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THE EFFECT OF ALKALI METAL CATIONS ON THE STRUCTURE OF DISSOLVED PRECURSORS TO ZEOLITES

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ABSTRACT

By means of ^{29}Si NMR spectroscopy, it is established that the distribution of silicate anions in alkaline silicate solutions is a moderate function of base composition. At a fixed SiO_2 concentration and silicate ratio, the proportion of Si present in oligomeric and cage-like structures increases in progressing from Li to Cs hydroxide. Interactions between alkali metal cations and silicate anions are investigated using NMR spectroscopy of the cations; in this way the concentration of ion pairs is measured as a function of cation size. As a result the silicate redistribution is ascribed to cation-silicate anion pairing and to a higher selectivity for ion pairing by large silicate anions as cation size increases.

INTRODUCTION

It is widely believed that the nucleation and growth of zeolites occur through the reactions of dissolved silicate and aluminosilicate anions [1,2]. Supporting this view, several experimental studies have shown that the structure of dissolved silicate species can influence the structure of solid aluminosilicate intermediates present in the gel from which a zeolite may form [3,4,5]. As a consequence, determination of the structure and distribution of such anionic species has become a subject of considerable interest. Studies utilizing ^{29}Si NMR have revealed a wide variety of silicate species in aqueous solutions of silica at high pH [1,6-10]. Anions resembling the secondary building units of zeolites have been observed and it has been shown that the concentrations of these species, as well as others, are highly sensitive to the pH of the solution [7,9]. The structures of aluminosilicates are less well known than those of silicates but some information about the simpler aluminosilicates has been obtained from ^{29}Si and ^{27}Al NMR [11,12].

Cation size and charge are known to influence the selectivity of zeolite synthesis [1]. For instance, faujasite synthesis is quite specific to sodium systems, whereas zeolite L is formed in the presence of potassium. The effects of cation composition on the distribution of silicate species has been examined by only a few authors. Ray and Plaisted [13], using trimethylsilation/ chromatography, have found that the proportion of silicon observed in oligomeric species increases as the base is changed from LiOH to CsOH. Differences in the distribution of silicate species of Na silicate and K silicate solutions can also be deduced from differences in the high resolution ^{29}Si NMR spectra of K silicates [8] and Na silicates [9].

The work presented here was aimed at establishing the influence of different alkali metal cations on the distribution of silicate anions in aqueous solutions such as those used in zeolite synthesis. Changes in the extent of silicate oligomerization were identified using ^{29}Si NMR spectroscopy. The results obtained indicate that the influence of cation composition is expressed through the formation of cation-anion pairs. Direct evidence for the presence of such ion pairs was obtained using alkali metal cation NMR spectroscopy.

EXPERIMENTAL

Alkali metal silicate solutions were prepared from Baker analyzed SiO_2 gel, reagent grade alkali metal hydroxides, and deionized water. Stock solutions at about 3 mol% SiO_2, $SiO_2/M_2O = 3$ (M = alkali metal) were aged in polypropylene bottles for periods of several weeks, to assure that all the SiO_2 had dissolved. Samples were then formulated with extra water and base to achieve a desired composition.

NMR spectra were obtained with a Bruker AM-500 spectrometer at 99.36 MHz. About 100 70^o pulses were used with relaxation delays of about 5 times the spin-lattice relaxation time, T_1. All spectra were recorded at room temperature.

RESULTS

Figures 1 and 2 show ^{29}Si NMR spectra of alkali metal silicate solutions with silicate ratios ($R = [SiO_2]/[M_2O]$) of R = 0.4 and 1.5. Each peak in these spectra represents a distinct silicon environment. In each figure, the chemical shift is referenced to that of the monomer in the Li silicate solution. The silicate solutions at R = 0.4 exhibit only three peaks, assignable to the monomer, dimer and cyclic trimer [9]. The larger cations produce higher concentrations of the cyclic trimer than do the smaller cations. The Li silicate spectrum in Fig. 1 ought not be compared directly with the other spectra, since a substantial amount of lithium inosilicate precipitated from the solution. At R = 1.5 the spectra display resonances in all of the connectivity regions except Q^4 (-34 ppm). As the cation size increases, silicon is displaced from lower connectivity states to states with Q^3_Δ and Q^3 connectivity. (Q^i indicates a silicate tetrahedron with i silicate bonds, and the subscript indicates a three-Si ring.)

