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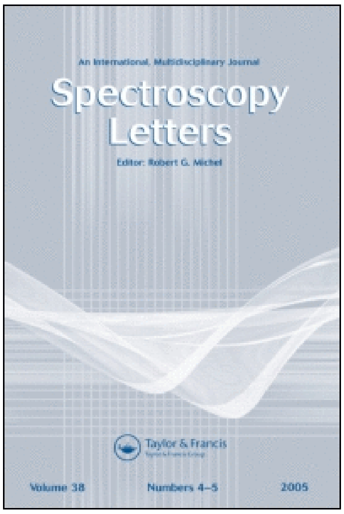

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Silicon-29 NMR Study of Alkaline Aqueous and Alcoholic Tri-butylmethyl Ammonium (TBMA) Silicate Solutions

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Silicon-29 NMR Study of Alkaline Aqueous and Alcoholic Tri-butylmethyl Ammonium (TBMA) Silicate Solutions

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ABSTRACT Silicon-29 NMR spectroscopy was used to characterize aqueous and alcoholic alkaline solutions of tri-butylmethyl ammonium (TBMA) silicates. The effect of TBMA cation on the equilibrium of silicate oligomers in aqueous alkaline silicate solutions was investigated using ^{29}Si NMR spectra. It was found that TBMA cation has a structure directing role and directs the silicate species to form minor amounts of silicate anion in the presence of high concentration of silicon. Silicon-29 NMR spectra of TBMA silicate solutions indicate that considerable changes occurred by changing the Si/TBMA ratio. The distribution of silicate species was affected by the presence of the alcohols, specifically methanol.

KEYWORDS alcoholic silicate solution, silicate species, ^{29}Si NMR spectroscopy, structure directing, tri-butylmethyl ammonium

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INTRODUCTION

The study of aqueous alkaline silicate solutions is of importance in understanding the formation and growth of zeolites and microporous materials on a molecular level.[1] To date, most of the information available has been derived from ^{29}Si NMR spectroscopic studies.[2,3] Much of the research has focused on the effects of adding various organic solutes to aqueous silicate solutions in order to replicate more accurately the conditions of actual zeolite synthesis.[3] Although changes in the silicate anion equilibria have been noted as a result, there have been very few reports of direct chemical interaction occurring between aqueous silicates and organic additives.[4]

Aqueous solutions of silicates rapidly equilibrate to a mixture of anionic species, including chains, branched systems, and cyclic units. Evidence for the existence of such polysilicate ions has come from Raman spectroscopy,[5] paper chromatography,[6] structure analysis of sodium silicate solutions,[7] and reaction with molybdic acid.[8] However, the situation is complicated because of the sensitivity of the equilibria to concentration and pH. Alkali silicates dissolve in water at high pH to form solutions in which a number of anionic species are present in dynamic equilibrium. Determination of the chemical structures of these species is difficult, but

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the technique of ^{29}Si NMR has recently achieved some prominence, following the introduction of pulsed methods involving Fourier transformation, and bids fair to give a better understanding of silicate solutions. Already a number of papers have been published on these topics.[9–14] However, beacuse ^{29}Si atoms have dilute spin systems (natural abundance 4.7%) and the hydroxyl protons exchange rapidly on the NMR timescale, each type of silicon environment normally gives a single resonance, so that assignments are problematic. To a considerable extent, this difficulty is overcome by the use of silica enriched in ^{29}Si.[15] Organic base silicate solutions have long been known to exhibit unique chemical and physical characteristics, including crystallization to distinctive clathrate hydrate structures.[16] As early as 40 years ago, organic base cations, specifically tetra alkyl ammonium (TAA) cations, were used as structure-directing agents in the synthesis of zeolite molecular sieves.[17] Today, tetra-alkyl ammonium cations are employed in the production of most commercially important zeolites, and thus, their interaction with aqueous silicates has a direct and significant impact on a variety of industries ranging from petroleum refining to pollution control.

