[CONTRIBUTION FROM THE LABORATORY FOR INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY OF LEIDEN]

The Nature of the Silicate Species in Sodium Silicate Solutions[1]

BY S. A. GREENBERG[2]

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An analysis of the literature data and e.m.f. and conductance measurements of the present study was made to determine the degree of polymerization of the silicate ions. It was concluded that in relatively dilute solutions and in solutions above pH 10.5, the silicate ion is monomeric. The pK_1 and pK_2 values for silicic acid $Si(OH)_4$ at 20° are 9.85 and 11.8, respectively. The equivalent conductance of the silicate ion $SiO(OH)_3^-$ was estimated to be 35 at 25°.

Although the nature of sodium silicate solutions is fairly well understood in its broad outlines, confusion exists as to the degree of polymerization of the silicate ions.[3] The literature data and e.m.f. and conductance measurements of this study were analyzed according to current theories to determine this information. The hypotheses were tested by evaluating the ionization constants of silicic acid $Si(OH)_4$ and the equivalent conductance of the silicate $SiO(OH)_3^-$ ions.

The equilibria associated with monomeric silicic acid and those active in sodium silicate solutions have not been treated adequately. For example, the negative logarithms of the dissociation constants of silicic acid have been reported[4-10] between 9 and 10 for pK_1 and between 12 and 14.3 for pK_2. The molecular weights of silicic acid in sodium silicate solutions have been determined by light scattering,[11] cryoscopic, diffusion and transference measurements[12] but no theory has been offered to explain the results.

In the present study the dissociation constants of silicic acid were calculated from e.m.f. measurements found in the literature[13] and from conductivity measurements on sodium silicate solutions with $Na_2O:SiO_2$ mole ratios of 1:0.5, 1:1, 1:1.5, 1:2 and 1:3. The electrical conductivity results and data taken from the literature were used to evaluate the equivalent conductance λ_0 of the $SiO(OH)_3^-$ ions.

Experimental

Equipment.—For the equilibrium studies a water-bath held constant to ±0.01° was employed. Conductivity measurements were made with a Philips (Eindhoven) Bridge No. GM4249 and both Philips and Industrial Instruments dip cells[14] with constants of approximately 1.0 and 0.5 $cm.^{-1}$.

Materials.—The sodium silicate solutions were made from spectroscopically-pure, special bulky silica[14] which contains 85.6% SiO_2 and water. Solutions made with analytical reagent grade sodium hydroxide were found to be of sufficient purity after the carbonate was removed. Water of low conductivity was prepared by passing distilled water through ion-exchange resins and filters.

Procedure.—The sodium silicate solutions were made by adding the silica to normal sodium hydroxide solutions at 40° and the solutions were stirred during the depolymerization reaction until the electrical conductivities were constant and the solutions were optically clear.[15] In some studies[13] the silicas were added to sodium hydroxide solutions at room temperature. Because of the relatively large activation energy involved in the depolymerization of silica by sodium hydroxide solutions,[15] it is not certain that equilibrium was reached in these solutions. Certainly the time effects observed by several authors[13,16] may be attributed to the non-equilibrium conditions.

The presence of carbon dioxide in the sodium silicate solutions was avoided by preparing them from carbon dioxide-free sodium hydroxide solutions and water and by storing the solutions in well-stoppered polyethylene bottles. The absence of turbidity in the sodium silicate solutions is evidence that the carbon dioxide content is very low.[11,17]

Theoretical

In silicic acid the silicon is usually considered to be tetrahedrally coördinated by four hydroxyl groups.[18,19] Monosilicic acid solutions are formed when silica dissolves in water.[3] The solubility increases in alkaline solutions and the limit has not yet been established.

