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Vibrational and ^{29}Si NMR Spectroscopies of Soluble Silicate Oligomers

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SUMMARY: Vibrational spectroscopy has been used to correlate the features of silicate solution spectra with ^{29}Si NMR spectra, as a function of SiO_2:Na_2O ratio and SiO_2 concentration. Assignments of infrared and Raman component bands have been made for different anion types and are consistent with results reported for crystalline silicates and silicate glasses. The extent of depolymerization of larger anions has been found to differ, depending on both the degree of dilution and alkalinity. The relative amounts of polymeric (Q^4) silica and larger three dimensional ($Q^3{}_{4R}$) anions are greater for the more siliceous solutions (3.3 and 2.95 ratio) at high concentrations. These large anions continue to be major contributors to the anion distribution even at 15 to 50 fold dilution. In the case of more alkaline solutions, especially below 2.5 ratio, the relative contribution of the large anions to the distribution drops rapidly, even with 2 or 3 fold dilution. At low concentrations, in very alkaline solutions, the anion distribution is mainly monomer, dimer and cyclic trimer. Vibrational spectroscopies show great promise for observing changes in anion distribution on a much shorter time scale than is possible with ^{29}Si NMR and can be useful for following reactions involving silicate solutions.

Introduction

^{29}Silicon nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful method for measuring the distribution of Si-O linkages in silicate anions where a silicon atom may be linked to one or more neighboring silicon atoms through Si-O bonds. The Q^i notation, developed by Engelhardt, et al.[1)] in which *i* indicates the number of neighboring silicon atoms linked, through intermediate oxygen atoms, to the atom in question, is standard usage for describing ^{29}Si spectra. These authors assigned ^{29}Si NMR peaks as follows: Q^0 ~ - 72 ppm, Q^1~ - 79 ppm, $Q^2{}_{(3R)}$ (cyclic trimer) ~ -82 ppm, $Q^2{}_{(4R)}$ and $Q^3{}_{(3R)}$(three ring) ~ -87 to-91 ppm, $Q^{3(4R))}$(four ring) ~ -96 to -98 ppm and Q^4 ~ -108 ppm(broad).

In this paper we use vibrational spectroscopy to correlate the features of silicate solution spectra with ^{29}Si NMR spectra, as a function of SiO_2:Na_2O ratio and SiO_2 concentration. All silicate solutions are prepared from silicate stock solutions which have consistent levels of impurities. The results will show that infrared and Raman spectroscopy serve as important

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techniques to gain insight into the complex chemistry of silicate solutions, especially since they are less expensive, with faster data acquisition, compared to ^{29}SiNMR.

Experimental

Materials. All solutions were made using PQ Corporation N® brand silicate, a commercial silicate solution, 8.9% Na_2O, 28.7% SiO_2 by weight, as a stock solution. Trace impurities in this solution are 300 ppm Al_2O_3, 55 ppm Fe_2O_3, 60 ppm TiO_2, 40 ppm CaO and 15 ppm MgO. The solutions were diluted with high purity (>10 megohm) water, and for those samples of lower ratio, reacted with JT Baker Analyzed Reagent 50% sodium hydroxide solution in appropriate amounts. Since the trace impurities in the NaOH solution total less than 10 ppm, impurity levels in the prepared solutions are proportionally reduced by dilution. Solutions were equilibrated at ambient temperature for at least 200 hours prior to analysis. DuPont LUDOX® SM-30 silica sol was obtained from Aldrich, Milwaukee, WI.

The most concentrated solutions were made at 6M in SiO_2 with SiO_2:Na_2O ratios ranging from 3.3 to 1.65. These are close to the concentrations of many commercial silicate solutions. Solutions with these ratios were also prepared at lower concentrations. When the SiO_2:Na_2O ratio is less than about 1.2, the solubility of silicate decreases sharply at room temperature as crystals of sodium metasilicate form. Therefore, solutions with SiO_2:Na_2O ratio of 1.03 and lower were prepared at concentrations of 1M or less.

Instrumentation. ^{29}Si NMR spectra were obtained on a 363 MHz spectrometer, operating at a ^{29}Si NMR frequency of 72.18 MHz. Data were collected with either Nicolet or Tecmag data acquisition systems, using a 10mm Cryomagnet Systems, Inc. probe with a quartz insert. Quartz NMR tubes (Wilmad) were employed for all samples. Spectra were obtained as neat liquids with a ca. 80° pulse, with a 5 second recycle delay. Recycle delay tests showed that the 5 second recycle delay yielded quantitative results, even for Q^4 silicon. Typically 700 to 6000 scans were accumulated for each sample, the number of scans was increased as the silica concentration decreased.

