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Thermochemistry of Aqueous Silicate Solution Precursors to Ceramics

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A quantitative understanding of the thermochemistry of silicate solution systems is necessary for the design, optimization and control of sol-gel, colloid and zeolite preparations. This review is intended to be a compendium of ready information for the growing number of chemical engineers active in solution-based materials synthesis. Experimental measurements of silica solubility, silicate speciation and silanol deprotonation in aqueous solutions are summarized and critiqued. The thermochemical properties of monomeric and dimeric silicate anions are also assessed. The trends that are then evident are compared with expectations from simplistic gas-phase molecular orbital calculations to illustrate the importance of solvation. Finally, the equilibrium behavior of simple silicate oligomers is rationalized, and the future direction to quantitative modeling of the behavior of more complex oligomers is suggested.

Need for Review of Silicate Thermochemistry

A fundamental premise of chemical engineering is that knowledge of thermodynamics, kinetics and transport can be utilized for rational, quantitative design of industrial processes. However, there is a serious lack of readily available quantitative thermochemical and kinetic data necessary to design solution-based ceramics syntheses. Here aqueous silicate thermochemistry is reviewed comprehensively. While this review is geared toward those practicing in the field, we refer those new to the field to several excellent earlier works (e.g., Iler, 1979; Barrer, 1982; Szostak, 1989; Brinker and Scherer, 1990) for a thorough introduction to issues related to sol-gel processing and molecular-sieve synthesis.

Recent reviews of trends in the designed synthesis of zeolites (Guth, 1992; Davis and Lobo, 1992; Feijen et al., 1994) and silica gels and colloids (cf. Bergna, 1994; Heaney et al., 1994) emphasize that future success in the design and control of synthesis processes will depend on a detailed and quantitative understanding of the distribution of oligomeric precursor species in these solutions. For example, let us consider the synthesis of zeolites. Even a clear aluminosilicate solution phase contains a host of silicate and aluminosilicate anions undergoing fast exchange, so that these species may be considered in equilibrium with each other on the timescale of zeolite growth processes. During solution-mediated crystal growth it is often assumed that the crystal growth rate depends on a concentration of a distinct aluminosilicate precursor in the adjacent solution phase. To make the precursor concept quantitative and useful, it is necessary to tie the precursor concentration to the solution composition, and this can only be accomplished using physically relevant models of silicate and aluminosilicate speciation in aqueous solutions (Šefčík and McCormick, 1997b). In situations where the product is formed by rearrangement of the network of a precursor gel (Davis and Lobo, 1992), the equilibria among the various liquid-phase precursors must become quantitatively understood for two reasons: these equilibria no doubt influence the structural evolution of the metastable gel, and understanding these equilibria among simple structures is prerequisite to and instructive in modeling the stability and structure of gels.

In this review we restrict our attention to the thermochemistry of stable aqueous solutions. Although several workers have characterized series of silicate solutions and have discussed the thermochemistry and kinetics of possible reaction networks (Kinrade and Swaddle, 1988; Knight et al., 1988), little attention has been devoted to explaining the thermochemistry to aid prediction of the behavior of complex and/or as-yet-unassigned structures in varying process conditions.

Rationalizing the thermochemistry of even the simplest species can yield a great deal of insight into the stability patterns of larger oligomers and of polymeric gels. Thus, we fo-

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cus on equilibria of reactions in aqueous silicate solution systems at room temperature, where we analyze equilibria between monomer and dimer anions in stable alkaline aqueous silicate solutions. To consider the reasons for the equilibrium behavior of simple silicate oligomers and thereby to anticipate the behavior of more complex structures, we qualitatively compare the observed thermochemical trends to expectations from gas-phase semiempirical molecular orbital calculations and a simple ion-solvation theory.

Silicate Speciation: What Reactions Should be Considered?

Several methods have been used to decide what species exist in solutions, and hence what types of reactions are possible and should be considered when modeling aqueous silicate solutions.

Indications from solubility studies

Thanks to careful attention from geological and inorganic chemists, the true solubility limit (as opposed to the colloidal stability limit) of silica has been measured in aqueous solutions containing various electrolytes and with various pH values. With the exception of vanadia, silica is the most soluble of the metal oxides at their respective isoelectric points (Baes and Mesmer, 1976) with a minimum solubility of 2 mM in pure water. At near-neutral pH, dissolved silica is present primarily as monomeric uncharged silicic acid $Si(OH)_4$. Hence we express the solubility equilibrium of amorphous silica as

$$SiO_2(\text{amorph.}) + 2H_2O \leftrightarrow Si(OH)_4.$$

The solubility of $Si(OH)_4$ depends strongly on the solvent dielectric constant, but only mildly on ionic strength (Dandurand and Schott, 1987).

The total silica solubility [including all dissolved forms, in addition to $Si(OH)_4$] is highly pH dependent. Solubility studies in aqueous solutions delineate a region in the composition field [Si]-pH where silicate solutions are truly homogenous and where reaction equilibria among the species present are established rapidly, as shown in Figure 1 (Alexander et al., 1954; Andersson et al., 1982; Zarubin and Nemkina, 1990). At moderate pH (between 1 and 9) most of the dissolved silica in aqueous solutions is present primarily as the monomeric silicic acid $Si(OH)_4$. At pH > 9 this monomer undergoes significant deprotonation and, with increasing concentration, condensation to oligomers (further discussion of processes involved in silica solubility can be found in, for example, Iler, 1979). Even these simple facts were not entirely evident until the application of Raman (e.g., Freund, 1973) and NMR (e.g., Harris and Newman, 1977) spectroscopy. We note below that there is still doubt in some cases as to the structure of certain polyanionic silicate species in aqueous solutions. In mixed-solvent systems the equilibrium speciation of even simple oligomers remains under investigation.

Indications from NMR

^{29}Si NMR spectroscopy has been especially useful for measuring the concentrations of specific silicon sites without disturbing the system. ^{29}Si NMR peaks in spectra of aqueous solution are separated into five bands according to their first coordination shell (owing to esterification, the bands can overlap substantially in mixed-solvent systems). Finer ^{29}Si chemical shifts allow one to distinguish silicon sites belonging to a number of specific small oligomers. The use of NMR relaxation and correlation techniques (Harris and Knight, 1983a,b; Knight, 1988; Knight et al., 1989) have led to the identification of peaks of more than 20 silicate species, including oligomers with up to 12 Si atoms. Even so, some structures remain to be definitively assigned. Many ^{29}Si NMR peaks remain without any specific assignment beyond the first coordination shell. Though Raman assignments remain somewhat ambiguous, the presence of cyclic structures has been clearly established (Freund, 1973).