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As mentioned, alkaline aqueous solutions of silicates contain a variety of anionic species in dynamic equilibrium. Silicon-29 NMR spectroscopy has proved to be the most valuable tool for obtaining information about the molecular structures, but isotopic enrichment in ^{29}Si is generally necessary in order to make diagnostic use of splitting patterns caused by (^{29}Si–^{29}Si) scalar coupling.[18,19] To date, some 23 anionic structures have been proposed.[18,20] As concentrations increase and the pH is lowered, many highly condensed species are presumably formed, so that resonance bonds overlap and information about individual anions is lost. In consequence, whereas oligomers containing Q^1, Q^2, and Q^3 silicon sites (where the superscript indicates the number of siloxane bridges) are well known, information on small Q^4-containing species is hard come by. However, the existence of the cubic octamer (Q_8^3) is well established, and it is known to be favored by the presence of substituted ammonium species as the gegenious. Zeolitic species occur that incorporate "four-membered" rings, such as are present in Q_8^3, so that zeolite synthesis involving the linking of Q_8^3 rings is conceivable, but such linking immediately implies the presence of Q^4 sites.

In the current work, we have used ^{29}Si NMR to investigate the effect of role of structure directing of tri-butylmethyl ammonium (TBMA) cation as template on the distribution of silicate species in alkaline aqueous solution. Also, the effect of addition of different alcohols is studied.

MATERIALS AND METHODS

Amorphous silicon dioxide was prepared by dropwise hydrolysis of silicon tetrachloride in water (deionized distilled water was used throughout these experiments). The resulting gel was dried at 110°C, crushed, and washed repeatedly with water (to neutrality of the washing).

Tri-butylmethyl ammonium chloride (Fluka Co., Switzerland) was converted to the hydroxide form by dissolving in minimum amount of water and passing down a column of Aldrich amberlite resin IRA-400 (OH). TBMA silicate solutions were prepared by dissolving SiO_2 in appropriate amounts of aqueous tri-butylmethyl ammonium hydroxide (TBMAOH). All of silicate solutions were prepared in 0.5 M this template. We prepared some solutions with different Si/TBMAOH mole ratio such as 0.30/0.50, 0.40/0.50, 0.50/0.50, 0.75/0.50, and 0.90/0.50 in a plastic bottle by dissolving appropriate amounts of SiO_2 in 0.5 M aqueous TBMAOH. Dissolution of the silica required between 1 and 2 weeks at a temperature of 60–70°C, yielding clear solutions.

Alcoholic silicate solutions were prepared by addition of 50% (v/v) methanol, ethanol, 1-propanol, 1-butanol, 1,3-propandiol, and glycerin to silicate solution with Si/TBMAOH = 1.0 (0.5/0.5) mole ratio.

All silicate solutions contain ca. 15% v/v D_2O (Aldrich Chemical Co., USA) to provide a field/frequency lock for the NMR. ^{29}Si NMR spectra were obtained using Bruker (Germany) AMX 500 NMR spectrometer operating at 99.36 MHz and ambient probe temperature (ca. 22°C). Chemical shifts are reported in ppm from the signal for external TMS.

RESULTS AND DISCUSSION

The Effect of Silica Concentration

Figure 1a shows 99.36 MHz ^{29}Si NMR spectrum of an aqueous tri-butylmethyl ammonium silicate