FTIR spectra were collected on a Nicolet (Madison, WI) Magna® 550 spectrometer using a SpectraTech (Shelton, CT) single/multibounce HATR accessory. A single bounce 45° ZnSe element was used for the 0.4 to 6M solutions. 300 scans were collected per sample at a resolution of 4 cm^{-1}. The spectra reported in this paper were obtained by subtracting a pure water spectrum from the sample spectrum and the baseline corrected in the region from 1300 to 650 cm^{-1}, using Nicolet's OMNIC™ software. Curve fitting was performed by transforming these spectra to the spc (Salem, NH) GRAMS/386™ software, and using its curve fit program. A Gaussian model is used for the component bands. The fit is considered satisfactory if chi^2 is less than 2.

Raman spectra were collected using a Kaiser Optical Systems, Inc. (Ann Arbor, MI) Holospec Raman microprobe excited by a frequency-doubled diode pumped Nd:YVO_4 laser (532.4 nm). Incident laser power was about 600 mW with integration times from 3 to 10 sec. The spectra reported in this paper were obtained by subtracting a pure water spectrum from the sample spectrum.

Results

NMR. Figure 1 represents the quantitative distribution of the several types of Si-O linkages described in the Introduction. It is based on integrated band intensities of the peaks reported by Bass and Turner[2)]. The relative stability of the larger anions in the 3.3 ratio silicate, compared to 2.07 ratio, is significant in many applications of silicates involving dilution.

When silicate solutions are diluted to 0.4 M, large three dimensional anions and polymer predominate at high ratios, smaller three dimensional and planar cyclics at intermediate ratios and small anions in the most alkaline silicates (Figure 2). The resolution of ^{29}Si NMR spectra of 0.4 M solutions is sufficient to make estimates of the relative amounts of individual anions, based on peak height[2)].

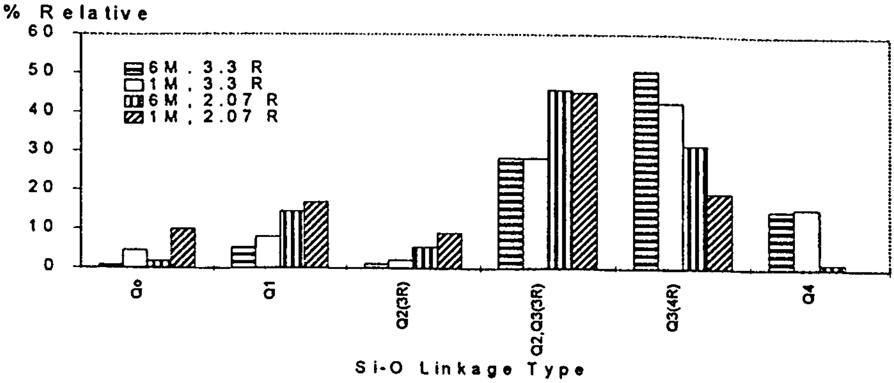

Fig. 1: Relative percentages of Si-O linkage types for 3.3 and 2.07 ratio silicates at different concentrations.

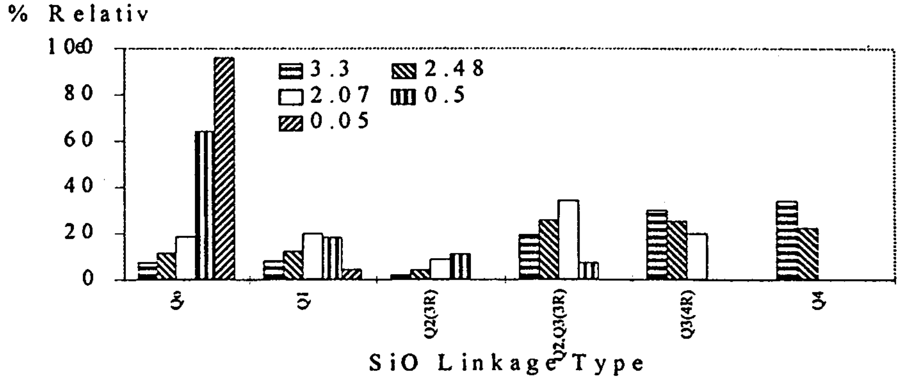

Fig. 2: Relative percentages of Si-O linkage types for 0.4M solutions, 0.05 to 3.3 ratio.

