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Monitoring the structure of water soluble silicates

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Abstract

Commercial 3.22 ratio sodium silicate glasses were dissolved in water at around 150 °C and 4.6 atm pressure and the process was followed by in situ and ex situ Raman spectroscopy. Both methods proved to be suitable for measuring the concentration of dissolved silicate as a function of time, but marked differences were observed in the spectra obtained in the two different ways. The in situ measured Raman spectra proved to be identical with those of the commercial silicate solutions mostly composed of ring structured nanoparticles. The rapid sample quenching generates terminal Si–O(H) bonds and hydrated monomer crystallites mostly by consuming the three member rings. In contrast to the common belief mostly polymer pieces seem to detach from the solid sodium silicate and only a negligible fraction is leached out in monomer form. Dilution of a 3 mol/L silicate solution to 0.2 mol/L at ambient conditions reduces the average particle size from about 10.5 $[SiO_4]$/mol to 1 $[SiO_4]$/mol which is reflected in the Raman spectra of these liquids.

Keywords: Sodium silicate; Nanoparticles; Dissociation; Hydrolysis; Average molweight; Raman spectroscopy; In situ

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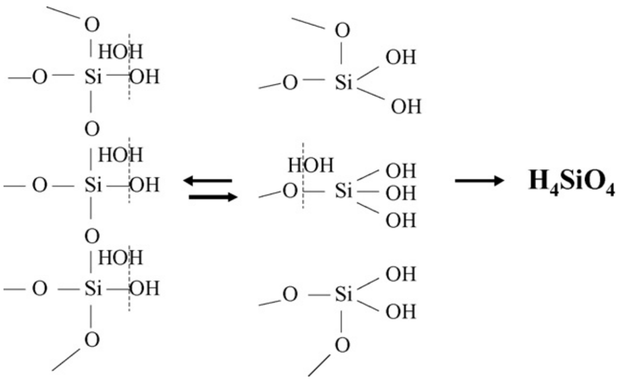
1. Introduction

The solubility of solid silicates in H_2O is important in biology, geology, and a variety of technical applications including synthesis of assorted catalysts and adsorbents [1–8]. It is usually assumed that the hydrolytic depolymerization of crystalline or amorphous silicates at elevated temperatures and pressures is a sequential surface process releasing monomers into the aqueous phase [3,5,9–13]:



Alkaline cations which are leached out prior to hydrolysis of alkaline silicates appear to catalyze this hydrolytic process [9–12,14,15].

Conversely to the proposed monomer formation, most commercial sodium silicate solutions made by dissolution of appropriate glasses are mainly composed of polymer silicate particles especially at $SiO_2/Na_2O > 2$ weight ratios (abbreviated as ratio) [1–4,16,17]. The appearance of polymers may be explained by a secondary polymerization process during a slow equilibration of silicate solutions that usually takes several hours or days [1–4]. At proper conditions the polymerization of monomers can take place even in highly alkaline aqueous solutions [18]. However, published experimental observations suggest that the polymers might not appear in the solutions as results of polymerization but might directly form from the solid silicates during the dissolution process. For example, larger than one $[SiO_4]$-unit size cavities were observed by in situ transmission electron microscopy in alkaline silicate glasses even in the early stage (<30 min.) of their dissolution indicating that these cavities did not form via sequential removal of $[SiO_4]$ tetrahedra [19]. Likewise, in situ Raman spectra of glass particles also suggested that polymers might leave the solid during the leaching process [20]. Model calculations also permit such direct polymer particle detachment by breaking simultaneously several stressed/deformed chemical bonds in the solid which are the preferred reaction sites for water [21,22].

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To learn more about the dissolution process we monitored the silica content in the aqueous solution of a dissolving sodium silicate glass using in situ Raman spectroscopy. It will be shown that this method provides more reliable structural data than the traditional external test of samples and direct polymer detachment is the major route in the manufacturing of high ratio commercial sodium silicates.

A large variety of sophisticated techniques have been employed for characterizing the structure of silicates in aqueous solutions while avoiding chemical interferences with the system. A major driving force for these studies is the great technical importance but poor understanding of the synthesis of zeolites and related microporous materials [8,23–26]. Nanometer to micrometer sized zeolite-precursor colloid silicate particles have been characterized by small angle X-ray and neutron scattering (SAXS and SANS) [27–29], wide angle X-ray scattering (WAXS) [29], energy dispersive X-ray dispersion (EDXRD) [30], pulsed electron-nuclear double resonance (ENDOR) spectroscopy [31], dynamic light scattering [32], and other methods many of which were also used for in situ studies.

