



Fig. 3. Comparison of predicted and observed quartz solubilities in the system $\text{SiO}_2\text{--H}_2\text{O--NaOH}$.

Fig. 3 represents partial conversion of NaOH to $\text{NaH}_3\text{SiO}_4(\text{aq.})$. For example, a curve representing 50% conversion of NaOH would lie approximately half way between the two limiting curves illustrated.

The actual experimental measurements of silica solubility lie very close to the predicted solubility curve of Fig. 3, and it thus follows that sodium-silica complexing can be of no quantitative significance under these conditions. It should be noted that this conclusion is dependent upon the accuracy of the analytic quartz solubility measurements, on the parameters $K_{\text{H}_2\text{O}}$, $K_{\text{H}_4\text{SiO}_4}$, K_{NaOH} , and on the assumed value of 1.0 for γ . It was further assumed that all aqueous species obeyed the Davies extension of the Debye-Hückel equation, and that the second acid dissociation constant of silicic acid had little effect on the observed solubilities. These last two assumptions, in particular, become increasingly tenuous as NaOH concentration is increased. It remains possible that some degree of sodium-silica complexing might yet exist in more concentrated solutions, or under conditions varying widely in temperature and pressure from the range considered here. Fig. 2 is intended to facilitate a similar test for sodium-silica complexing for anyone working with the same system within the temperature-composition region covered by the plot.

The degree of polymerization of solvated silica

The solvation reaction of quartz with water has been given by eq. 1. Under the temperature–pressure equilibrium conditions of present concern, the value of the polymerization factor “ y ” of the silica complex has generally been considered to be 1.0, (see Brintzinger and Brintzinger, 1931; Alexander et al., 1954; Kitahara, 1960b, 1960c, and Morey et al., 1962). This value of y has been adopted largely because of the very good agreement between solubilities as given by the silicomolybdate colorimetric method and those obtained by other methods, combined with the fact that the silicomolybdate method has been shown to be sensitive to the monomeric silica species alone (Alexander, 1953). Recently, Weill and Bottinga (1970) have reconsidered this problem and concluded that cristobalite and quartz solubility data are better explained if one assumes the presence of a polymerized species in an amount which varies with temperature. The concentration of polymerized species proposed by them, however, is too small to be detected by the method described below.

An independent test for the value of y is possible using the computing routines outlined in the previous section. First, eq. 2–8 may be solved using values of y differing from 1.0. As an example, Table IV contains total quartz solubilities predicted by the model for the case where y equals 2.0. The predictions are incorrect being far higher than the observed solubilities, and the discrepancy widens as y is increased. Only when y is close to 1.0 are predictions consistent with the observed data. Note that this conclusion still obtains if sodium–silica complexing should occur in the system. This latter effect would tend to raise the net observed solubility above that predicted by the model (which ignores sodium–silica complexing), and would further increase the discrepancy between observed and predicted silica solubilities for values of y differing from 1.0.

TABLE IV

Predicted quartz solubilities in the system $\text{SiO}_2\text{--H}_2\text{O--NaOH}$ at 0.01 NaOH molality for the case where “ y ” equals 2.0

Temperature (°C)	Observed quartz solubility in the system $\text{SiO}_2\text{--H}_2\text{O}$ (p.p.m. SiO_2)	Observed quartz solubility in the system $\text{SiO}_2\text{--H}_2\text{O--NaOH}$ (p.p.m. SiO_2)	Predicted quartz solubility in the system $\text{SiO}_2\text{--H}_2\text{O--NaOH}$ (p.p.m. SiO_2)
225	344	689	1020
176	158	617	961
125	83	529	835

Values of y are also calculated using a program similar in format to the quartz solubility model. The same eq. 2 to 8 were used, but in this case, “Total Silica” (total analytic silica as measured in the system $\text{SiO}_2\text{--H}_2\text{O--NaOH}$) was considered a given parameter, and y an unknown whose value would be determined from the solution of the equations. Solutions for y at three separate temperatures are given in Table V. Note that all values approximate 1.0. This test is obviously crude enough to allow for a small amount of polymerization as proposed by Weill and Bottinga (1970).