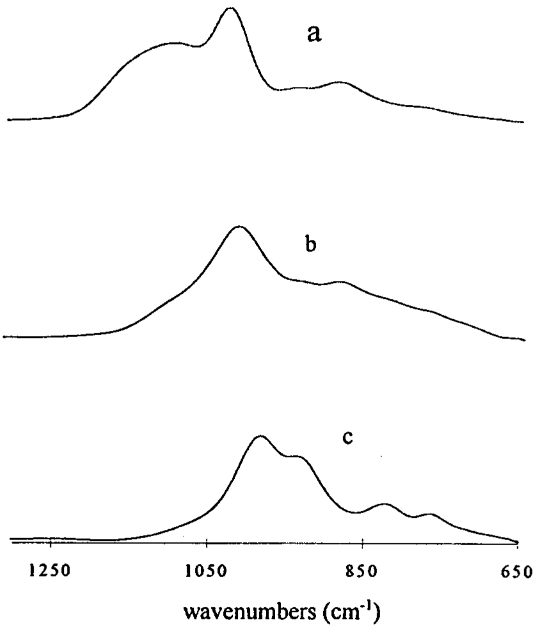

Fig. 3: FTIR spectra of 0.4 M solutions. (a) 3.3 ratio, (b) 1.07 ratio, (c) 0.51 ratio

FTIR. Infrared absorption bands of sodium silicates are observed between 1250 and 700 cm^{-1}. Although absorption bands for sodium silicate glasses have been observed below 700 cm^{-1}, the ZnSe ATR element becomes totally absorbing near 600 cm^{-1}. Also, a broad, intense water band in this region makes observation of bands in the *solution* spectra far more difficult to observe.

Silicate FTIR spectra typically show a relatively sharp peak in the region from 1120 to 900 cm^{-1} superimposed on a broad band covering the range mentioned previously. The high frequency edge of the broad band shifts to lower frequency as the silica:alkali ratio decreases, at constant silica concentration, or as the concentration decreases at constant ratio. Figure 3 compares the spectra of 0.4M solutions ranging in silica:alkali ratio from 3.3 to 0.5. The location of maximum absorption moves to *lower* frequency. The shape of the band also changes with ratio. Similar results are observed for other concentrations. However, when we compare the spectra of solutions of the same SiO_2:Na_2O ratio as they are diluted, the location of maximum absorption shifts to ***higher*** frequency. The band shapes also change with dilution.

Figure 4 shows the result of using the GRAMS/386™ software on the infrared spectrum of 0.4M, 2.07 ratio solution. The silicate absorption band is resolved into nine component bands at this concentration and ratio. Although the curve fit shows bands below 850 cm^{-1}, the strong absorption of water makes determination of band location and area very uncertain, so the significance of these bands will not be discussed. The number of component bands, band areas and peak maxima locations vary with ratio and concentration.

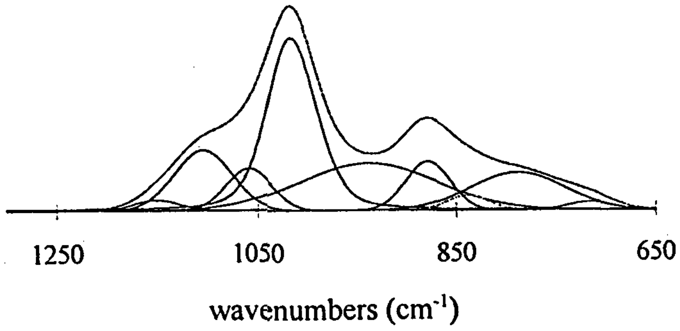

Fig. 4: Curve fit of observed silicate band, 2.07 ratio, 1 M, to component bands using GRAMS/386 software.

Raman. Raman peaks in the silicate absorption region are sharper than those seen in the FTIR spectra. Water does not absorb as strongly below 700 cm^{-1} so bands can be seen as low as 400 cm^{-1}. Figure 5 compares 6M 3.22 ratio with 6M 2.0 ratio. The high frequency shoulder is much smaller than in FTIR spectra. The more alkaline silicate has stronger bands below 800 cm^{-1}. The low frequency bands are even more relatively intense in 0.4 molar solutions.

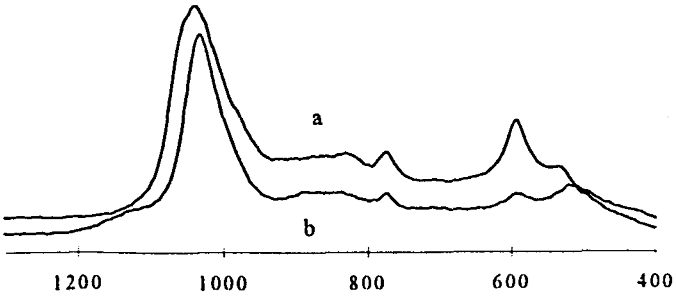

Fig. 5: Raman spectra of (a) 6 M 2.07 ratio and (b) 6 M 3.3 ratio sodium silicates.

Discussion

Effect of SiO_2:Na_2O Ratio. As ratio increases the condensation of monomer to first linear, then planar cyclic, then three dimensional anions and finally polymeric silica takes place. This results in progressively broader FTIR bands, with considerably more absorption above 1000 cm^{-1}. Raman spectra have fewer or less intense bands in the lower frequency region as ratio increases but the band near 1020 cm^{-1} increases in intensity.