Only NMR and vibrational spectroscopy have been able to provide information on the structure of dissolved sub-nanometer sized silicate molecules thus far. High resolution (HR) ^{29}Si NMR spectroscopy [16,17,33–40] and its further advanced versions like 2D correlation spectroscopy (COSY) [25] and incredible natural abundance double quantum transfer experiment (INADEQUATE) [41] have been preferred for such investigations because these techniques can distinguish and quantitatively compare many versions of Q_2 and Q_3 connected [SiO_4] tetrahedra which have been assigned to about 30 different silicate rings [40,41]. The widely used Q_i nomenclature was introduced by Engelhard et al. [42,43] to mark the "*i*" number of direct connections of a [SiO_4] tetrahedron to other [SiO_4] neighbors. Unlike in solids, Q_4 connections have never been found in considerable amount in aqueous silicate solutions and the Q_0 and Q_1 species are not characteristic on the siloxane polymer structure. Unfortunately the HR ^{29}Si NMR is not yet applicable to follow the glass dissolution process in situ due to the need of ^{29}Si-enrichment and problems associated with sampling and mobility [39,44].

Albeit at lower resolution, Raman and IR spectra can also characterize the Q_i connectivities of silicates [16,17,45–49] and they have been also extensively used to identify ring vibrations in various silicates [50–69]. Both of these vibrational spectroscopic methods have been employed to follow zeolite synthesis in situ [29,56,61,64]. The Si–O vibration related Raman spectra of silicates are usually better resolved than the corresponding IR spectra and Raman can also characterize the O–Si–O bending vibrations of various siloxane ring systems at $<400\ cm^{-1}$ which are not accessible for the commonly used mid-IR spectrometers. A fiber optic cable connected Raman probe head can be submerged into the sticky, aqueous, occasionally turbulent, hot, and pressurized silicate solutions forming from commercial sized glass cubes while keeping the spectrometer in a large (up to about 100 m) distance. These capabilities render Raman spectroscopy unique to follow the glass dissolution process in situ.

2. Materials and methods

Approximately 3 cm edged cubes of commercial 3.22 ratio sodium silicate glass were treated with water at about 150 °C and 465 kPa (4.6 atm) in a 53 L stainless steel reactor until the solid disappeared. Silicate solutions with 0.2, 0.5, 1, 2, and 3 mol SiO_2/L were diluted from commercial N® silicate [1] solutions and equilibrated for at least 48 h.

Raman spectra were obtained on a Kaiser Holo Probe spectrometer (200 mW frequency doubled Nd:YAG laser source; CCD detector at −40 °C) connected to the autoclave via fiber optic cable. Further details of our spectroscopic capabilites and methods have been reported elsewhere [18,70–72].

The dissociation of dissolved silicate ions was determined both from electrical conductivity and ionselective electrode measurements using a YSI Model 32 conductometer and a Model 86-11 sodium selective electrode, respectively. Details of these measurements along with the determination of average molecular weight (AMW) using a Wescor Type 5500 osmometer have been reported before [18].

3. Results and discussion

The first Raman signals typically appeared in the liquid phase of glass dissolver after about ~20 min heating when the pressure attained steady state 55 psig (~4.6 atm). With the limited <1 min sampling time relatively noise-free spectra were obtained after about 35 min. As some normalized spectra in Fig. 1 illustrate, the relative intensity of Raman bands changed with the progress of dissolution but new bands did not appear. Note however that occasionally the peak positions changed within about $\pm 10\ cm^{-1}$ interval presumably as a consequence of some turbulence in the reactor.

The absolute intensities of spectra monotonically increased with time. Without specifying the various Raman bands in Fig. 1, one can focus on the most intense one near $1050\ cm^{-1}$ and set up the spectrometer for scanning the liquid automatically at preset time intervals. Fig. 2 shows an example for the growth of silicate concentration in the aqueous phase monitored in situ by the Raman spectrometer. The same trend

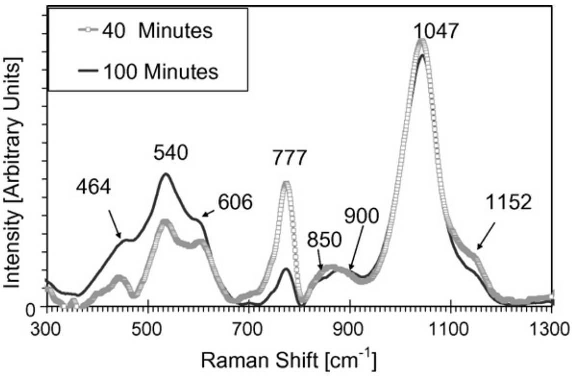

Fig. 1. In situ Raman spectra of the aqueous phase during the dissolution of 3.22 ratio sodium silicate glass after leaching for 40 and 100 min at 150 °C and 4.6 atm. Spectra were normalized to compare the relative size of bands.

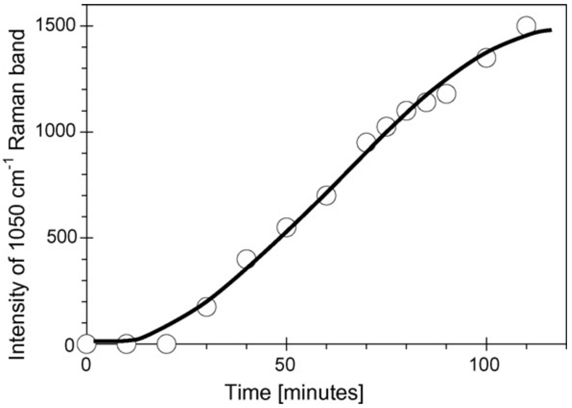

Fig. 2. The intensity of 1050 cm^{-1} Raman band indicates the progress of silicate dissolution.

was obtained from spectra of samples taken periodically from the autoclave and tested externally. Fig. 3 points to good linear correlation between the absolute intensity of the Raman band and the silicate concentration calculated from the specific gravity of samples measured externally. These experiments demonstrate that Raman spectroscopy is well suited for controlling the glass dissolution process.