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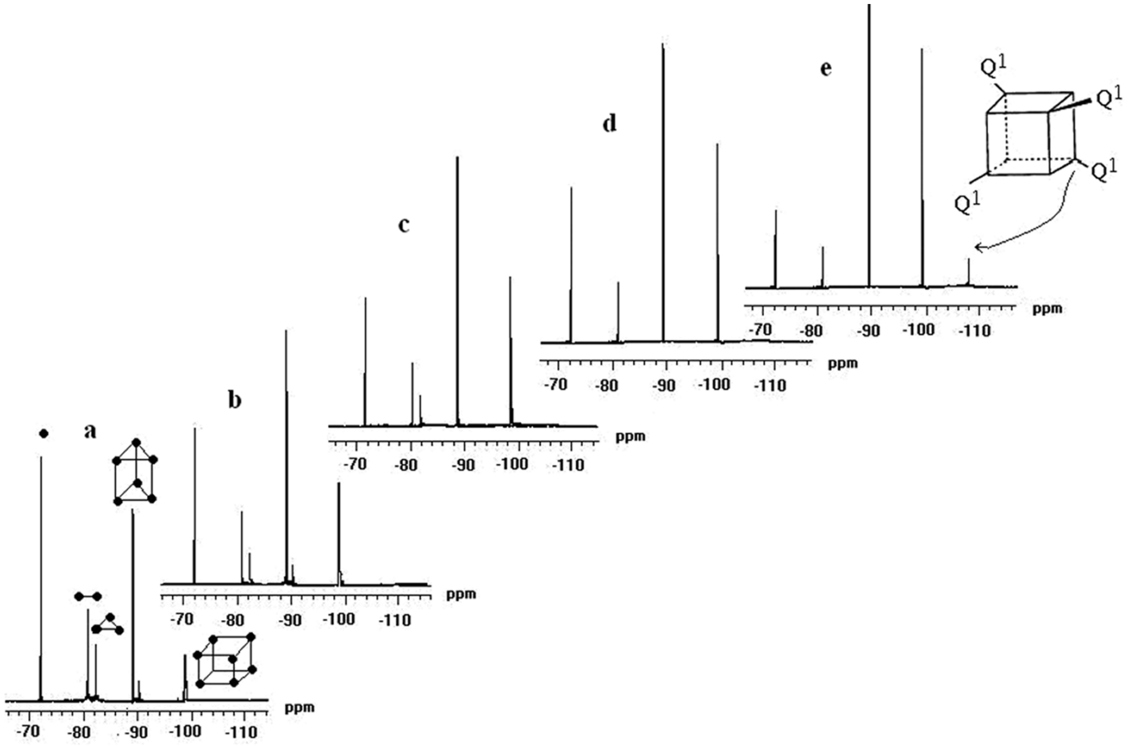

FIGURE 1 ^{29}Si NMR spectra (at 99.36 MHz) of TBMA silicate solutions with different [Si]:[TBMA] mole ratio, (a) 0.60, (b) 0.80, (c) 1.00, (d) 1.50, and (e) 1.80, at 22°C. Spectral width, 9920.64 Hz; acquisition time, 1.65 s; recycle delay, 30.0 s; pulse angle, 30 degrees (5.0 s); number of repetitions, 2048.

solution with [Si]/[TBMA] = 0.60 ([Si] = 0.3 M and [TBMA] = 0.5 M) indicating the presence of a number of different silicate anions. The spectra were expected to pertain to fully equilibrated solutions because they were recorded ca. 2 weeks after preparation. Clearly, the spectrum is complex and exhibits a series of NMR signals, for instance at chemical shifts of −72, −80, −82, −89, and −99 ppm, which indicates the presence of Q^0 (monomer), Q^1_2 (dimmer), Q^2_Δ (cyclic trimer), Q^3_6 (prismatic hexamer), and Q^3_8 (cubic octamer), respectively.

Figure 2 represents the structures of some silicate species that occurred in solution.

Figure 1b displays 99.36 MHz ^{29}Si NMR spectrum of an aqueous tri-butylmethyl ammonium silicate solution contain 0.4 M SiO_2 and 0.5 M TBMAOH ([Si]/[TBMA] = 0.8). It has been noted that an increase to concentration of Si causes an increase to quantity of Q^3_6 and drop to Q^0 intensity signal, and therefore in higher concentration of SiO_2, polymerization of lower order silicate anions occurred and go to form higher order silicate species such as Q^3_6 and Q^3_8. As mentioned, with increase to concentration of SiO_2, formation probability of higher order silicate species is increased, so that in 0.90 M SiO_2, we observe a small signal at ca. 108 ppm, which describes the Q^4 unit (see Fig. 3 for its structure), which is observed in Fig. 1e.

The existence of Q^4, was shown by R. K. Harris and co-workers.[21] However, the percentage of Q^4 in solution compared with that of the other silicate species is very low. It is clear that the only structure to be in accord with the evidence of chemical shifts and splitting patterns is the symmetrically substituted cubic octamer, so the Q^1_4, Q^3_4, Q^4_4 species contain Q^1, Q^3, and Q^4 sites in equal numbers and show three signals in NMR spectrum.

Figure 4 shows the variation of some silicate species percentage with increase to SiO_2 concentration. The correlated data is presented in Table 1. It is clear from the plots that with increase of SiO_2 concentration, the percentage of Q^0 is decreased and percentages of Q^3_6 and Q^3_8 are increased, and it is shown that at high SiO_2 concentration, the degree of polymerization of silicate units is increased.