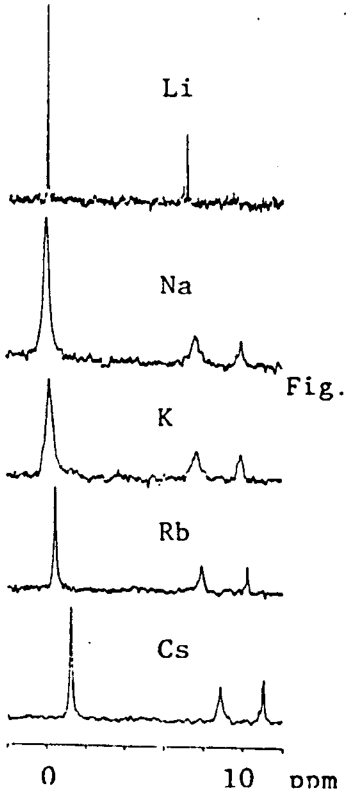

Fig. 1. ^{29}Si NMR spectra of 1.75 mol% SiO_2, R = 0.4 alkali metal silicate solutions.

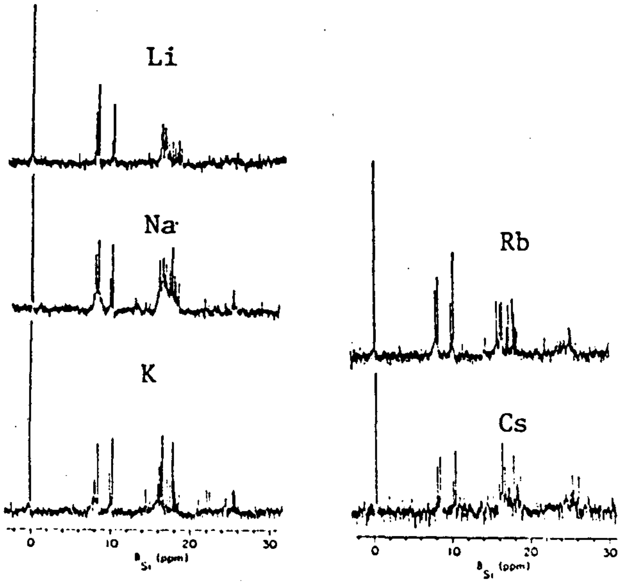

Fig. 2. ^{29}Si NMR spectra of 3.0 mol% SiO_2, R = 1.5 alkali metal silicate solutions.

The chemical shift and the linewidth of the cation NMR spectra were recorded with series of solutions with increasing cation size. Such a series of spectra is shown in Fig. 3. These spectra each display only one line due to the fast chemical exchange of the cation between the hydrated and the silicate-paired environment. These values were reduced as described in ref. 19 to reveal the trend in the concentration of paired cation with increasing cation size.