We have not found an unambiguous guideline in the literature for the interpretation of Raman spectra of silicate solutions. One can calculate from data in Figs. 2 and 3 that the 40 min spectrum in Fig. 1 corresponds to an approximately 2 mol SiO_2/L silicate solution. Fig. 4 compares its Raman spectrum with those of a 2 and a 0.1 M Na_2SiO_3 solution which contain mostly $Na_2H_2SiO_4$ monomers, partly dissociated into $NaH_2SiO_4^{-}$ and $H_2SiO_4^{2-}$ ions, respectively [18]. The 930 cm^{-1} band can be assigned to ν_s symmetric stretching of HO–Si–ONa [18]. Its absence from the spectrum of the autoclave liquid suggests that it cannot contain $NaH_2SiO_4^{-}$ in measurable amount. The Raman shifts near 780 cm^{-1} are likely due to the δ_{as} asymmetric bending of polarizable (H)O–Si–O(H) groups that can be present on the surface of any silicate or silica including monomers and polymers [18,73–76]. These non-bridging oxygens can be negatively charged ions or their charge might be compensated with protons. The Raman scattering near 450 cm^{-1} is presumably associated with δ_s symmetric deformation vibrations of O–Si–O groups [18,73,74,76]. A Raman band near 600 cm^{-1} has been frequently reported in studies on Na_2SiO_3 solutions [18,77–81] and has been assigned to δ_{as} NaO–Si–ONa vibration in $Na_2H_2SiO_4$ monomers [18]. Considering that the 3.22 ratio silicate contains much less Na_2O per mole than does the Na_2SiO_3, it is reasonable to assume that the 608 cm^{-1} band in the autoclave fluid is at least partly associated with non-monomer silica related δ_{as} O–Si–O deformations. Many studies assign such bands to Q_2 type linear or three-member ring silicate structures in the solution [17,62,74,76,81–88].

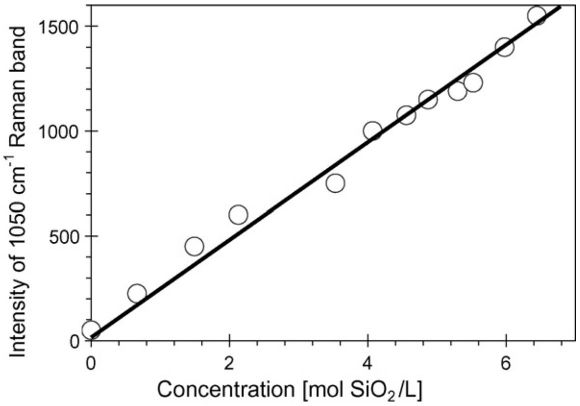

Fig. 3. The intensity of 1050 cm^{-1} Raman band correlates well with the concentration of silicate.

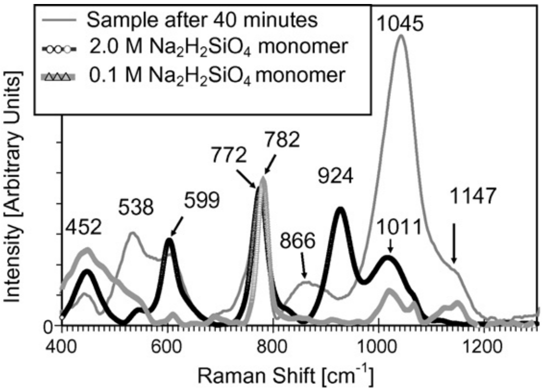

Fig. 4. Comparison of the in situ measured Raman spectrum of dissolved 3.22 ratio glass after 40 min of water treatment with the Raman spectra of 2 and 0.1 mol/L Na_2SiO_3 solutions. Normalized spectra.

Although one cannot exclude that some monomers are present in the autoclave, Fig. 4 clearly demonstrates that the most intense Raman bands of the autoclave liquid do not originate from any of the mentioned dissociated or non-dissociated sodium metasilicate monomers. The bands at around 1050 and 1150 cm^{-1} are typical delocalized or inter-tetrahedral (bridging) and localized or intra-tetrahedral ν_{as} phonon modes in crystalline silicates, respectively [76,89,90]. However, they usually appear only in the IR spectra which are more sensitive for asymmetric vibrations than the Raman [18,71,72,76]. Our nanoparticles do not allow long range phonon vibrations hence the intense 1050 cm^{-1} Raman band must indicate highly polarizable, asymmetric Si–O bonds which occur in Q_1 and Q_2 type [SiO_4] tetrahedra. Likewise, the 1150 cm^{-1} band has been suggested to represent ν_{as} Si–O–Si bridging vibrations in a 3D network of Q_3 and Q_4 type [SiO_4] tetrahedra [18,51,81,91,92]. Bass and Turner [16,17] associated the increasing IR absorption bands in the 850–1200 cm^{-1} range with increasing bond complexity of dissolved silica nanoparticles. On the other hand, it was shown recently that the 1145 cm^{-1} band is the most intense vibration in the 200–1300 cm^{-1} range of Raman spectra of crystalline sodium metasilicate $Na_2SiO_3\cdot 9H_2O$ which certainly does not contain linked [SiO_4] tetrahedra hence this band was associated with ν_{as} Si–O$^-$ and/or Si–OH vibrations [18]. Thus, the Raman scatterings near 1150 cm^{-1} might represent some hydrated metasilicate crystallites in the solution.