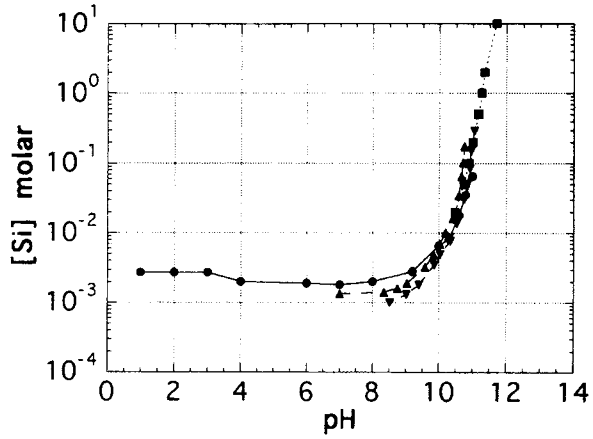

Figure 1. Amorphous silica solubility vs. pH in NaCl aqueous solutions with varying ionic strength.

Circles: ionic strength, $I = 0$ (Alexander et al., 1954); squares: $I > 3$ M (Andersson et al., 1982); triangles: $I = 1$ M (Zarubin and Nemkina, 1990); inverted triangles: $I = 3$ M (Zarubin and Nemkina, 1990).

Even with these limitations, various workers have obtained quantitative distributions of silicate oligomers for a wide range of stable (reviewed in McCormick and Bell, 1989; Swaddle et al., 1994; and Sjöberg, 1996) and metastable solutions (reviewed in Šefčík and McCormick, 1997a). We recommend the principal references found in these reviews, particularly Harris and Knight (1983b); McCormick et al. (1987); Pouxviel et al. (1987); Devreux et al. (1990); Sanchez et al. (1996). It is clear from the literature that the silicate speciation is strongly influenced by pH, by organic cosolvents, and by the specific structure of dissolved cations (e.g., tetraalkylammonium) (Hendricks et al., 1991).

Besides NMR, light scattering and colligative property measurements have also been used to detect silicate oligomers of varying size (cf. Iler, 1979). The distribution of silicate oligomers has been quantitatively determined by gas chromatography and mass spectroscopy of silylated oligomers (Dent Glasser and Lachowski, 1980; Ray and Plaisted, 1983). These studies confirm many of the NMR assignments, particularly in that the dissolved species are compact polyoxoanions, not extended polymer structures.

Indications from potentiometry

Potentiometric studies have been employed to quantify the degree of deprotonation of the silanol groups. The average charge per silicon $\langle Z \rangle$ has been evaluated with pH for various dilute solutions. At low Si concentration these curves become independent of concentration, so it was deduced that only monomers are present. Working in this low concentration limit, Busey and Mesmer (1977) and Sjöberg et al. (1981; 1983) accurately determined the first two deprotonation constants of the monomeric silicic acid as a function of temperature and of ionic strength.

For somewhat higher Si concentrations, the behavior of $\langle Z \rangle$ with pH clearly indicates the presence of oligomers. In fact, the wide scatter of previously published acidity data for monomeric silicic acid has been attributed (Ingri, 1978) to the use of solutions that were too concentrated to ensure the presence only of monomer, coupled with the use of speciation models that were overly simplistic. It was originally assumed by Lagerström (1959) and Ingri (1959) that there is only a single predominant oligomer—the cyclic tetramer. Moreover, it was assumed that there were only two possible negative charges: -2 or -4. Under these assumptions even the best fit of the speciation model to the experimental data left much room for improvement.

Previously proposed reaction schemes

Sjöberg and coworkers (1985) used ^{29}Si NMR in conjunction with potentiometry to identify the full range of oligomers in solutions of concentration similar to those studied by Lagerström and Ingri. By NMR they identified and measured the concentration of the silicate monomer, dimer, cyclic trimer, and cyclic tetramer. Using potentiometry they determined a number of oligomerization equilibrium constants β_{-pq} for reactions of the type

$$q\ \mathrm{Si(OH)_4} \xleftrightarrow{\beta_{-pq}} p\mathrm{H}^+ + q\text{−mer}^{p-}.$$

They found, however, that the total intensity of the NMR signal from these species accounted for only half of the silicon present (based on a calibration with a concentrated sample). To account for the missing signal and to fit the potentiometric data, they suggested that the most predominant species in solution was probably a linear or branched tetramer. However, it is not clear why the signal from such a tetramer would go undetected in the ^{29}Si NMR spectra, even when a ^{29}Si enriched silicon source was used. [The pulse repetition time was apparently long enough to allow for complete relaxation of Si nuclear spins in solvated oligomers; the spin lattice relaxation times T_1 were evaluated by the inversion recovery method and were reported as between 20 and 25 s for the monomer, dimer, and cyclic trimer. The relaxation times in concentrated sodium silicate solutions are substantially lower; $T_1 = 4$ to 5 s for small oligomers (including tetramers) and $T_1 = 12$ to 15 s for larger cage structures at 25°C (Kinrade and Swaddle, 1986). However, the presence of large cage structures in dilute solutions, such as those studied by Sjöberg and coworkers (1985), is not likely (see below).]

In a similar study, but now of concentrated silicate solutions (Svensson et al., 1986), a large number of oligomerization equilibrium constants were estimated, and these constants reasonably reproduce several experimental silicon connectivity distributions with pH between 11 and 14. However, it is not clear whether the apparent constants found are necessarily unique, and the constants reported do not predict the observed depolymerization of silicate oligomers with increasing silicate ratio $R = \mathrm{SiO_2/Na_2O}$ at high pH (cf. Engelhardt et al., 1975).

Caullet and Guth (1989) assembled a model that reproduced the distribution of silicate anions in several solutions at pH between 11 and 14 with a reasonable success. The model included condensation reactions between uncharged silicic acid and monomers, leading to various oligomers and deprotonation reactions of monomers and oligomers. A number of simplifications, however, were employed. First, the condensation equilibrium constants were assumed to be independent of the structure of the oligomer. Second, at a given silicon site, the free energy of deprotonation was assumed to increase linearly for each successive deprotonation, according to a linear free-energy relationship. Finally, the free energy of successive deprotonation occurring on neighboring silicon sites was assumed to follow an empirical algebraic form, whose physical origin is as yet unclear. The resulting model does accurately account for the distribution of small anions in several dilute alkaline solutions, but it does not accurately predict the distribution of larger oligomers.

Reactions of Monomers and Dimers

We want to rationalize thermochemistry of aqueous silicates so that we do not need the ad hoc assumptions of previous solution models. We will now consider separately and in detail two different classes of reactions—condensation and deprotonation—of small silicate oligomers—monomers and dimers—in aqueous solutions.

Condensation

Rationalizing the behavior of even monomers and dimers can yield a great deal of insight into the stability patterns of larger oligomers and perhaps even gels. Since the number of possible species in the monomer–dimer subsystem is small (5 monomers and 7 dimers), the number of independent equilibrium constants is only 11. For the purpose of equilibrium studies one can choose to write the reactions however one likes, regardless of actual reaction mechanisms involved. By restricting our attention to a few reaction equilibrium constants rather than to literally thousands that would be needed for complex solutions, we ensure both accuracy and the ability to deduce meaningful trends.