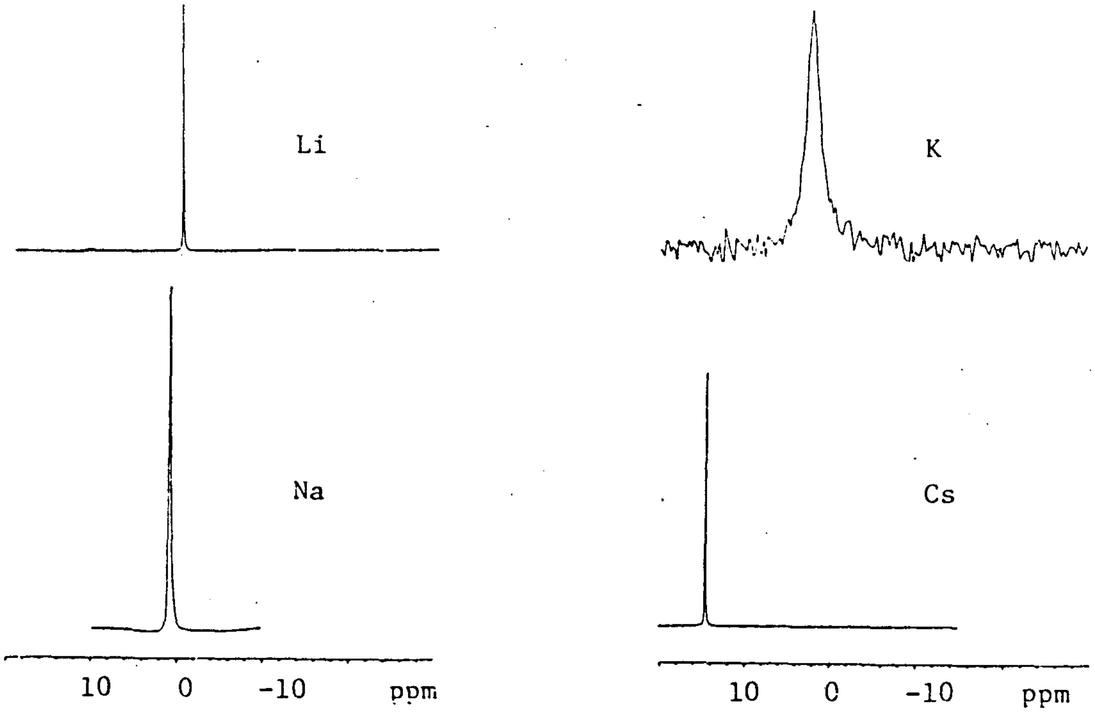

Fig. 3. Cation NMR spectra of alkali metal silicate solutions with 3 mol% SiO_2 and R = 1.5. The chemical shift reference is the fully hydrated cation in dilute chloride salt solution.

DISCUSSION

The results presented in Figs. 1 and 2 demonstrate that the distribution of silicate anions in alkaline silicate solutions is affected to a moderate degree by the choice of the alkali metal cation. The proportion of Si present in single and double rings increases progressing from Li to Cs, i.e., in the direction of increasing cation radius. The present results are consistent with those of Ray and Plaisted [13], who showed by means of trimethylsilation/chromatography that the fraction of Si present in oligomeric structures increases with increasing cation size. Also, in agreement with the trends of the present work, these authors observed that the addition of KCl to a Na silicate solution resulted in a modest increase in the degree of silicate oligomerization.

Since pH is known to influence strongly the distribution of silicate anions in alkaline solutions [7,9], one might expect the observed changes in silicate anion distribution with cation size to be a result of changes in pH. However, the pH of the solutions was not observed to increase with cation size, as might be expected from a consideration of hydroxide dissociation constants [15]. This suggests that the influence of cation composition is a consequence of direct cation-anion interactions, rather than an effect of pH.

It is well known that cation-anion pairs can form in concentrated solutions of ionic compounds [16]. The extent of ion pair formation increases with increasing ion concentration, decreasing cation size, and decreasing dielectric strength of the solvent [16]. Kinrade and Swaddle have invoked the proximity of alkali metal cations to silicates to explain anomalously short ^{29}Si spin lattice relaxation times [17].

The way in which cation-anion pairs might influence the distribution of silicate anions can be illustrated with the aid of reactions 1-3 below:

1. $M + M^- = D^- + H_2O$
2. $M^- + C^+ = CM$
3. $D^- + C^+ = CD$

Here M^- and D^- represent the anionic species $Si(OH)_3O^-$ and $(HO)_3SiOSi(OH)_2O^-$, respectively, and M and D are the corresponding neutral species $Si(OH)_4$ and $(HO)_3SiOSi(OH)_3$. C^+ is the cation and CM and CD are cation-anion pairs formed with M^- and D^-, respectively.

Reactions 2 and 3 represent the formation of cation-anion pairs. If the equilibrium constants for these reactions, K_2 and K_3, are identical, cation-anion pair formation will have no influence on the extent of dimerization at a fixed pH. On the other hand, if $K_3/K_2 > 1$, then the formation of dimers will be enhanced. The question to be posed, then, is what is the effect of cation size on K_2 and K_3, and more importantly, on K_3/K_2.

Based on Bjerrum's model of ion pairing [16], it is expected that the equilibrium constant for ion pair formation of a given anion with a cation decreases with increasing cation size. As a consequence K_2 and K_3 would both be expected to decrease in magnitude as one proceeds from Li^+ to Cs^+. Direct experimental confirmation of this trend is not available, but support for it can be inferred from the following observations. First, the precipitation of the Li inosilicate salt at solution compositions (R = 0.4) which remain stable in the presence of larger cations indicates that Li^+ cations bind to small silicate anions more strongly than do larger cations. Second, using a Born-

Haber cycle and measured heats of formation of alkali metal orthosilicates [19], we have estimated that the heat of formation of a $Li^{+-}OSi$ ion pair is 25.5 kcal/mol higher than that of a $K^{+-}OSi$ pair in the absence of the moderating effects of hydration. From this we would infer that K_2 for Li^+ is larger than for K^+.