The relative size of δ_{as} (H)O–Si–O(H) bending vibration at 777 cm^{-1} decreases with increasing concentration (Fig. 1) which suggests an increasing number of connections between [SiO_4] tetrahedra. This is in line with the increased relative intensities of 464, 540, and 606 cm^{-1} bands that can be associated with deformation vibrations of 6, 4, and 3 [SiO_4]-member rings, respectively [18,62,65,72,88,93–96]. Based on the average molecular weight data (vide infra) most dissolved particles likely contain a combination of double six, double four, six-three, etc. rings. The intense 540 cm^{-1} band hints at the dominating presence of four member rings.

The broad band between 800 and 950 cm^{-1} is also missing from the spectra of sodium metasilicate monomers (Fig. 4). It is likely associated with ν_s Si–O stretches which must be scarce in the inherently asymmetric bond environment of silica nanoparticles. McMillan [75] associated a band at around 900 cm^{-1} with terminal $–SiO_3^{3-}$ (Q_1 type) groups and one at 850 cm^{-1} with fully dissociated SiO_4^{4-} (Q_0 type) monomer ions in molten silicates. However, there is a low probability that the dissociation of silica particles would go beyond $H_2SiO_4^{2-}$ in alkaline aqueous solutions [2,3,18].

Thus, the overall takeaway from these in situ Raman spectroscopic measurements is that the dissolution of sodium silicate glass proceeds mainly via detachment of polymer silicate particles from the solid and only very little monomer enters the aqueous phase. Although the Raman signal was below the detection limit during the first 20 min of the dissolution process, there is no reason to believe that monomers prelude the appearance of polymers during this period because this does not happen even in the course of the measurable dissolution process from 20 to 100 min when the overwhelming majority of glass goes into solution. Moreover, even the partial transition of monomers into polymers in concentrated solutions takes place only after weeks of storage [18].

The external Raman measurements of samples taken in a traditional way from the same autoclave also confirmed the overwhelming presence of polymers at every stage of the dissolution process. However, there was a surprising difference between the in situ and external Raman spectra. As an example in Fig. 5 illustrates, the 1142 cm^{-1} vibration is substantially more intense in the latter one, i.e., it contains an increased number of freely vibrating, presumably terminal $Si–O^-$ and/or Si–OH bonds which might be generated by increased dissociation of Na^+ ions and/or hydrolysis of Si–O–Si bonds. This is in line with the significant decrease of the δ_{as} 606 cm^{-1} band which can be related to the above discussed vibrations of non-dissociated NaO–Si–ONa bonds and/or vibrations of the most stretched, three member rings. These changes along with the shifts of other deformation vibrations toward lower wavenumbers, i.e., toward larger, especially four member (540 cm^{-1}) rings, must be caused by the quick cooling and/or pressure drop of samples taken from the autoclave because the Raman spectra of slowly cooled, commercial, 3.22 ratio sodium silicate solutions are fairly similar to the in situ measured Raman spectra.

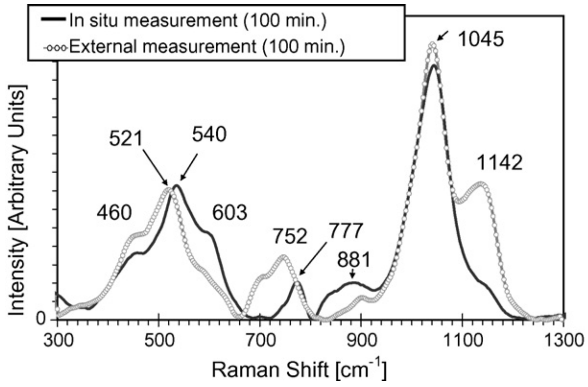

Fig. 5. Comparison of in situ and externally measured Raman spectra of the aqueous phase after 100 min leaching of 3.22 ratio glass with water at 150 °C and 4.6 atm. Normalized spectra.

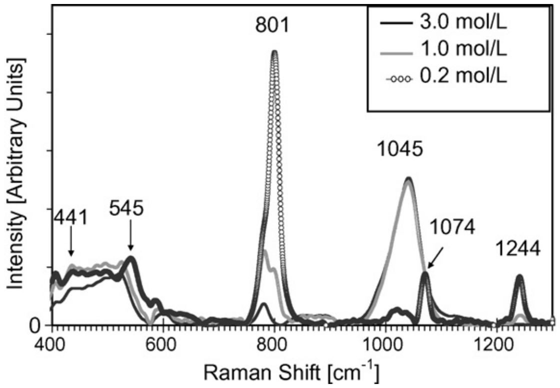

Fig. 6. Raman spectra of variously diluted commercial N®-silicate solutions. Normalized spectra.