The equilibrium constant K for the dimerization reaction (N.B.: written for uncharged species),

$$2\mathrm{Si(OH)_4} \xleftrightarrow{K} \mathrm{Si_2O(OH)_6} + \mathrm{H_2O}$$

is best identified unambiguously by minimizing the content of charged monomers and dimers. In this way one avoids coupling between condensation and deprotonation equilibria (Sjöberg et al., 1985). Cary and coworkers (1982) examined ^{29}Si NMR of a very dilute ^{29}Si-enriched silicate solution ([Si] = 0.0016 M, very low ionic strength) at equilibrium with amorphous silica at pH = 7 and temperature 25°C. They found that about 6% of silicon was in the form of dimer. Moreover, Sjöberg and coworkers (1981) showed that in these conditions these species are essentially neutral. Therefore, the dimerization equilibrium constant can be correctly estimated as $K = 20$.

Applin (1987) suggested that because the apparent diffusion coefficient of very dilute silicic acid ([Si] < 0.0015 M, pH = 5.5, $t = 25°C$) decreased with increasing silicic acid concentration, an equilibrium distribution of silica between monomer and dimer must be present. Using several simplifying assumptions, K was estimated at 300. This dimerization constant estimate seems much too high for two reasons. First, it corresponds to about 40%(!) of silicon in the form of dimer at [Si] = 0.0015 M (cf. Dove and Rimstidt, 1994, where this is suggested as reasonable), but ^{29}Si NMR results show not more than 25% of soluble silicon in the form of dimer for [Si] ≤ 0.05 M (cf. Figure 3). Second, we will see shortly that a value higher than about 100 would suggest that the silicic acid dimer acidity is lower than the monomer acidity, in contrast to the expectation for inorganic polyacids that acidity increases with degree of condensation (Iler, 1979).

Deprotonation

Unlike in acidic conditions, in alkaline aqueous solutions the equilibrium distribution of silicate species is to a significant degree governed by deprotonation equilibria. We define monomer and dimer deprotonation constants as follows:

$$\mathrm{SiO}_{i-1}(\mathrm{OH})_{5-i}^{(i-1)-} \xleftrightarrow{K_m^i} \mathrm{SiO}_i(\mathrm{OH})_{4-i}^{i-} + \mathrm{H}^+$$

$$\mathrm{Si}_2\mathrm{O}_i(\mathrm{OH})_{7-i}^{(i-1)-} \xleftrightarrow{K_d^i} \mathrm{Si}_2\mathrm{O}_{i+1}(\mathrm{OH})_{6-i}^{i-} + \mathrm{H}^+.$$

These could also be represented by the thermodynamically equivalent set of reactions (cf. Busey and Mesmer, 1977).

$$\mathrm{SiO}_{i-1}(\mathrm{OH})_{5-i}^{(i-1)-} + \mathrm{OH}^- \xleftrightarrow{\kappa_m^i} \mathrm{SiO}_i(\mathrm{OH})_{4-i}^{i-} + \mathrm{H}_2\mathrm{O}$$

$$\mathrm{Si}_2\mathrm{O}_i(\mathrm{OH})_{7-i}^{(i-1)-} + \mathrm{OH}^- \xleftrightarrow{\kappa_d^i} \mathrm{Si}_2\mathrm{O}_{i+1}(\mathrm{OH})_{6-i}^{i-} + \mathrm{H}_2\mathrm{O}$$

$$\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{H}^+ + \mathrm{OH}^-.$$

There is a great deal of discrepancy among reported monomer deprotonation constants. An excellent review of treatments before 1978 is provided by Ingri (1978). Ingri indicates that some studies used silicate solutions too concentrated or at too low a pH to ensure that monomers are the only species present in solution. Data reported before spectroscopic techniques were successfully applied to silicate solutions are to be regarded with care. The interference of other reactions brings the reported thermochemical values into serious question; the interpretation of experiment is highly model dependent. Other studies used sufficiently dilute and basic solutions, but the calculation of deprotonation constants was based on the questionable assumption that only a few of the five degrees of deprotonation are possible (we will see, though, that these assumptions are on occasion correct).

Busey and Mesmer (1977) and Sjöberg et al. (1981, 1983) used potentiometry to carefully evaluate dependence of the first two monomer deprotonation constants on ionic strength ([Na] from 0 to 3 molar) and temperature (from 20°C to 100°C). These monomer deprotonation constants are expressed in terms of concentrations rather than activities:

$$K_m^1 = \frac{[\mathrm{SiO}_1(\mathrm{OH})_3^-][\mathrm{H}^+]}{[\mathrm{Si}(\mathrm{OH})_4]}$$

$$K_m^2 = \frac{\left[\mathrm{SiO}_2(\mathrm{OH})_2^{2-}\right][\mathrm{H}^+]}{[\mathrm{SiO}_1(\mathrm{OH})_3^-]},$$

so they should depend on the solution ionic strength I. A modified Davies equation for activity coefficients of ions has been successfully used to describe the medium dependence of numerous ionization equilibria (Baes and Mesmer, 1976) and has been applied to monomer deprotonation equilibria (Sjöberg et al., 1983) to obtain

$$pK_m^1 = 9.84 - 1.022\frac{I^{1/2}}{1+I^{1/2}} + 0.11I$$

$$pK_m^2 = 13.43 - 2.044\frac{I^{1/2}}{1+I^{1/2}} + 0.20I,$$

where ionic strength I is expressed in molar units. The ion product of water $K_w = [\mathrm{H}^+][\mathrm{OH}^-)]$ at ionic strength I and at room temperature is appropriately described (Sjöberg et al., 1983) using the equation:

$$pK_w = 14.01 - 1.022\frac{I^{1/2}}{1+I^{1/2}} + 0.22I.$$

Figure 2 shows that for I between 0 and 3 the uncharged monomer is more acidic than the first deprotonated monomer, which in turn is more acidic than water. The uncharged monomer is slightly more acidic than the most acidic small alcohol – phenol ($pK_a = 9.9$, Trémillon, 1974).

Sjöberg and coworkers (1985) also investigated dilute alkaline sodium silicate solutions with the aid of ^{29}Si NMR and potentiometric methods, and from these measurements they extracted the first two deprotonation equilibrium constants for the dimer, defined here as

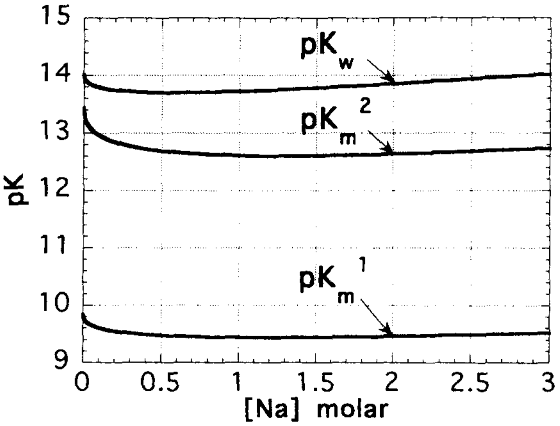

Figure 2. Deprotonation equilibrium constants vs. ionic strength in NaCl aqueous solutions.

$$K_d^1 = \frac{[\mathrm{Si_2O_2(OH)_5^-}][\mathrm{H^+}]}{[\mathrm{Si_2O(OH)_6}]}$$

$$K_d^2 = \frac{[\mathrm{Si_2O_3(OH)_4^{2-}}][\mathrm{H^+}]}{[\mathrm{Si_2O_2(OH)_5^-}]}$$

at ionic strength $I = 0.6$ and at the ambient temperature. However, it was assumed that there is only one degree of deprotonation present for each specific oligomer at a given pH. For example, when the measured average (negative) charge per Si atom in the solution was near 1, it was assumed that the monomer is present solely with charge 1 and that the dimer is present solely with charge 2. Although this assumption was consistent with experimental data, it is by no means necessary, and we will see shortly that it affects the precision in determining the deprotonation constants. Even so, this investigation, along with the monomer deprotonation constants and the dimerization constant (Cary et al., 1982) already discussed, suggests that $pK_d^1 = 9.05$ and $pK_d^2 = 10.25$ in these conditions.