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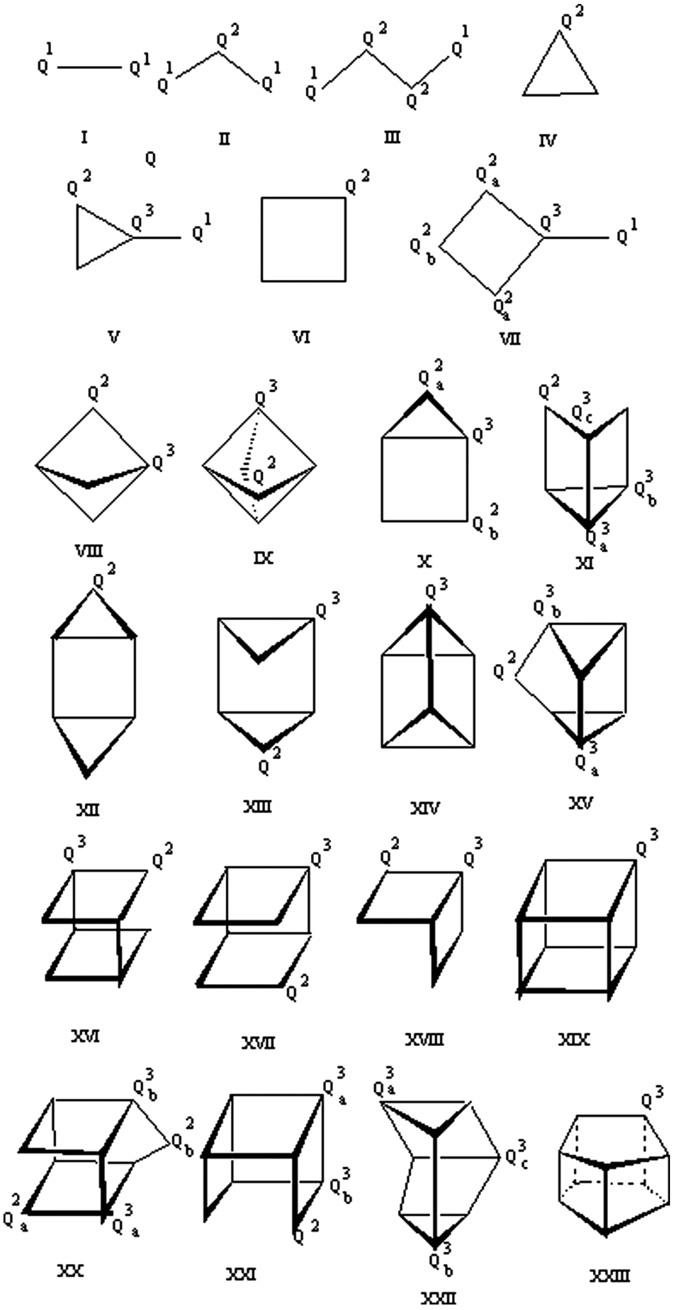

FIGURE 2 Structures of some silicate species.

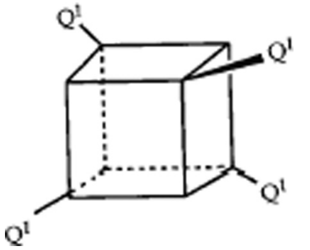

FIGURE 3 Schematic representation of the silicate anion containing a Q^4 unit.

The Effect of Different Alcohols on Distribution of Silicate Species

Figure 5a–f shows the 99.36 MHz ^{29}Si NMR spectra of aqueous tri-butylmethyl ammonium silicate solutions with the mole ratio of [Si]/[TBMA] = 1.0 (0.5 M SiO_2) containing 50% (v/v) methanol, ethanol, 1-propanol, 1-butanol, 1,3-propandiol, and glycerin, respectively. Spectra reveal that the distribution of the silicate anions significantly depend upon the