Fig. 6 shows the Raman scatterings of a commercial 3.22 ratio N-silicate at different dilutions. Since it was shown that the dissociation level can dramatically change the Raman spectra of aqueous Na_2SiO_3 solutions [18], we measured the dissociation degrees of these N-silicates as well. Fig. 7 shows that the dissociation of this high ratio silicate lags slightly behind the dissociation levels of NaOH and Na_2SiO_3 in the 3–0.2 M concentration range. Fig. 8 indicates that in contrast to the all monomer Na_2SiO_3 solutions, the dilution of N-silicate

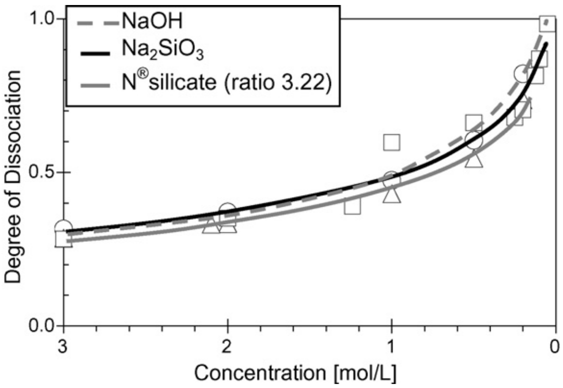

Fig. 7. Concentration dependent dissociation in aqueous solutions of various sodium compounds. Concentration units for silicates and sodium hydroxide are [mol SiO_2/L] and [mol NaOH/L], respectively. The dissociation is related to Na^+ ions dissociating from the molecule. One represents the value when every sodium ion is in the solution and zero represents the value when zero Na^+ is in the solution.

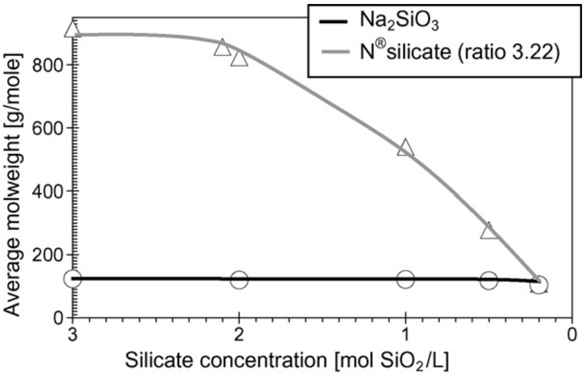

Fig. 8. Variation of the average molweight of silica nanoparticles as a function of concentration in aqueous solutions of Na_2SiO_3 and N®-silicate.

reduces dramatically its average molweight (AMW) from about 10.5 to 1 [SiO_4] tetrahedra/mol. This split of Si–O–Si bonds is reflected in Fig. 6 as increasing relative intensity of δ_{as} (H)O–Si–O(H) bands at 801 cm^{-1} and diminishing ν_{as} and δ_s vibrations at 1045 cm^{-1} and 400–650 cm^{-1}, respectively. The 10.5 [SiO_4]/mol AMW in the 3 mol SiO_2/mol solution fits well to a near 50–50% split of particles with double six (12 × [SiO_4]) and double four (8 × [SiO_4]) ring systems. Such nanoslabs are considered to be thermodynamically more stable than the corresponding straight chains and can serve as primary building blocks for the synthesis of zeolites [44,65,94–98]. In agreement with this view, we have not found a Raman band around 973 cm^{-1} which is the most intense vibration of the chain-structured crystalline Na_2SiO_3 [18]. To explain the molweight change with dilution, one can assume that the more concentrated solutions do not have sufficient water for reaction and hydration of an increasing number of anions as proposed before [18]. This view is also in line with the well known practical experience that solutions of N-silicate and other high ratio silicates which, as we just saw, are made directly from polymer particles can be stable for over 1 year while the similarly concentrated but monomer based Na_2SiO_3 solutions tend to polymerize within a few weeks [1,18].

Fig. 9 compares the Raman spectra of 0.2 mol/L monomer silicate solutions obtained from Na_2SiO_3 and the high ratio N-silicate. This latter one seems to contain some crystalline silicates for which bands near 1074 and 1244 cm^{-1} are characteristic transverse-optic and longitudinal optic (TO-LO) ν_{as} O–Si–O vibration pairs [18,76,99,100]. The remaining 450–550 cm^{-1} bands suggest predominant six-ring and four-ring structures for these crystals. The more intense 1030 cm^{-1} band in the Raman spectrum of the Na_2SiO_3 solution might indicate that it contains more $Si(OH)_2O_2^{2-}$ ions than the other material [18]. This is understandable considering the large amount of Na^+ to compensate the charge of these anions in the Na_2SiO_3. Probably also the lower number of $^-$O–Si–O$^-$ bonds and/or higher number of non-dissociated HO–Si–OH bonds are responsible for the shift of the δ_{as} vibration from about 777 to 801 cm^{-1} in the solutions of Na_2SiO_3 and N-silicate, respectively. At certain concentrations we have observed these Raman bands simultaneously in solutions made from $Na_2SiO_3 \cdot 9H_2O$ [18].