Svensson et al. (1986) investigated concentrated silicate solutions ($[\mathrm{Si}] > 4$ M, $R > 1$, $I < 10$) with both ^{29}Si NMR and potentiometry. They were not able to distinguish the NMR signal corresponding to the dimer from the signal corresponding to other chain-end groups; hence their calculated first deprotonation equilibrium constant for the dimer predicts unreasonably high dimer acidity. Other deprotonation equilibrium constants determined, though, are in reasonable agreement with those determined by Sjöberg and coworkers (1985).

Summary and critique of thermochemical data

We now summarize the experimental data to date that are suitable for and lend confidence to the identification of monomer and dimer deprotonation equilibrium constants, and then we can reexamine the values of $pK_d^1 = 9.05$ and $pK_d^2 = 10.25$ provided by Sjöberg and coworkers. Even in solutions where the monomer and dimer are not the only silicate species, we can nevertheless consider the 11 possible mutual equilibria among the variously charged monomer and dimer species as determining the proportional distribution of silicon among these sites. Of course, we cannot hope that equilibrium constants identified solely from strongly lumped data such as these will be necessarily unique. Nevertheless, experimental data providing quantitative total concentration of monomer, dimer, and hydroxide ion are suitable for consistency tests of the monomer and dimer deprotonation constants obtained in dilute systems.

We have found three previous studies where suitable data for sodium silicate systems are available (Dent Glasser and Lachowski, 1980; Sjöberg et al., 1985; and McCormick, 1987, with pH data from Caullet and Guth, 1989; see Figure 3). In Figure 3 we plot these data together with other comparative data at undetermined pH and data from potassium silicate aqueous solutions. As an independent variable we choose the concentration of silicon present as either monomer or dimer; as a dependent variable we choose the mole ratio of silicon present as monomer. The average negative charge per silicon $\langle Z \rangle$ is calculated from reported pH values. Values of $\langle Z \rangle$ in these systems ranged between 0.6 and 1.8. This is a wide enough range that we choose not to *a priori* exclude any particular degree of deprotonation of monomer (Z up to 4) or dimer (Z up to 3). The deprotonation constants vary only slightly in the range of ionic strengths covered by the systems considered here ($0.2 \leq I \leq 3.3$). Therefore we further assume that in this range of ionic strength and at room temperature, all deprotonation constants of monomer and dimer are independent of the ionic strength and pH.

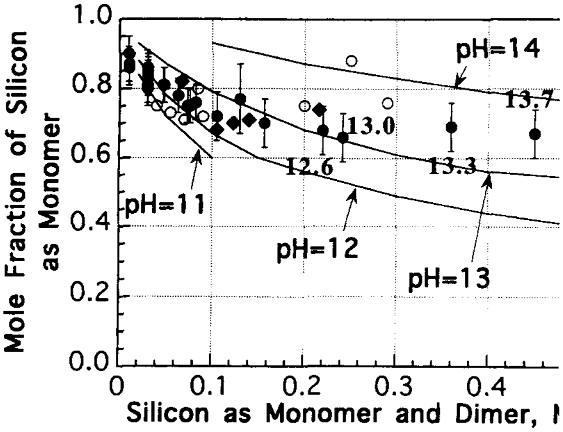

Figure 3. Distribution of silicic acid between the monomer and the dimer.

Mole fraction of silicon as monomer vs. silicon concentration as monomer and dimer. Filled circles: experimental points at various values of pH (from 11 to 12.5), or as indicated (for pH > 12.5). (Data from Dent Glasser and Lachowski, 1980; Sjöberg et al., 1985; McCormick, 1987; Caullet and Guth, 1989.) Open circles: experimental points with undetermined pH. (Data from Hasegawa et al., 1986; Kinrade and Pole, 1992.) Filled diamonds: data from potassium silicate aqueous solutions (Harris and Knight, 1983b). Lines are calculated for the indicated values of pH between 11 and 14, using the thermochemical model summarized in Table 1.

We consider the monomer deprotonation constants determined by Sjöberg et al. (1983) highly reliable, and as a means of predicting the observed monomer–dimer distributions, we will mainly use a variation of the dimer deprotonation constants. To proceed further we postulate a linear free-energy relationship (cf. Caullet and Guth, 1989) so that pK_m^i, pK_d^j are linear functions of respective degrees of deprotonation of monomer, i, and dimer, j. We will discuss the strengths and limitations of this postulate shortly. Since we fixed the monomer deprotonation constants, we have only two parameters, pK_d^1, pK_d^2, available for achieving a fit with all of the experimental data. Examination of the two-dimensional parameter space $pK_d^1 - pK_d^2$ shows only a small region producing a fit (within experimental error bars) to both the pH and the mole fraction of silicon in monomer for the data in Figure 3 (except one point from a sodium silicate system):

$$pK_d^1 = 9.0 \pm 0.1, \qquad pK_d^2 = 10.7 \pm 0.1.$$

Notice that these values are close to those reported by Sjöberg et al. (1985): $pK_d^1 = 9.05$ and $pK_d^2 = 10.25$. Our value of pK_d^2 is somewhat higher because we allowed higher degrees of deprotonation than $Z = 1$ to occur.

Table 1. Equilibrium Constants in the Silicate Speciation Model*

i	1	2	3	4	5	6
pK_m^i	9.5	12.6	15.7	18.8	—	—
pK_d^i	9.0	10.7	12.4	14.1	15.8	17.5

*Dimerization equilibrium constant: $K = 20$.

Hence we have obtained a model:

$$2\mathrm{Si(OH)_4} \overset{K}{\longleftrightarrow} \mathrm{Si_2O(OH)_6} + \mathrm{H_2O}$$

$$\mathrm{SiO_{i-1}(OH)_{5-i}^{(i-1)-}} \overset{K_m^i}{\longleftrightarrow} \mathrm{SiO_i(OH)_{4-i}^{i-}} + \mathrm{H^+}$$

$$\mathrm{Si_2O_i(OH)_{7-i}^{(i-1)-}} \overset{K_d^i}{\longleftrightarrow} \mathrm{Si_2O_{i+1}(OH)_{6-i}^{i-}} + \mathrm{H^+},$$

with the dimerization and deprotonation equilibrium constants summarized in Table 1.