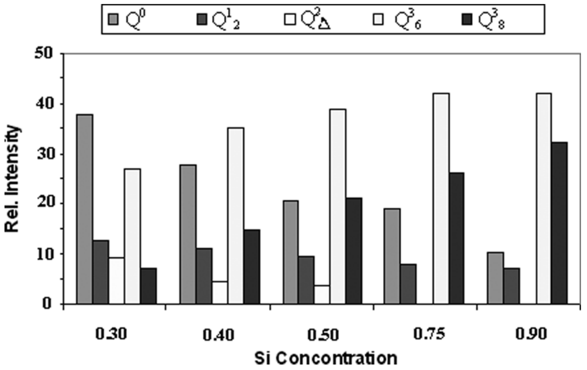

FIGURE 4 Quantitative variation of some silicate species (Q^0, Q^1_2, Q^2, Q^3_6, and Q^3_8) with the silicon concentration.

kind of alcohols. As Fig. 5a shows, only four signals can be observed in the spectrum, indicating silicate anions in the methanol are intended to polymerize, so that the Q^3_6 and Q^3_8 species are highly dominated in this solution. By increasing the length of the alkyl chain (i.e., CH_3CH_2OH, $CH_3CH_2CH_2$, OH, and $CH_3CH_2CH_2CH_2OH$), the oligomerization effect of the alcohol is reduced and consequently more signals can be observed in the spectra (Fig. 5b–d). Figure 6a illustrates the relative intensity of some silicate species with different alcohols with one hydroxyl group. As a result, methanol can exert specific distribution of the silicate species and

TABLE 1 Data on the Peak Area (Relative Intensity) for Silicate Species at Different SiO_2 Molar Concentrations

C_{SiO_2}	% Q^0	% Q^1	% Q^2_Δ	% Q^3_6	% Q^3_8
0.30 M SiO_2	40.0	13.5	10.0	28.8	7.7
0.40 M SiO_2	29.5	11.7	5.0	37.4	16.4
0.50 M SiO_2	21.9	10.1	4.1	41.2	22.6
0.75 M SiO_2	20.4	8.6	0.0	44.6	27.9
0.90 M SiO_2	11.2	7.8	0.0	44.6	34.4

especially stabilize Q^3_6 and Q^3_8 in presence of TBMOH, hence it can be concluded that methanol plays a role in structure directing.

Figure 5c, e, f show silicon-29 NMR spectra of the silicate solutions with 50% 1-propanol, 1,3-propandiol, and propantriol (glycerin), respectively. As can be realized, by increasing the number of hydroxyl group, silicate anions are directed to more polymerization, and silicate species with higher molecular weight are formed, so that prismatic hexamer and cubic octamer are highly dominated in the silicate solution with 50% propantriol. Figure 6b presents the distribution of some of the silicate species in silicate solutions containing 1-propanol, 1,3-propandiol, and propantriol (i.e., different number of hydroxyl groups and same carbon atoms). Therefore, glycerin (such as methanol) can also plays

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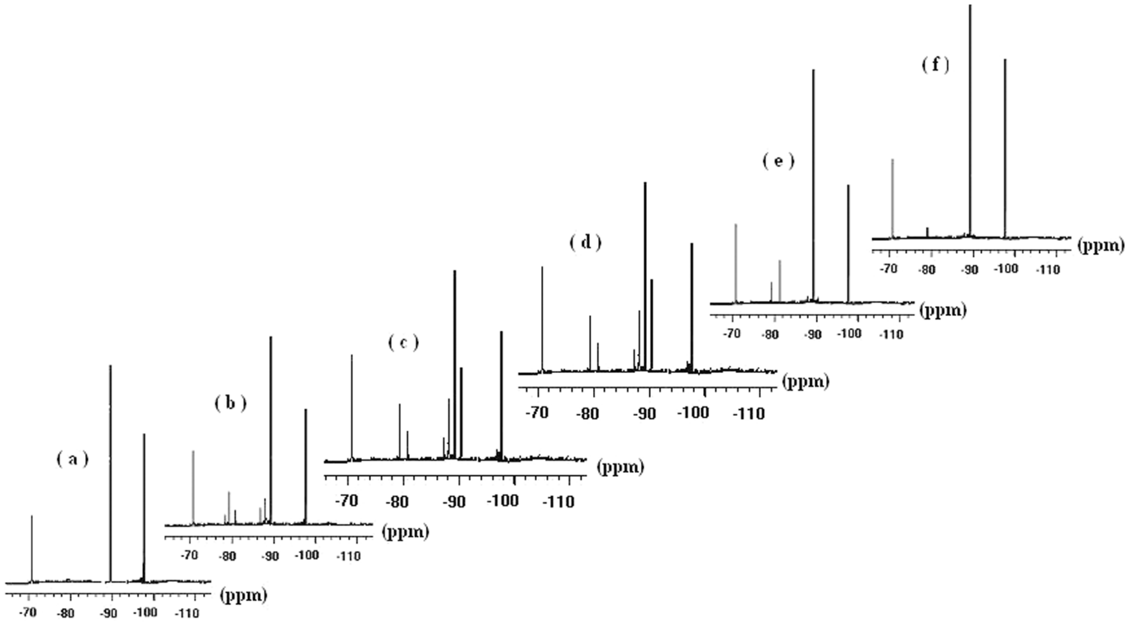