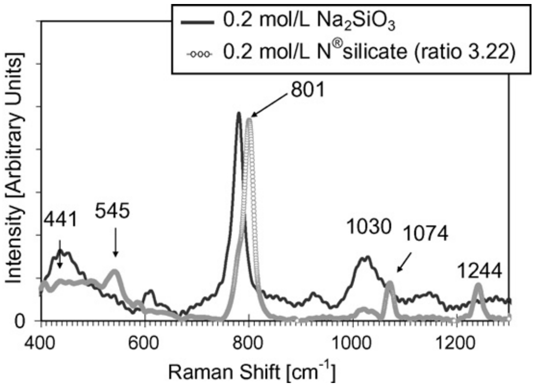

Fig. 9. Raman spectra of monomer silicates in 0.2 mol/L aqueous solutions of Na_2SiO_3 and N®-silicate.

4. Conclusions

1. Raman spectroscopy is adequate to measure the concentration of dissolved silicates and can be used in situ for controlling the dissolution of sodium silicate glasses in water.
2. The dissolution of 3.22 ratio sodium silicate glasses proceeds via direct detachment of ~900 g/mole AMW polymer silicate particles from the solid into the solvent. These nanoparticles seem to contain mostly double and mixed 6, 4, and 3 silicate rings, similar to the commercial N-silicate solutions. Quick quenching leads to less compact silicate structures containing more asymmetric, polarizable Si–O$^-$ and Si–OH bonds than the N-silicate.
3. Dilution of 3 mol/L N-silicate solutions to 0.2 mol/L results in hydrolysis into monomers. Only about 50% of the total sodium is dissociated to Na^+ even in this diluted material which must also contain largely non-dissociated H_4SiO_4 particles.

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References

[1] www.pqcorp.com.
[2] J.G. Vail, Soluble Silicates, ACS Monograph Ser, Reinhold Publ., NY, 1952.
[3] R.K. Iler, The Chemistry of Silica J., Wiley & Sons, NY, 1979.
[4] H.E. Bergna, W.O. Roberts (Eds.), Colloidal Silica, Surfactant Science Series 131, CRC Taylor & Francis, Boca Raton/London/NY, 2006.
[5] H.H. Weldes, K.R. Lange, Ind. Eng. Chem. 61 (29) (1969).
[6] N. Zotov, H. Keppler, Chem. Geol. 184 (2002) 71.
[7] E. Senderov, R. Hinchey, I. Halasz, U. S. Pat. Appl. Publ. Provisional Ser No. 387 945 (2003).
[8] J.D. Rimer, J.M. Fedeyko, D.G. Vlachos, R.F. Lobo, Chem. Eur. J. 12 (2006) 2926.