In all preceding calculations we have assumed that deprotonation constants are independent of solution ionic strength I. To estimate the magnitude of the effect that an ionic strength dependence of deprotonation constants would have on the monomer–dimer distribution, we assume a modified Davies equation for activity coefficients of ions with charge z,

$$\ln \gamma_{\pm} = -0.51 z_{\pm}^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.1 \times I \right)$$

(in the original Davies equation there is 0.3 instead 0.1; cf. Levine, 1988), so that we get a close agreement with the ionic strength dependence of pK_{m1} and pK_{m2} from Sjöberg et al. (1983). With this model we calculate how the monomer–dimer distribution changes with the solution ionic strength, and we find that this effect is mild compared to the effect of pH. For example, with [Si] = 0.1 M (silicon as monomer or dimer) we get the mole ratio of monomer from 0.60 (at $I = 0.5$) to 0.63 ($I = 3$) at pH = 12 and from 0.68 ($I = 0.5$) to 0.72 ($I = 3$) at pH = 13. We can see that the pH change from 12 to 13 is clearly more significant than the ionic strength change from 0.5 to 3.0. It seems to be a reasonable approximation, then, to assume that deprotonation constants are not strong functions of the solution ionic strength.

Now we discuss strengths and limitations of the postulate that pK_m^i and pK_d^j are linear functions of respective degrees of deprotonation of monomer, i, and dimer, j. This postulate is equivalent to an assumption that free energies of successive deprotonation of monomer and dimer are linear functions of their degree of deprotonation (cf. Caullet and Guth, 1989). In the case of silicates the linearity seems consistent with observed values of average charge on silicon $\langle Z \rangle$ from 1.4 to 2 at pH between 13 and 14 (Dent Glasser and Lachowski, 1980; Svensson et al., 1986; Caullet and Guth, 1989). A sublinear dependence of monomer deprotonation constants pK_m^i on i, as suggested by Babushkin (1985) and Flint and Wells (1934),

$$pK_m^1 = 9.7, \qquad pK_m^2 = 11.7, \qquad pK_m^3 = pK_m^4 = 12.0,$$

would predict average charge $\langle Z \rangle \geq 3.5$ at the monomer for pH > 12, which is contrary to experimental results. Therefore we concur with Caullet and Guth that the postulated linearity pK_m^i and pK_d^j is a suitable approximation for predicting anion distributions in aqueous silicate solutions.

Inspection of discussed equilibrium constants shows that the free energy of dimerization is small compared to the free energy of the various deprotonation reactions. The distribution of monomers and dimers is governed primarily by the stability of the variously charged ions and by the activity of the hydroxide ion. Dimerization occurs only when the activity of the hydroxide anion is low enough that the hydroxide is no longer driven to ionize as many silanol groups as can be provided by monomers. Therefore, it is clear that we need to understand the deprotonation energy in great detail in order to model oligomer distributions.

Implications for Larger Oligomers

Although we do not currently have equilibrium data for uncharged oligomers larger than trimers (Hoebbel et al., 1979; Cary et al., 1982), we can estimate the thermochemical trend for silica polymerization to larger clusters by using the size dependence of the solubility of silica particles. We calculate free energies of larger clusters from reported solubilities for particle diameters 1.4, 2.0, and 6.25 nm, corresponding to estimated numbers of silicon atoms $n = 32$, 90, and 2,800, respectively (Iler, 1979). In Figure 4 we plot the estimated free energy of oligomerization reactions

$$n\mathrm{Si(OH)_4} \overset{\Delta G_{n,m}}{\longleftrightarrow} \mathrm{Si}_n\mathrm{O}_{4n-m}\mathrm{H}_{4n-2m} + m\mathrm{H_2O}.$$

Figure 4 shows that subsequent condensations are thermodynamically favorable, but they become less so with increasing size. We caution that Figure 4 should be read with care: there is no indication whether there are intermediate species that are particularly stable, and we will see shortly that among

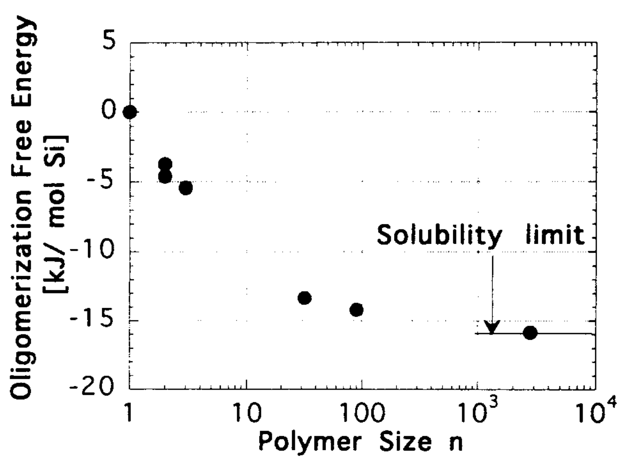

Figure 4. Free energy of the oligomerization reaction $n\mathrm{Si(OH)_4} = \mathrm{Si}_n\mathrm{O}_{4n-m}\mathrm{H}_{4n-2m} + m\mathrm{H_2O}$ vs. polymer size n.

Free energies of oligomerization to dimer and linear trimer are calculated from data by Hoebbel et al. (1979) and Cary et al. (1982). Free energies of larger clusters are calculated from solubility data reported by Iler (1979).

Table 2. Enumeration of Silicate Oligomers

No. of Si Atoms	No. of Structures
1	1
2	1
3	2
4	6
5	10
6	29
7	64
8	194
9	531
10	1,733

deprotonated oligomers, the closure of linear species to form rings and cages is thermodynamically favorable.

Of course, there are multiple oligomers with different topologies with given values n and m, and our notation should be understood as shorthand for a specific oligomer. To get an idea how many distinct silicate oligomers there could possibly be, we apply a computer-assisted enumeration algorithm to count them. The algorithm by Kvasnička and Pospíchal (1991) works with a class of the so-called adjacency matrices that are in a one-to-one correspondence to molecular graphs of silicate oligomers. It turns out that a population of possible silicate structures grows rapidly with a number of silicon atoms that they contain, even when no fully condensed sites and no two-membered rings are allowed (Table 2). Clearly, any attempt to model a silicate solution while keeping track of all possible species gets out of hand quickly.

We can now reconsider some previously calculated distribution diagrams for silicate oligomers in alkaline aqueous solution as a function of pH. The distribution of variously charged monomeric species is governed by pH in a simple fashion (Figure 5). In very dilute solutions, where the proportion of larger oligomers is negligible, this is the complete story of species distribution, as has been correctly pointed out by Baes and Mesmer (1976). However, in more concentrated systems with substantial oligomer formation, a simple model assuming a single predominant oligomer (Baes and Mesmer, 1976) fails badly in comparison with experiment (Dent Glasser and Lachowski, 1980). Figure 6 shows that the simple model underpredicts the monomer mole ratio by 50%! It is thus clear that if one wants to quantitatively model the distribution of silicate anions in concentrated solutions of technical interest, it is necessary to include the full range of anionic oligomer species in the equilibrium model.