FIGURE 5 ^{29}Si NMR spectra (at 99.36 MHz) of TBMA silicate solutions with [Si]/[TBMA] = 1.0 containing (a) 50% methanol, (b) 50% ethanol, (c) 50% 1-propanol, (d) 50% 1-butanol, (e) 50% 1,3-propandiol, and (f) 50% glycerin, at 22°C. Spectral width, 9920.64 Hz; acquisition time, 1.65 s; recycle delay, 30.0 s; pulse angle, 32 degrees (5.0 s); number of repetitions, 2048.

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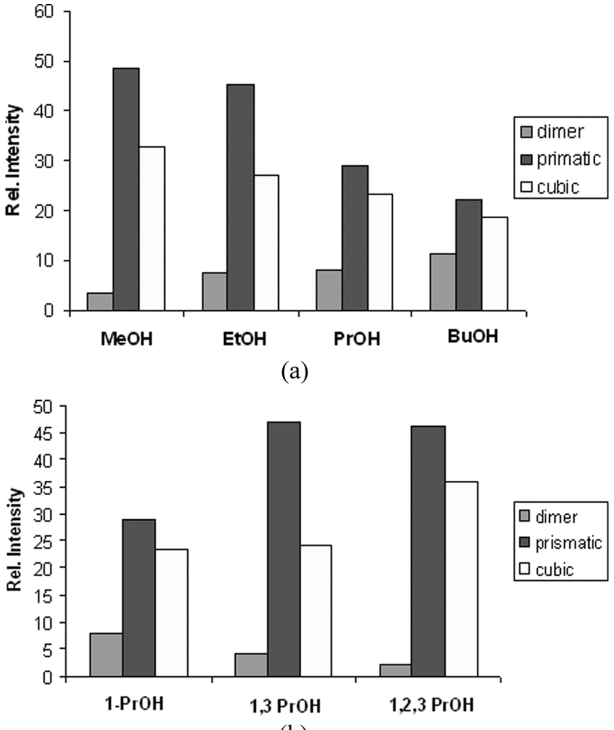

(a)

(b)

FIGURE 6 Quantitative variation of the different silicate species (Q_2^1, Q_6^3, and Q^{38}) percentage at TBMA silicate solution with [Si]/[TBMA] = 1.0 and containing (a) 50% methanol, 50% ethanol, 50% 1-propanol, 50% 1-butanol, and (b) 50% 1-propanol, 50% 1,3-propandiol, and 50% glycerin, respectively.

a role in structural directing and consequently index specific distribution of the silicate anions.

The Effect of Methanol Concentration

Figure 7a–f displays the 99.36 MHz ^{29}Si NMR spectra at the presence of different methanol percentage. Clearly by increasing concentration of the methanol, the number of signals is diminished, so that in very high concentration of methanol (i.e., 100%), only two signals are detected (see Fig. 7f). Figure 8 presents the distribution of some silicate species, Q_2^1, Q_6^3, and Q_8^3, in different methanol concentration. Also, correlated data is listed in Table 2.