[9] B.C. Bunker, D.R. Tallant, T.J. Headley, G.L. Turner, R.J. Kirkpatrick, Phys. Chem. Glasses 29 (1988) 106.
[10] P.W.J.G. Wijnen, T.P.M. Beelen, J.W. deHaan, C.P.J. Rummens, L.J.M. van de Ven, R.A. van Santen, J. Non-Cryst. Solids 109 (1989) 85.
[11] I. Horvath, Olaj Szappan Kozmetika 39 (1990) 112.
[12] P.M. Dove, J.D. Rimstidt, Rev. Miner. 29 (1994) 259.
[13] A.C. Lasagna, Rev. Mineral. 31 (1995) 23.
[14] S.A. Gold, V.A. Burrows, J. Electrochem. Soc. 151 (2004) G762.
[15] P.M. Dove, N. Han, J.J. De Yoreo, PNAS 102 (2005) 15357.
[16] J.L. Bass, G.L. Turner, J. Phys. Chem. 101B (1997) 10638.
[17] J.L. Bass, G.L. Turner, M.D. Morris, Macromol. Symp. 140 (1999) 263.
[18] I. Halasz, M. Agarwal, R. Li, N. Miller, New J. Chem., submitted for publication.
[19] B.C. Bunker, T.J. Headley, S.C. Douglas, Mat. Res. Soc. Symp. Proc. 32 (1984) 41.
[20] G.J. Exarhos, W.E. Conaway, J. Non-Crystaline Solids 55 (1983) 445.
[21] T.A. Michalske, B.C. Bunker, J. Appl. Phys. 56 (1984) 2686.
[22] L.J. Criscenti, J.D. Kubicki, S.L. Brantley, J. Phys. Chem. A 110 (2006) 198.
[23] J.L. Provis, D.G. Vlachos, J. Phys. Chem. B 110 (2006) 3098.
[24] J. Osswald, K.T. Fehr, J. Mater. Sci. 41 (2006) 1335.
[25] C.T.G. Knight, J. Wang, S.D. Kinrade, Phys. Chem. Chem. Phys. 8 (2006) 3099.
[26] C.H. Rüscher, N. Salman, J.-Chr. Buhl, W. Lutz, Micropor. Mesopor. Mater. 92 (2006) 309.
[27] J.N. Watson, L.E. Iton, R.I. Keir, J.C. Thomas, T.L. Dowling, J.W. White, J. Phys. Chem. B 101 (1997) 10094.
[28] J.M. Fedeyko, D.G. Vlachos, R.F. Lobo, Langmuir 21 (2005) 5197.
[29] D. Grandjean, A.M. Beale, A.V. Petukhov, B.M. Weckhuysen, J. Am. Chem. Soc. 127 (2005) 14454.
[30] A.T. Davies, G. Sankhar, C.R.A. Catlow, S.M. Clark, J. Phys. Chem. B 101 (1997) 10115.
[31] D. Arieli, A. Delabie, M. Groothaert, K. Pierloot, D. Goldfarb, J. Phys. Chem. B 106 (2002) 9086.
[32] V.R. Rani, R. Singh, P. Payra, P.K. Dutta, J. Phys. Chem. B 108 (2002) 20465.
[33] E. Lippmaa, M. Magi, A. Samonson, G. Engelhardt, -R.A. Grimmer, J. Am. Chem. Soc. 102 (1980) 4889.
[34] R.K. Harris, C.T.G. Knight, J. Chem. Soc. Faraday Trans. 2 (79) (1983) 1525.
[35] R.K. Harris, C.T.G. Knight, J. Chem. Soc. Faraday Trans. 2 (79) (1983) 1539.
[36] A.V. McCormick, A.T. Bell, C.J. Radke, Zeolites 7 (1987) 183.
[37] A.V. McCormick, A.T. Bell, Catal. Rev. Sci. Eng. 31 (1989) 97.
[38] W.J.G. Wijnen, T.P.M. Beelen, R.A. van Santen, Surfactant Sci. Ser. 131 (2006) 597.
[39] C.C. Egger, A.W. Anderson, G.J.T. Tiddy, J.L. Casci, Phys. Chem. Chem. Phys. 7 (2005) 1845.
[40] H. Cho, A.R. Felmy, R. Craciun, J.P. Keenum, N. Shah, D.A. Dixon, J. Am. Chem. Soc. 128 (2006) 2324.
[41] M. Haouas, F. Taulelle, J. Phys. Chem. B 110 (2006) 3007.
[42] G. Engelhardt, H. Jancke, D. Hoebbel, D. Wiecker, Z. Chem. 14 (1974) 109.
[43] G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel, W. Wieker, Z. Anorg. Allg. Chem. 418 (1975) 17.
[44] J. Perlo, V. Demas, F. Casanova, C.A. Meriles, J. Reimer, A. Pines, B. Blümich, Science 308 (2005) 1279.
[45] B.O. Mysen, J.D. Frantz, Chem. Geol. 96 (1992) 321.
[46] N. Umesaki, M. Takahashi, M. Tatsumisago, T. Minami, J. Mater. Sci. 28 (1993) 3473.
[47] J.D. Frantz, B.O. Mysen, Chem. Geol. 121 (1995) 155.
[48] V.L. Zholobenko, S.M. Holmes, C.S. Cundy, J. Dwyer, Micropor. Mater. 11 (1997) 83.
[49] P. Colomban, M.-P. Etcheverry, M. Asquier, M. Bounichou, A. Tournie, J. Raman Spectrosc. 37 (2006) 614.
[50] B.D. Saksena, K.C. Agarwal, G.S. Jauhri, Trans. Faraday Soc. 59 (1963) 276.
[51] W.C. Beard, Adv. Chem. Ser. 121 (1973) 162.
[52] M.V. Borisov, B.N. Ryzhenko, Geokhimiya (1974) 1367.
[53] C.S. Blackwell, J. Phys. Chem. 83 (1979) 3251.
[54] C.S. Blackwell, J. Phys. Chem. 83 (1979) 3257.
[55] F. Roozenboom, H.E. Robson, S.S. Chan, Zeolites 3 (1983) 321.
[56] W.R. Moser, J.E. Cnossen, A.W. Wang, S.A. Krouse, J. Catal. 95 (1985) 21.