The effects of cation size on K_3/K_2 cannot be determined directly, since the necessary thermochemical information is unavailable. Indirect evidence for an increase in K_3/K_2 with increasing cation size can be drawn, however, from NMR observations of the interactions between alkali metal cations and silicate anions. These studies indicate that oligomeric anions shield the nucleus of Cs^+ more efficiently than Na^+ and that Cs^+-silicate pairing exhibits higher selectivity for large oligomers than does Na^+-silicate pairing (see Fig. 4, in which large silicate anions are present at the solution stability limit described in ref. 18). Thus we conclude that the concentration of ion pairs increases somewhat with increasing cation size in the presence of large silicate anions.

CONCLUSIONS

The distribution of silicate anions in alkaline silicate solutions changes with the composition of the base. At a fixed SiO_2 concentration and silicate ratio, the proportion of Si present in high molecular weight and cage-like structures increases in progressing from Li to Cs hydroxide. This trend is ascribed to cation-silicate anion pairing and to the higher selectivity to ion pairing by large silicate anions as cation size increases. An elementary estimate of the energetics of ion pairing and cation NMR confirm that major differences in pairing equilibrium are to be expected as the cation size is changed.

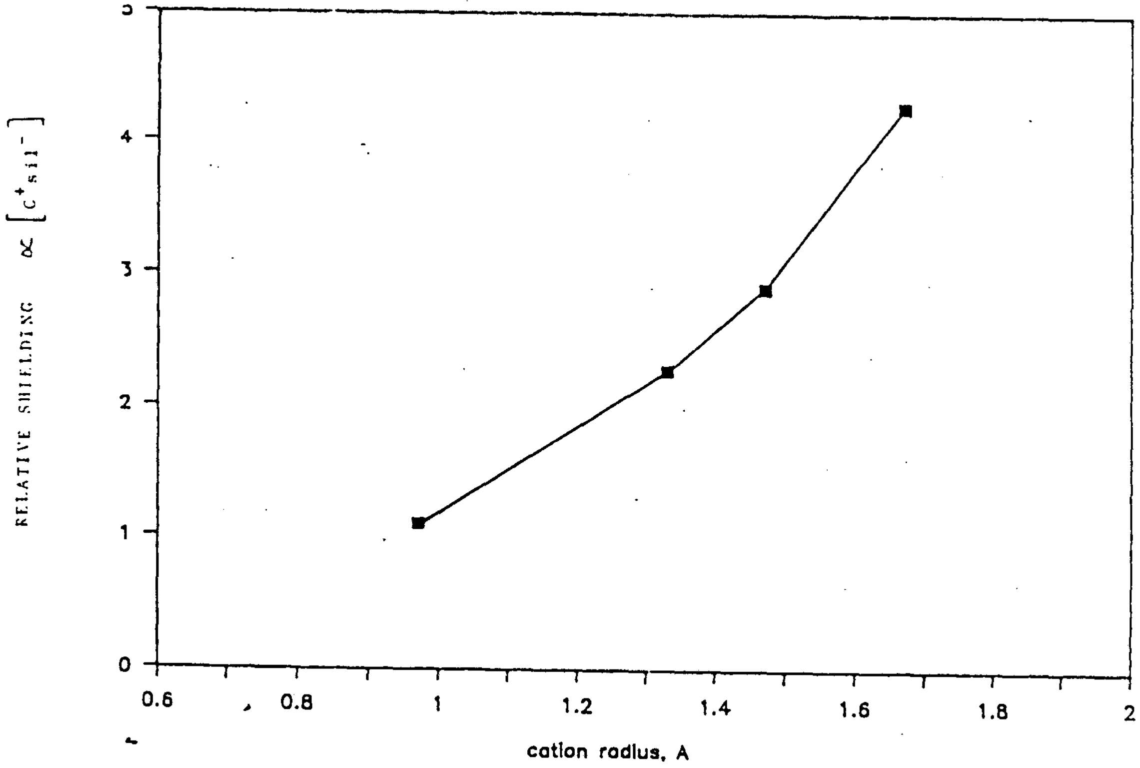

Fig. 4. Normalized shielding of the alkali metal cation due to pairing with the silicate anion, as a function of cation size. The normalized shielding is proportional to the concentration of cation-silicate ion pairs [19].

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