The results presented above clearly demonstrate that organic solvents influence the distribution of silicate oligomers in tri-butylmethyl ammonium silicate solutions. Results reveal that by addition of alcohols, the distribution of silicate at the expense of smaller oligomers leads to increase in concentration of the Q_6^3 and Q_8^3. The extent to which this occurs varies from solvent to solvent, and percentage of one solvent clearly depends on solvent structure and composition. Consideration of the physical–chemical phenomena involved suggests that at least two processes are relevant: mass action equilibration and

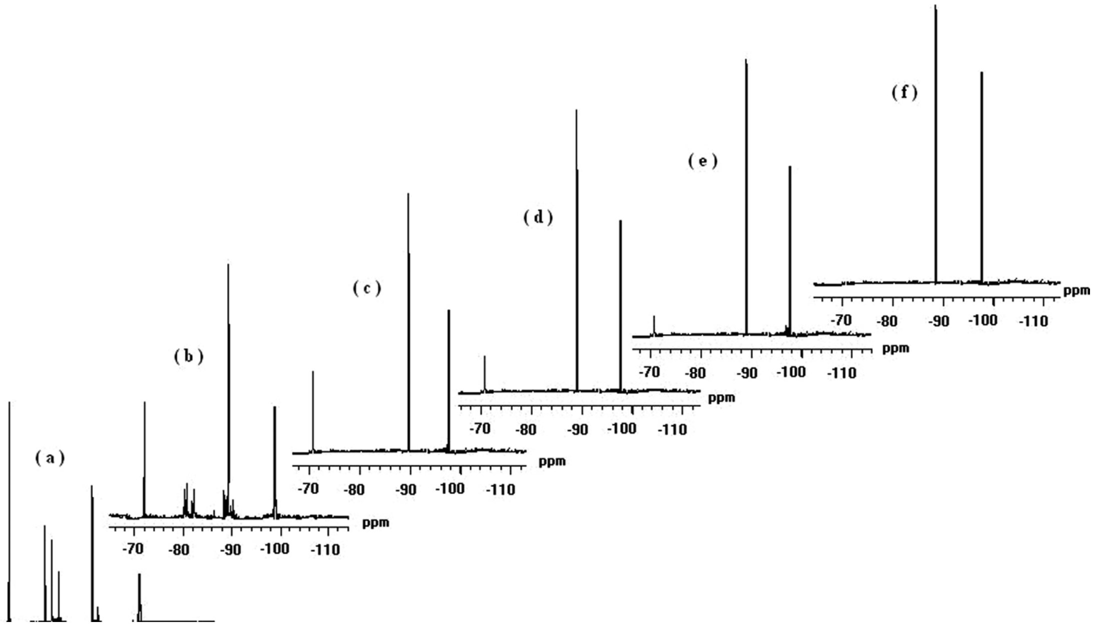

FIGURE 7 ^{29}Si NMR spectra (at 99.36 MHz) of 2-HETMA silicate solutions with [Si]/[TBMA] = 1.0 containing (a) 0% methanol, (b) 25% methanol, (c) 50% methanol, (d) 75% methanol, (e) 90% methanol, and (f) 100% methanol, at 22°C. Spectral width, 9920.64 Hz; acquisition time, 1.65 s; recycle delay, 30.0 s; pulse angle, 32 degrees (5.0 s); number of repetitions, 2048.

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TABLE 2 **Data on the Peak Area (Relative Intensity) for Silicate Species at Presence of Different Alcohols (50%) in Silicate Solutions**

Type of alcohol	Q_2^1%	Q_6^3%	Q_8^3%
Methanol	3.5	48.5	32.8
Ethanol	7.5	45.3	27.1
1-Propanol	8.1	29.0	23.4
1-Butanol	11.3	22.1	18.5
1,3-Propandiol	4.3	47.1	24.0
Glycerin	2.1	46.3	35.8

water structuring. Condensation of silanol oxygen atoms to form a siloxane bridge may be represented schematically as:

$$2(-\mathrm{SiOH}) \longleftrightarrow \text{-SiOSi} - +\mathrm{H_2O}. \qquad (1)$$

Consideration of this equilibrium reaction indicates that extent of condensation will increase if a portion of water in solution is replaced with an organic solvent.[22] This mass action effect is expected to vary slightly from solvent to solvent in solutions that contain a constant mole percent of organic solvent because the solvents have different molecular weights and densities and, therefore, different concentrations.

