methanolic aluminate solution (Sample No. 4) 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



the number of aluminosilicate species are increased than the others solutions (samples No. 1, 2 and 4). Figure 4, *c* shows the decrease in low order aluminosilicate species (q^0 and q^1) and increase the amount of high order of aluminosilicate species (q^3 and q^4).

Figure 4, *b* shows the ^{27}Al NMR spectrum of sample No. 2 with four bands at chemical shifts of 79.5, 74.5, 70 and 65 ppm. A methanolic silicate solution was used for the preparation of the aluminosilicate solution; however, there are no significant differences between Fig. 4, *a* and *b* (Samples No. 1 and 2, respectively). The ^{27}Al NMR spectrum of the aluminosilicate solution prepared with methanolic aluminate and an aqueous silicate solution (Sample No. 3) is presented in Fig. 1, *c*. The spectrum shows several resolved bands located at chemical shifts of ca. 80, 75, 70, 64 and 58 ppm, assigned to q^0 , q^1 , q^2 and q^3 , respectively. It is pertinent to mention that the band located at a chemical shift of 64 ppm is significantly sharper than the others, presumably indicating that the electric field gradient at aluminum is significantly smaller for some environments giving rise to the sharp peaks. Harris and co-workers [40] assigned this signal to the substituted cubic octameric aluminosilicate species. It should be noted that signals at chemical shifts of 80 and 75 ppm are well separated revealing that the exchange rate between q^0 and q^1 is slow on the NMR time scale. Results obtained from this experiment reveal that at the same concentration of silicon and aluminum, the formation and distribution of aluminosilicate species are strongly dependent on the solvent in the silicate and aluminate solutions. Comparison of Fig. 4, *b* (sample No. 2) and Fig. 4, *c* (sample No. 3) indicates that although the final compositions of the aluminosilicate solutions are the same, the features of the spectra are totally different. As a result, the solvent plays an important role in the reaction between the silicate and aluminate ions. In both aqueous and methanolic silicate solutions, there are a number of silicate species, such as the monomer (Q^0), dimer (Q_2^1), cyclic trimer (Q_3^2), cyclic tetramer (Q_4^2), prismatic hexamer (Q_6^3) and cubic octamer (Q_8^3). It is proposed [40] that formation of aluminosilicate species is accomplished by interaction of aluminate anions with silicate species in different ways such as, addition (addition of aluminate ion to any silicate species to produce an aluminosilicate species with one aluminum q^1 site); substitution (replacement of silicon by aluminum to create q^n with any value of n) and chelation (this would imply ring or cage formation). Figure 4, *c* shows that a number of aluminosilicate species were produced by mixing aqueous silicate and methanolic aluminate solutions, indicating that this mixing condition favors interaction of silicate species with aluminate ions. As Fig. 4, *c* shows, one can deduce that replacement of silicon by aluminum through substitution and chelating is highly efficient and hence creation of aluminosilicate species such as q^3 and q^4 is favored (see also Table 2). It can be said that in methanolic aluminate solutions there are aluminate species such as, $\text{Al}(\text{CH}_3\text{CH}_2\text{OH})_4^{3+}$,

Table 2

Peak area (relative intensity) of different aluminosilicate species in different aluminosilicate solutions

| Sample No. | Figure | q^0 , % | q^1 , % | q^2 , % | q^3 , % | q^4 , % |
|------------|--------|-----------|-----------|-----------|-----------|-----------|
| 1 | 1a | 0.323 | 0.119 | 0.0 | 90.90 | 0.43 |
| 2 | 1b | 0.336 | 0.131 | 39.12 | 52.04 | 0.0 |
| 3 | 1c | 0.341 | 0.130 | 39.06 | 51.02 | 9.85 |
| 4 | 1d | 0.374 | 0.146 | 87.27 | 2.78 | 0.0 |

$\text{AlOH}(\text{CH}_3\text{CH}_2\text{OH})_3^{2+}$ or $\text{Al}(\text{OH})_2(\text{CH}_3\text{CH}_2\text{OH})_2^+$ which have a positive charge. The formation of these species from reaction of aluminate and methanol was approved in our previous work [40]. On the other hand, silicate species such as the prismatic hexamer (Q_6^3) and cubic octamer (Q_8^3) carry negative charges (6- and 8-, respectively). Consequently, interaction between aluminate and silicate species should be more efficient.