These changes are correlated with the increase in $Q^2_{(4R)}$ (four ring) and $Q^3_{(3R)}$ (three ring) ~ -87 to -91 ppm, $Q^3_{(4R))}$ (four ring) ~ -96 to -98 ppm and Q^4 ~ -108 ppm (broad) that are shown in Figure 2. Therefore we can clearly assign the high frequency bands in both FTIR and Raman to the larger anions. In both spectroscopies the peak around 1000 cm^{-1} is a composite of bands due to several different large anion types. Curve fitting shows that the portion of the FTIR silicate band between 980 and 1250 cm^{-1} can be resolved into five to seven bands, depending on ratio and concentration.

In the Raman spectra the band near 770 cm^{-1} increases with decreasing ratio indicating it is due to Q^0 and Q^1 linkages. The band around 920 cm^{-1} is observed only for 1.03 and 0.51 ratio which indicates it should be assigned to more highly ionized small anions where the charge is balanced by sodium ions rather than protons. The Raman band near 600 cm^{-1} can be assigned to $Q^2_{(3R)}$ (three ring) anions based on its absence in 3.3, but presence in lower ratios.

Effect of Concentration. The progressive increase to higher frequency for the location of the maximum absorption in FTIR is attributed to complex changes in the relative absorption of the high frequency component bands2). In contrast, the peak absorption band only moves from 1033 to 1030 cm^{-1} for 3.3 ratio and from 1031 to 1026 cm^{-1} when concentration is decreased from 6 to 0.4M. Figures 1 and 2 suggest that this can be explained by the stability of large anions to hydrolysis at lower alkalinity. The relatively higher absorption of the 770 and 600 cm^{-1} bands as both 3.3 and 2.07 ratio are diluted is consistent with the higher relative amounts of Q^0 and Q^0 linkages assigned to the 770 cm^{-1} Raman peak, and in small cyclics for the 600 cm^{-1} Raman peak, also consistent with Figures 1 and 2.

Conclusions

Although infrared, and to a lesser extent, Raman spectroscopic data are a complex composite of absorption bands, contributed by several anion types, trends observed with changes in concentration and/or alkalinity closely follow the trends observed by ^{29}Si NMR. Assignments of infrared and Raman component bands for different anion types, less specific than NMR assignments, are summarized in Table 1. The band locations are consistent with results reported for crystalline silicates and silicate glasses3-5). Vibrational spectroscopies show great promise for observing changes in anion distribution on a much shorter time scale than is possible with ^{29}Si NMR. This can be useful for following reactions involving silicate solutions which have many important commercial applications.

Our results also show that the extent of depolymerization of larger anions differs, depending on both the degree of dilution and alkalinity. The relative amounts of polymeric (Q^4) silica and larger three dimensional (Q^3_{4R}) anions are greater for the more siliceous solutions (3.3 and 2.95 ratio) at high concentrations. These large anions continue to be major contributors to the anion distribution, relative to the smaller monomeric, linear chain and

Tab. 1. Assignments of Infrared Component Band Regions to Anion Types

Anion Type	Component Band Region
polymer	1300 to 1100 cm^{-1}
$Q^3_{(4R)}$ rings	1120 to 1050
$Q^3_{(3R)}$, $Q^2_{(4R)}$ rings, linear Q^2	1070 to 1030
$Q^2_{(3R)}$ rings	1050 to 1020
SiO^{-1} cyclic anions	1020 to 1010
linear Q^1 (dimer, trimer, tetramer) + monomer	1055 to 995, 985 to 965
monomer + dimer	950 to 910
SiO^{-1} small anions	900 to 850
ring structures	625 to 400

planar cyclic anions, in these solutions, even at 15 to 50 fold dilution. In the case of more alkaline solutions, especially below 2.5 ratio, the relative contribution of the large anions to the distribution drops rapidly, even with 2 or 3 fold dilution. At low concentrations, in very alkaline solutions, we find that the anion distribution is mainly monomer, dimer and cyclic trimer.

References

1) G. Engelhardt, D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites,* John Wiley: New York, Chapter 3 (1987)
2) J.L. Bass, G.L. Turner, *J. Phys Chem. (B),* **101**, 10638 (1997)
3) E.I. Kamitsos, J.A. Kapoutsis, H. Jain, C.H. Hsieh, *J. Non-Crys. Solids,* **171**, 31 (1994)
4) W.P.Griffith, *J. Chem. Soc (A),* **1969**, 1372 (1969)
5) M. Bartsch, P. Bornhauser, G. Calzaferri, R. Imhof, *Vibrational Spectroscopy,* **8**, 305 (1995).