It will be assumed that all the silica in the sodium silicate solutions under discussion is present as monomeric $Si(OH)_4$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^=$ which may also be referred to for convenience as H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^=$. The thermodynamic dissociation constants for the equilibria will be

$$H_4SiO_4 = H^+ + H_3SiO_4^- \qquad (1)$$

$$H_3SiO_4^- = H^+ + H_2SiO_4^= \qquad (2)$$

represented by K_1 and K_2 and the concentration values by K_1^* and K_2^*

$$K_1 = \frac{a_{H^+}a_{H_3SiO_4^-}}{a_{H_4SiO_4}} = \frac{(H^+)(H_3SiO_4^-)}{(H_4SiO_4)}\frac{f_{H^+}f_{H_3SiO_4^-}}{f_{H_4SiO_4}} \qquad (3)$$

$$K_2 = \frac{a_{H^+}a_{H_2SiO_4^=}}{a_{H_3SiO_4^-}} = \frac{(H^+)(H_2SiO_4^=)}{(H_3SiO_4^-)}\frac{f_{H^+}f_{H_2SiO_4^=}}{f_{H_3SiO_4^-}} \qquad (4)$$

where a is the activity, ( ) is the concentration in moles/l. and f is the activity coefficient.

In non-colloidal solutions of sodium silicate the electroneutrality relation holds

$$(Na^+) + (H^+) = (OH^-) + (H_3SiO_4^-) + 2(H_2SiO_4^=) \qquad (5)$$

where (H^+) is small and can be neglected. The total amount of silica in solution (SiO_2) is equal to the concentration of the various species of silicic acid. When (OH^-), (Na^+) and (SiO_2) are known

$$(SiO_2) = (H_3SiO_4^-) + (H_2SiO_4^=) + (H_4SiO_4) \qquad (6)$$

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 130th meeting of the American Chemical Society, Atlantic City, New Jersey, 1956.

[2] Portland Cement Association, Skokie, Illinois.

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the other quantities can be calculated by assuming that the concentration of $H_2SiO_4^{=}$ is negligible below a pH of 11.8 and that the concentration of H_4SiO_4 can be neglected above this pH value. The pH value of 11.8 can be derived[20] by using approximate pK_1^* and pK_2^* values (10.3 and 13.3 at 20°) in the relationship $(H^+) = (K_1^* \times K_2^*)^{1/2}$. The hydroxyl ion concentration (OH^-) can be estimated from pH measurements where $pH = -\log a_{H^+}$; $K_w = a_H a_{OH}$; $pK_w = 14.167$ at 20°; $a_{H^+} = (H^+) f_{H^+}$; and $\log f = -0.505\mu^{1/2}$ (at 20°) according to the Debye–Hückel equation.

Discussion of Results

E.m.f. Measurements.—The published data on these measurements were discussed by Bacon and Wills.[13] Only the 20° data of Bacon and Wills, the 25° data of Harman[10] and the 30° data of Bogue[8] were examined in this study.

The procedure for evaluating ionization constants of weak acids from cells with liquid junctions has been described.[21–23] The hydrogen ion activity is expressed in terms of the measured electromotive force E by the equation

$$E = E^0 - (RT/F) \ln a_{H^+} \qquad (7)$$

where E^0 is the standard potential of the cell and RT and F have their usual meanings. Use is also made of the equation $\log f_i = -AZ_i^2\mu^{1/2} + c\mu$, where A and C are constants, Z is the charge on the ion and μ is the ionic strength. By means of eq. 3–7 it is possible to derive

$$pK_1^* = pH - \log \frac{(H_3SiO_4^-)}{(H_4SiO_4)} + A\mu^{1/2} = pK_1 + C_1\mu \qquad (8)$$

for the pH range <11.8 and

$$pK_2^* = pH - \log \frac{(H_2SiO_4^{=})}{(H_3SiO_4^-)} + 3A\mu^{1/2} = pK_2 + C_2\mu \qquad (9)$$

for the pH range>11.8.

The values for pK_1^* and pK_2^* at 20° (eq. 8 and 9) were plotted as a function of μ. In Fig. 1 the pK_1^* *versus* μ curve is shown. It may be seen that the points on the curve may be extrapolated to a pK_1 value of 9.85. A pK_2 value of 11.8 was estimated. The closeness of pK_1 and pK_2 also was indicated by the titration curves of silica which show only one broad break rather than the two expected from dibasic acids with K_1 and K_2 values which show a ratio $K_1/K_2 > 10^3$.[20]

Although Bacon and Wills[13] considered the pH data of Harman[10] and Bogue[8] unreliable, eq. 8 and 9 were applied to these data to obtain pK_1 and pK_2 values at 25 and 30°. The (OH^-) values were in these cases given by the authors. The 25° values for pK_1 and pK_2 were found by extrapolation to be 9.7 and 11.9, respectively. From the data of Bogue, pK_1 and pK_2 were estimated to be 9.1 and 11.9 at 30°.