[57] E.J.J. Groenen, C.A. Emeis, J.P. van den berg, P.C. de Jong-Versloot, Zeolites 7 (1987) 474.
[58] H. Yoshino, K. Kamiya, H. Nasu, J. Non-Cryst. Solids 126 (1990) 68.
[59] C.C. Perry, X. Li, D.N. Waters, Spectrochim. Acta 47A (1991) 1487.
[60] M. Bartsch, P. Bornhauser, G. Calzaferri, R. Imhof, Vib. Spectrosc. 8 (1995) 305.
[61] D.C. Calabro, E.W. Valyocsik, F.X. Ryan, Micropor. Mater. 7 (1996) 243.
[62] A. Pasquarello, R. Car, Phys. Rev. Lett. 80 (1998) 5145.
[63] W. Mozgawa, M. Sitarz, M. Rokita, J. Mol. Struct. 511 (1999) 251.
[64] C.E.A. Kirschhock, R. Ravishankar, F. Verspeurt, P.J. Grobet, P.A. Jacobs, J.A. Martens, J. Phys. Chem. B 103 (1999) 4965.
[65] Y. Yu, G. Xiong, C. Li, F.-S. Xiao, Micropor. Mesopor. Mater. 46 (2001) 23.
[66] H. Mikosch, E.L. Uzunova, G.St. Nikolov, J. Phys. Chem. B 108 (2004) 13200.
[67] B. Mihailova, S. Mintova, K. Karaghiosoff, T. Metzger, T. Bein, J. Phys. Chem. B 109 (2005) 17060.
[68] B. Mihailova, V. Valtchev, S. Mintova, A.-C. Faust, N. Petkov, T. Bein, Phys. Chem. Chem. Phys. 7 (2005) 2756.
[69] H.Y. Jung, R.K. Gupta, E.O. Oh, Y.H. Kim, C.M. Whang, J. Non-Cryst. Solids 351 (2005) 372.
[70] I. Halasz, M. Agarwal, E. Senderov, B. Marcus, Appl. Catal. A: Gen. 241 (2003) 167.
[71] I. Halasz, M. Agarwal, E. Senderov, B. Marcus, W. Cormier, Stud. Surf. Sci. Catal. 158 (2005) 647.
[72] I. Halasz, M. Agarwal, B. Marcus, W. Cormier, Micropor. Mesopor. Mater. 84 (2005) 318.
[73] G.B. Wilmot, The Raman spectra and structure of silica and the soda-silica glasses, Ph.D. Thesis, MIT, 1951.
[74] A.N. Lazarev, Vibrational Spectra and Structure of Silicates, c/b Consultants Bureau, NY/London, 1972.
[75] P. McMillan, Am. Miner. 69 (1984) 622.
[76] R.A. van Santen, D.L. Vogel, Adv. Solid State Chem. 1 (1989) 151.
[77] D. Fortnum, J.O. Edwards, J. Inorg. Nucl. Chem. 2 (1956) 264.
[78] J.E. Earley, D. Fortnum, A. Wojcicki, J.O. Edwards, J. Am. Chem. Soc. 81 (1959) 1295.
[79] E. Freund, Bull. Soc. Chim. Fr. 7–8 (1973) 2238.
[80] A. Mariangeli, M.A. Morelli, R. Simoni, A. Bertoluzza, Can. J. Spectrosc. 23 (1978) 173.
[81] J.L. Bass, ACS Symp. Ser. 194 (1982) 17.
[82] F.L. Galeener, Kinam 4 (Serie C) (1982) 83.
[83] D.W. Matson, S.K. Sharma, J.A. Philpotts, J. Non-Cryst. Solids 58 (1983) 323.
[84] F.L. Galeener, R.A. Barrio, E. Martinez, R.J. Elliott, Phys. Rev. Lett. 53 (1984) 2429.
[85] F.L. Galeener, in: J.A. Blackman, J. Taguena (Eds.), Disord. Condens. Matter. Phys. 57HXAE Conference, Oxford Univ. Press, Oxford, UK, 1991, p. 45.
[86] R.A. Barrio, F.L. Galeener, E. Martinez, R.J. Elliott, Phys. Rev. B. 48 (1993) 15672.
[87] H. Imai, M. Yasumori, H. Hirashima, K. Awazu, H. Onuki, J. Appl. Phys. 79 (1996) 8304.
[88] Y. Borodko, J.W.A. Ager III, G.E. Marti, H. Song, K. Niesz, G.A. Somorjai, J. Phys. Chem. B 109 (2005) 17386.
[89] J.J. Fripiat, A. Leonard, N. Barake, Bull. Soc. Chim. Fr. (1963) 122.
[90] E.M. Flanigen, H. Kathami, H.A. Szymanski, Advances in Chemistry Series, 101, Am. Chem. Soc, Washington DC, 1971, p. 16.
[91] E.R. Lippincott, A.V. Valkenburg, C.E. Weir, E.N. Bunting, J. Res. Natl. Bureau Stand. 61 (1958) 2885.
[92] R. Szostak, Molecular Sieves, van Nostard Reinhold Catalysis Series (1989).

[93] P.K. Dutta, D.C. Shieh, Zeolites 5 (1985) 135.
[94] P.K. Dutta, D.C. Shieh, M. Puri, J. Phys. Chem. 91 (1987) 2332.
[95] H. Mikosh, E.L. Uzunova, G.St. Nikolov, J. Phys. Chem. B108 (2004) 13200.
[96] H.Y. Yung, R.K. Gupta, E.O. Oh, Y.H. Kim, C.M. Whang, J. Non-Cryst. Solids 351 (2005) 372.
[97] C.E.A. Kirschhock, R. Ravishankar, L. van Looveren, P.A. Jacobs, J.A. Martens, J. Phys. Chem. B103 (1999) 4972.
[98] S. Caratzoulas, D.G. Vlachos, M. Tsapatsis, J. Am. Chem. Soc. 128 (2006) 596.
[99] C.T. Kirk, Phys. Rev. B38 (1988) 1255.
[100] P. Lange, J. Appl. Phys. 66 (1989) 201.