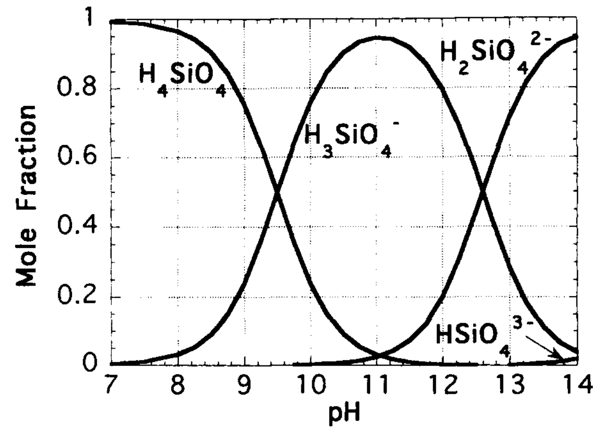

Figure 5. Distribution of monomeric anions vs. pH.

Calculated for the ionic strength $I = 1$ M using the deprotonation constants summarized in Table 1.

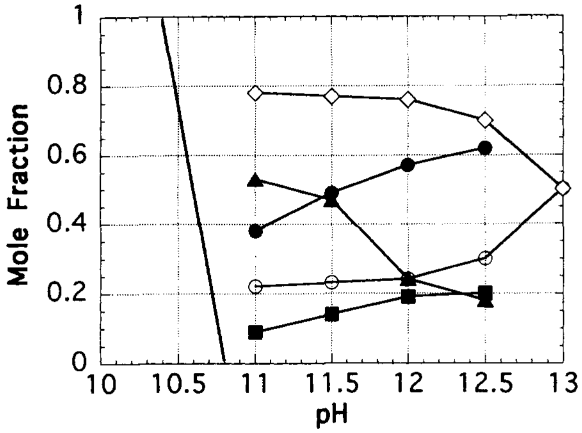

Figure 6. Distribution of silicate species vs. pH at [Si] = 0.1 M.

Filled symbols: experimental data from Dent Glasser and Lachowski (1980); open symbols: calculated from a simple model (Baes and Mesmer, 1977); circle: monomer; square: dimer; diamond: tetramer; triangle: polymer; line at left: amorphous silica solids.

Finally, we comment on previously published formation constants for larger silicate anions (cf. Sjöberg et al., 1985; Svensson et al., 1986; Caullet and Guth, 1989). Caullet and Guth postulated a set of assumptions for values of deprotonation constants of individual silicon sites regardless of oligomer structure beyond distinguishing linear and cyclic species (see Table 3). Sjöberg and Svensson evaluated, from experimental data, anion formation constants, lumping condensation and deprotonation equilibria. We converted their deprotonation constants to the cumulative deprotonation constants K_i (see Table 3) for individual oligomers as per the reaction scheme

$$\text{oligomer} \overset{K_i}{\Leftrightarrow} \text{oligomer}^{i-} + i\text{H}^+,$$

Table 3. Cumulative Deprotonation Constants of Silicate Oligomers

Species	Data Source	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8
Dimer	C&G'89*	9.4	19.7	30.8	42.7				
	Sv&al'86**	6.3	18.0		42.1				
	Sj&al'85†	9.05	18.0						
	This work	9.0	19.7	32.1	46.2				
Trimer Linear	C&G'89	9.4	19.7	30.8	42.7	55.5	69.2		
	Sv&al '86			27.8			65.6		
	Sj&al'85			28.0					
Trimer Cyclic	C&G'89	9.4	20.5	31.6	43.6	57.3	71.0		
	Sj&al'85			30.3					
Tetramer	C&G'89	9.4	19.7	30.8	42.7	55.5	69.2	83.7	98.2
	Sv&al'86		12.8		36.4				88.0
	Sj&al'85			28.6††	36.7				

*Caullet and Guth.
**Svensson et al.
†Sjöberg et al.
††Cyclic tetramer.

assuming that the free energy of siloxane bond formation is constant (following Caullet and Guth, 1989).

The general pattern in Table 3 supports linear free-energy relationships for deprotonation, but we can also see that there is a substantial quantitative disagreement between values of deprotonation constants from various sources. Some values are particularly suspicious. The first deprotonation constant for dimer given by Svensson and coworkers (1986), $pK_1 = 6.3$, is unreasonably low, as it would make the dimer even more acidic than silica gel ($pK_a = 6.8$, Iler, 1979). Similarly, the second deprotonation constant of tetramer given by the same authors, $pK_2 = 12.8$, would suggest that the first deprotonation constant of tetramer would be as low as $pK_1 = 6.4$, again an unreasonably low value. However, it is likely that the acidity pK_1 of the first deprotonated silanol does depend on a degree of condensation, with more condensed silicon sites carrying more acidic silanols (Iler, 1979).

So far, we have critically evaluated thermodynamic values for simple silicate species, so that they are consistent with observed species distributions for a broad range of alkaline silicate solutions. If larger species are included in the description, many more thermochemical values have to be specified, and their accuracy and uniqueness is in doubt without some understanding of the behavior of even the simplest anions. For this reason, we will explore whether it is possible to rationalize the observed thermodynamic trends using gas-phase semiempirical molecular orbital calculations and solvation theory.

Role of Solvation

Are the thermochemical trends we have just seen due to peculiarities of silicate bonding, or is there a role for solvation effects in this? We can use thermochemical predictions, obtained from semiempirical molecular-orbital calculations, in a guarded fashion to discriminate between the roles of intramolecular bonding and ion solvation effects in governing silicate speciation in aqueous solutions. [Numerous semiempirical molecular-orbital calculations of silicates have been performed within the last decade using MNDO, AM1, and PM3 Hamiltonians introduced by Dewar, Stewart, and others (Dewar and Thiel, 1977; Dewar et al., 1986; Stewart, 1989; Dewar et al., 1990). For example, hydrolysis of the trisiloxane ring has been studied (West and Wallace, 1993), and the gas-phase enthalpies of formation and vibrational frequencies have been calculated for cyclic species with up to seven silicon atoms (West and Hench, 1995). Interactions between $Si(OH)_4$ and hydroxide anion, water molecule, and another $Si(OH)_4$ molecule have also been extensively studied (Burggraf and Davis, 1986; Davis and Burggraf, 1988; Burggraf et al., 1992). All results reported here are for structures optimized under the constraint of perfect tetrahedral silicon coordination by oxygen. All examined thermochemical trends were qualitatively the same using either MNDO or PM3 calculations, and thus we report results for MNDO calculations only.] We will merely compare experimentally observed trends to those suggested by MNDO calculations of silicate anions and neutral molecules. It must be emphasized that no solvation effects have been included in these calculations. This has been done on purpose; to the extent to which these calculations disagree with the solution behavior, that is the extent of the role of solvent and ionic interactions.