The effect of solvent concentration on the equilibrium distribution of silicate oligomers was investigated by Hendricks et al.[22] Expressions for the equilibrium constant for the formation of cyclic trimer, D3R (Q_6^3) and D4R (Q_8^3), from the monomer are written on the basis of the following equilibria (M = monomer, W = water):

$$6\ \mathrm{M} = \mathrm{D3R} + 9\ \mathrm{W} \qquad \mathrm{K_{D3R}} = \mathrm{C_{D3R}}\ \mathrm{C_W^9}/\mathrm{C_M^6} \qquad (2)$$

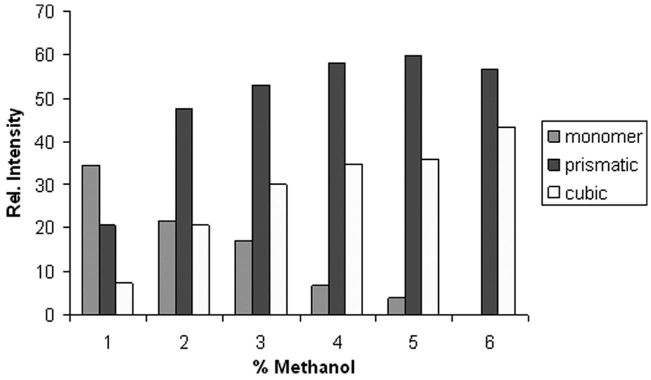

FIGURE 8 **Variation of the different silicate species (Q^0, Q_6^3, and Q_8^3) percentage in aqueous TBMA silicate solution with [Si]/[TBMA] = 1.0 and containing 0.0%, 25%, 50%, 75%, 90%, and 100% (v/v) methanol (1 to 6, respectively).**

$$8\ \mathrm{M} = \mathrm{D4R} + 12\ \mathrm{W} \qquad \mathrm{K_{D4R}} = \mathrm{C_{D4R}}\ \mathrm{C_W^{12}}/\mathrm{C_M^8} \qquad (3)$$

To write these expressions, it is assumed that the ratios of activity of coefficients do not change appreciably with solvent composition. It is clear from the above expression that with addition of alcohol concentration (displacement of water by alcohol), oligomerization of silicates increased and causes formation of high-order silicate species. But, from the above discussion, we conclude that mass action effects alone cannot explain the observed influence of alcoholic solvents on distribution of silicate oligomers. This leads to further consideration of the ways in which the presence of organic solvents can affect silicate speciation by promoting the structuring of water. In order to accomplish this, it is first necessary to consider the behavior of water molecules in the vicinity of hydroxyl functional groups.

Thermodynamic data for the dissolution of normal alkanes in water indicate that this process is exothermic and becomes more exothermic as the chain length increases.[23] In addition, the dissolution process results in a decrease in the entropy of the system that increases with increasing chain length. The interpretation of these observations is that the presence of the alcohol promotes the formation of a three-dimensional hydrogen-bonded structure of water, which becomes more pronounced as the chain length of the alkyl group increases. The influence of alcohols on the structuring of water is commonly attributed to "hydrophobic interactions."[24] Thus, if one imagines that water molecules exist in two-state equilibrium

$$\mathrm{H_2O}_{free} \longleftrightarrow \mathrm{H_2O}_{H\text{-}bonded} \qquad (4)$$

the presence of organic molecules in solution shifts the equilibrium of reaction (4), which will shift to the right.

The influence of hydrophobic interactions on the condensation of silicate ions can be investigated by considering the equilibrium of reaction (2). If the introduction of organic solvent molecules causes the chemical potential of water to decrease, then the equilibrium for reaction (2) will shift to the right and the extent of silicate condensation will increase.

As discussed earlier, both mass action and water structuring effects influence the condensation of silicate anions and the formation of siloxane bridges. But the number of hydroxyl group and carbon chain length can affect the hydrophobic interactions and consequently the degree of polymerization of silicate units to form higher order silicate anions.

CONCLUSIONS

The Silicon-29 NMR spectroscopy is a useful method for presentation of structure directing effect of tri-butylmethyl ammonium cation. The condensation of silicate species in TBMA silicate solution is affected by several parameters such as alcohols concentration, specifically methanol, concentration of Si, and type of template. In high silicon concentration and presence of tri-butylmethyl ammonium as template, a signal for Q^4 species appeared. On the other hand, by increasing concentration of the methanol, the number of signals decreased, and ^{29}Si NMR spectrum of silicate solution with the highest methanol concentration (ca. 100%) shows only two signals. Also, with variation of distribution of anionic silicate species, it can affect the structure of zeolite, which may be formed from such solutions.

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