Figure 4, *d*, displays a ^{27}Al NMR spectrum of the methanolic aluminosilicate solution prepared by mixing both methanolic silicate and aluminate solutions (sample No. 4) with three separate signals observed at chemical shifts of 79, 70 and 65 ppm. The signal at the highest frequency located at a chemical shift of 79 ppm reveals that the q^0 species is more concentrated than the others (Table 2). Results obtained from this experiment establish that interaction between the aluminate ion and the silicate species in methanolic solution is unfavorable and, therefore, formation of the aluminosilicate species is less feasible.

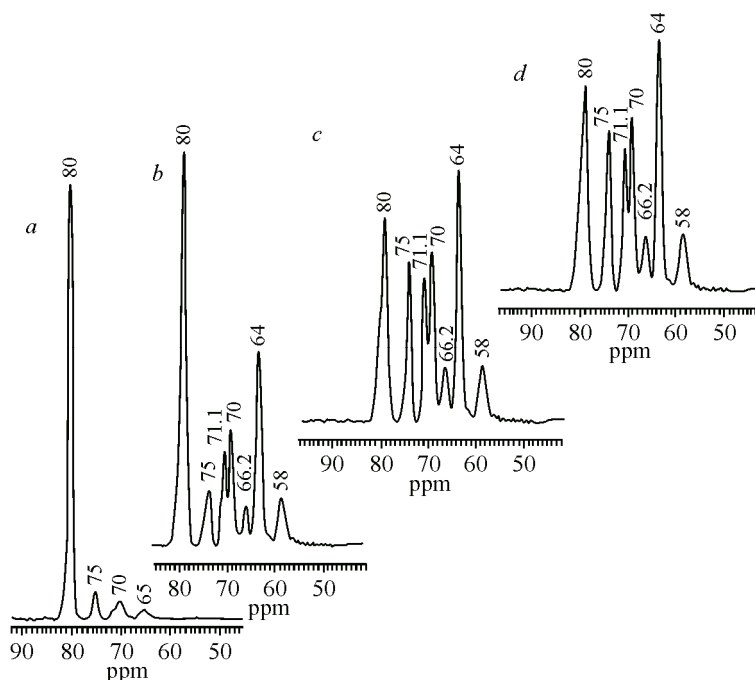
The evolution of ^{27}Al NMR spectra with time. The aim of this part of experiment was to provide some insight into the effects that aluminate/silicate replacement processes have on the appearance of ^{27}Al NMR spectra, and to show how these effects may be exploited in assigning structures and determining reaction mechanisms. The aluminosilicate solution was made by adding aqueous TPhA silicate solution to the methanolic TPhA aluminate solution to achieve an Al/Si ratio of 10 without using any 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.

1) Recording ^{27}Al NMR spectrum soon after mixing the solution, (2) a spectrum after 0.5 h, (3) a spectrum after 8 h and (4) a spectrum after 18 h.

Figure 5, *a* displays the ^{27}Al NMR spectrum immediately following mixing of aqueous TPhA silicate and methanolic TPhA aluminate solutions with an Al/Si ratio of 10 and 0.12 molar Si at 22 °C. The major peak, ca. 80.0 ppm, may be assigned primarily to free aluminate (q^0). However, peaks at ca. 75.1, 70.2 and 65.1 ppm represent q^1 , q^2 and q^3 environments, respectively, which are clearly present very quickly after mixing.

Figures 5, *b*–*d* represents the ^{27}Al NMR spectra, the mixing of aluminate and silicate solutions after 0.5, 8 and 18 hours 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 , q^3 and q^4 are substantial at the end of the evolution time (i.e., after 12 hours). This suggests that the aluminate anions react with the silicate anions in different ways depending on the individual silicate species involved. As explained elsewhere [23] formation of the aluminosilicate linkages is not necessarily step by step, i.e., building up the aluminum 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 [11–12], e.g., monomer, dimer, cyclic trimer, linear trimer, prismatic hexamer, and cubic octamer. The silicate solution used for this particular experiment was made one week before it was utilized. Therefore, it is likely 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

Fig. 5. ^{27}Al NMR spectra at 130.32 MHz of TPhA 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 hour; (c) 8 hours; (d) 16 hours, Spectral conditions: Spectral width, 15576.3 Hz; acquisition time, 0.1 s; recycle delay, 0.20 s; pulse angle, 9090 °C (14 μs)



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., 1–8 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.

CONCLUSIONS

The present work shows the formation of aluminosilicate anions through the reaction of aluminate and silicate anions using tetraphenyl ammonium hydroxide (TPhAOH) as a base without any alkaline metal. The results obtained from this study specify that there are two stages for the formation of aluminosilicate. Also, in this study methanol plays an important role in formation of aluminosilicate species when we used from aqueous silicate and methanolic aluminate solutions. 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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