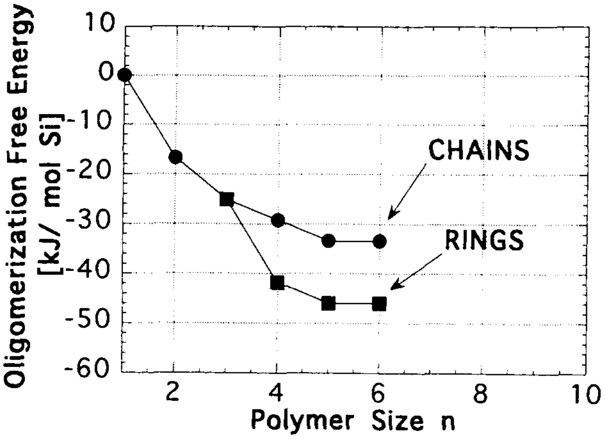

Figure 7. Free energy of the oligomerization reaction $n\mathrm{Si(OH)_4} = \mathrm{Si}_n\mathrm{O}_{4n-m}\mathrm{H}_{4n-2m} + m\mathrm{H_2O}$ vs. polymer size n; MNDO calculations in the gas phase for linear and cyclic oligomers.

We would like to see whether the trend in free enegies of oligomerization calculated by MNDO for species in the gas phase parallels the trend observed in solution for a set of oligomerization reactions:

$$n\mathrm{Si(OH)_4} \xleftrightarrow{\Delta G_{n,m}} \mathrm{Si}_n\mathrm{O}_{4n-m}\mathrm{H}_{4n-2m} + m\mathrm{H_2O}$$

In Figure 7 we show the calculated free energy of oligomerization of uncharged monomer to uncharged silicate oligomers, namely chains and rings. The standard free energy of formation of water in the gas phase (−56.7 kcal/mol) comes from thermochemical tables (Levine, 1988). Values of free energy are reported per mol of Si rather than per mol of species, because we wish to compare the stability of a silicon site in each environment. The calculated trend in $\Delta G_{n,m}$ is consistent with the qualitative picture based on experimental data (Figure 4). Moreover, it is predicted that ring closure of small linear species (larger than the trimer) is thermodynamically favorable.

Next we would like to see whether a trend of free energies of deprotonation in the gas phase matches the trend observed in solution. In the case of deprotonation reactions

$$\mathrm{SiO}_{i-1}(\mathrm{OH})_{5-i}^{(i-1)-} \leftrightarrow \mathrm{SiO}_i(\mathrm{OH})_{4-i}^{i-} + \mathrm{H}^+$$

$$\mathrm{Si_2O}_i(\mathrm{OH})_{7-i}^{(i-1)-} \leftrightarrow \mathrm{Si_2O}_{i+1}(\mathrm{OH})_{6-i}^{i-} + \mathrm{H}^+,$$

we can merely look at the free energy of formation from elements for monomeric and dimeric silicate anions. According to MNDO calculations, each anion becomes less stable with increasing charge, largely because deprotonation increases the Coulombic repulsion energy between atomic centers, and subsequent deprotonations become less favorable. However, calculations in the gas phase predict faster than linear increase in free energy of formation with the extent of deprotonation for both monomer (Figure 8) and dimer (Figure 9), qualitatively contradicting experimental solution data. This means that gas-phase calculations gravely underpredict acidity values of monomer and dimer anions. This discrepancy

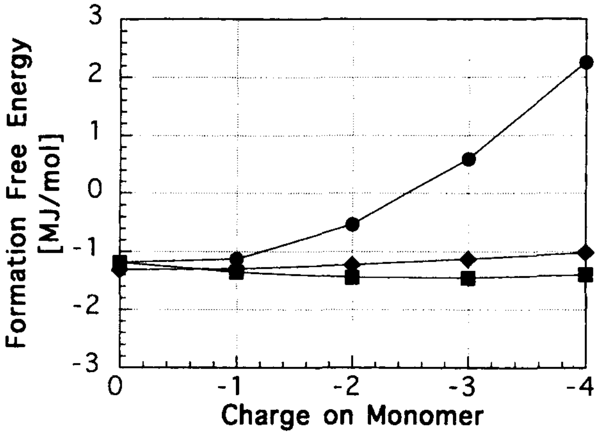

Figure 8. Standard free energy of formation from elements for monomer anions vs. anion charge.

Diamond: data calculated from the deprotonation constants (Table 1); circle: data calculated by MNDO; square: data calculated by combining MNDO with the Born theory.

stems from the role of the solvent in stabilizing silicate anions.

We feel that the role of solvent in deprotonation reactions is the key to understanding speciation in zeolite synthesis and alkaline sol-gel processing. In the Appendix we show that even a simple solvation model allows us to account for much of the discrepancy between calculated gas-phase and experimental solution acidities. Although various computational packages are becoming available for calculation of solvation free energies, we found that, for silicates, they have not yet significantly outperformed a simple Born model (see the Appendix).

Implications for Nonequilibrium and Mixed-solvent Systems

We now offer several thoughts on implications for nonequilibrium and mixed-solvent systems. Cyclization and cage formation are widespread among silicates in both acidic and basic systems. In acidic conditions the silicate oligomers are uncharged and metastable toward forming silica gel. We conjecture that cyclic and cagelike uncharged oligomers in aqueous solutions are thermodynamically more stable than their linear uncharged counterparts. Solvation does not seem to play a deciding role in stabilizing uncharged cyclic structures, since their stability is predicted by gas-phase molecular orbital calculations. In contrast, solvation is decisive in stabilizing charged silicate oligomers.

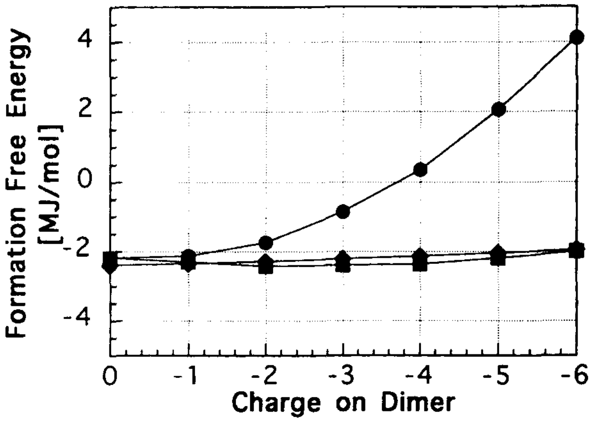

Figure 9. Standard free energy of formation from elements for dimer anions vs. anion charge.

Diamond: data calculated from the deprotonation constants (Table 1); circle: data calculated by MNDO; square: data calculated by combining MNDO with the Born theory.

The solubility of silica has been measured in a series of mixed solvents (water with polar organics). The logarithm of silica solubility in mixed solvents varies linearly with the inverse of the solvent relative permittivity. For this reason it is thought that the solvation excess free energy follows a Born-like expression corresponding to a dipole–solvent interaction (Dandurand and Schott, 1987). It is not clear, though, what the role of esterification is in these systems. Silicic acid can undergo esterification in acidic water/alcohol solvent systems, but silanol esterification has not been demonstrated in neutral or alkaline systems (cf. Šefčík and McCormick, 1997a). We are not aware of any experimental data regarding deprotonation equilibria for esters of silicic acid.

Otherwise, equilibrium data from mixed-solvent systems are confined to highly alkaline systems containing the tetramethylammonium (TMA) cation (Hasegawa et al., 1987, 1989; Knight, 1989; Hendricks et al., 1991). The presence of the TMA cation shifts the equilibrium between silicate oligomers in alkaline aqueous solution toward the cubic octamer (cf. McCormick and Bell, 1989). There is very likely a specific ionic interaction between the deprotonated cubic octamer and the TMA cations, which tends to stabilize the cubic cage. This stabilization is especially striking when the solvent becomes less polar, for example, by increasing the alcohol content, when virtually all of the soluble silicate finally ends up as the cubic octamer (Hendricks et al., 1991). That means that the magnitude of the solvation free energy of the deprotonated cubic octamer in TMA solutions does not decrease with increasing alcohol content, that is, with decreasing solvent relative permittivity, nearly as much as it does for monomer and other small oligomers.

Metastable silicate solutions are easily prepared by acidifying stable alkaline aqueous silicate solutions or by hydrolysis of silicic acid esters, for example, tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The time evolution of metastable solutions prepared by both methods is qualitatively similar (cf. Andersson et al., 1982; Pouxviel et al., 1987; Devreux et al., 1990). The behavior of metastable silicate solutions results from an interplay of condensation and phase separation. The precipitation of silicic acid in basic and neutral solutions is fast compared to condensation (cf. Iler, 1979). Precipitated silica in more alkaline systems stays in colloidal form due to deprotonation of surface silanol groups, and the colloids undergo a slow process of Ostwald ripening in pseudoequilibrium with solution silicate species, while in neutral and slightly acidic solutions the precipitated silica aggregates and forms a heterogeneous, mesoporous gel (Klein and Woodman, 1995). However, phase separation fails to occur in modestly acidic systems (pH between 1 and 3), even when supersaturation with respect to amorphous silica gel is very high (Andersson et al., 1982). Silicic acid then undergoes homogeneous step growth polymerization to a homogeneous, microporous gel, with strongly nonideal, complex kinetics. We hypothesize that the suppression of precipitation is primarily a kinetic effect. The nucleation rate in acidic systems is much lower than the silanol condensation rate. The rate of monomer condensation decreases with increasing pH, and for pH about 3.5 and higher precipitation outpaces condensation.

Silica polymerization is sufficiently slow under acidic conditions that the time evolution of small oligomer species can be quantitatively monitored with ^{29}Si NMR spectroscopy, and rate and equilibrium constants of siloxane condensation can be identified (cf. Šefčík and McCormick, 1997a, for a review of TEOS polymerization kinetics). It is of great interest to investigate under what conditions homogeneous silica polymerization is primarily kinetically driven, and whether there are some polymerization intermediates, such as cyclic and cage-like structures, that are thermodynamically favored.

Conclusions

The thermochemical trends confirmed in this study are consistent with data reported by some workers. The following points of physical insight regarding silicate speciation are obtained:

1. Each subsequent deprotonation of a silicate species in solution grows more difficult in a complex fashion that represents the interplay of two factors: (a) destabilization of the molecules as charge increases (which can be predicted with gas-phase molecular orbital calculations), and (b) favorable energetic interactions between the ion and solvent (which can be qualitatively predicted by a judicious use of the Born theory; see the Appendix).
2. The distribution of silicate oligomers in alkaline aqueous solutions is governed primarily by deprotonation equilibria.

While ion-solvent interactions are very difficult to model, the dominance of ion-solvent terms indicates that future success in predicting the behavior of silicate and aluminosilicate species will rely on further development in modeling of ion-solvent interactions. The most promising method seems to be molecular simulation (Monte Carlo or molecular dynamics) with appropriate atomic potentials (cf. Garofalini and Martin, 1994; Hill and Sauer, 1995; Rustad and Hay, 1995). For example, the free energy of deprotonation of hydrated silicic acid has been reasonably predicted in a recent molecular dynamics study (Rustad and Hay, 1995), and there is clearly need for further work.

Acknowledgments

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Appendix

Here we consider ion-solvent interactions using the Born model (cf. Bockris and Reddy, 1970). Born originally suggested that the solvent can be approximated as a dielectric continuum and the ion can be approximated as a charged sphere. The free energy of transfer is the sum of the work of creating a cavity within the continuous dielectric medium and of transferring the charged sphere from vacuum into the cavity:

$$\Delta G = -\frac{N_A e_0^2}{2r} Z^2 \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon} \right),$$

where N_A is Avogadro constant, e_0 is electron charge, ϵ_0 is dielectric constant in vacuum, ϵ is dielectric constant of the solvent, Z is charge, and r is radius of the ion.

As a simple approximation, we estimate the silicate ionic radius as the sum of (1) the average distance from the center of a silicate structure to the centers of oxygen atoms at the outer edges, and (2) the crystallographic radius of the oxygen ion. This leads to $r = 3$ Å for the monomer and $r = 4$ Å for the dimer.

It is remarkable that, despite major simplifications, the Born model is capable of fitting a substantial number of experimental data. The major simplifications of the Born model are (1) the solvent permittivity in the vicinity of the ion is assumed to be the same as in the bulk solvent (dielectric saturation is ignored), and (2) the work required to compress the solvent around the ion is assumed to be negligible (electrostriction is ignored).

Moreover, it is not immediately clear what values should be taken for ionic radii. Bockris and Reddy (1970) suggest the use of an "effective" ion radius that encompasses a portion of the solvent experiencing dielectric saturation (whereby the large electric field around the ion causes saturation of the solvent orientational polarizability). They suggested that the opposing effects of dielectric saturation and electrostriction may cancel each other, and molecular simulations by Jayaram et al. (1989) confirm that for ions of charge up to 1.1 the Born form holds. More highly charged ions continue to respond by quadratic increase in the free energy of solvation with increasing charge, although the free energy is lower than predicted by the Born model, as dielectric saturation outweighs electrostriction. Hirata and coworkers (1988), using the extended "reference interaction site model" (RISM) integral equations, suggested that the effective ionic radii be derived from the solute-solvent radial distribution function.

Now we calculate the standard free energy of formation of aqueous monomer and dimer anions from elements. To do that, we add the Born solvation free energy to the standard free energy of formation from elements in gas phase calculated using MNDO. As we can see for both monomer (Figure 8) and dimer (Figure 9), these values are much more satisfactory than those calculated in the gas phase alone, since they represent the competition between unfavorable anion destabilization (gas phase MNDO prediction) and favorable ion–solvent interactions. It is clear that the balance between intermolecular destabilization and solvation stabilization is essential. Even so, the predicted values of free energy are not quantitative; they predict that silicic acid is a strong acid.

It is clear that the stability of silicate anions arises from a balance of bonding vs. ion-solvent interactions. The Born model fails to quantitatively predict a solvation contribution to free energies, mainly because it inadequately models such a complex interaction. However, gas-phase semiempirical molecular orbital calculations combined with the Born model are qualitatively consistent with experimental thermochemical trends regarding deprotonation and condensation of silicates in aqueous solutions. It will be useful in the future to attempt more refined predictions using solvation treatments such as SMx (cf. Hawkins et al., 1996) or COSMO (Klamt and Schüürmann, 1993), provided appropriate parametrization is available.

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