A heat of ionization at infinite dilution for silicic acid of 3.3 kcal./mole was estimated by comparing the pK_1 values at 20, 25[24] and 35°[24] by means of the van't Hoff equation. From the heat of solution of amorphous silica (2.65 kcal./mole)[25] and the heat of ionization, it was possible to estimate the heat of neutralization as −7.6 kcal./mole, assuming the heat of ionization of water is −13.6 kcal./mole at 25°.

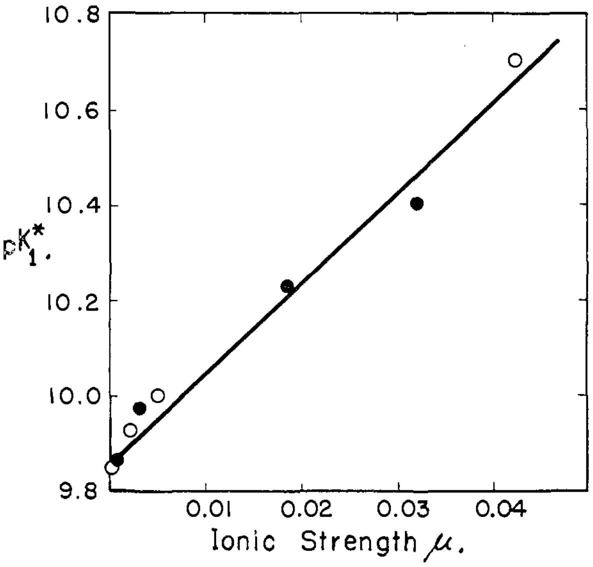

Fig. 1.—The plot of pK_1^* as a function of ionic strength μ: ○, $Na_2O:SiO_2$, 1:1.508: ●, $Na_2O:SiO_2$, 1:1.996.

Conductivity Measurements.—Figure 2 summarizes the conductivity data of the present study on sodium silicate solutions of $Na_2O:SiO_2$ mole ratios 1:0, 1:0.5, 1:1, 1:1.5, 1:2 and 1:3. The results agree fairly well with those of Harman[16] except for the sodium hydroxide and Na_2O:0.5 SiO_2 solutions. For these solutions the results of Harman show considerable scatter.

The concentration constant K_1^* can be evaluated from the equivalent conductance data [Λ_{NaOH} and $\Lambda_{NaH_3SiO_4}$ (Fig. 2)] on solutions with the same sodium ion concentrations. From eq. 5 and 6 an equation can be derived relating the equivalent conductance of the solutions with those of the ions λ_{OH^-}, λ_{Na^+} and $\lambda_{H_3SiO_4^-}$ and the hydrolysis constant K_H which is equal to K_w/K_1^*

$$\Lambda_{NaOH} - \Lambda_{NaH_3SiO_4} = (\lambda_{OH^-} - \lambda_{H_3SiO_4^-})\left[1 - \left\{\frac{K_w}{K_1^*(SiO_2)}\right\}^{1/2}\right] \qquad (10)$$

Here use is made of the assumption that the degree of hydrolysis of $H_3SiO_4^-$ is small in the pH range 11.2 to 12 and that in this pH range the concentration of hydrogen and $H_2SiO_4^-$ ions may be ignored. It is possible to neglect the hydrolysis because the constant is of the order of magnitude of only 10^{-4}. By plotting known values of the difference $\Lambda_{NaOH} - \Lambda_{NaH_3SiO_4}$ as a function of $[SiO_2]^{-1/2}$ a difference $\lambda_{OH^-} - \lambda_{H_3SiO_4^-}$ in the equivalent conductances of the ions of 145 was obtained as an intercept and from the slope of the curve a pK_1^* of 9.9 was calculated. This value of 9.9 is quite consistent with the pK_1 of 9.77 at 25° derived from solubility and pH measurements.[24]

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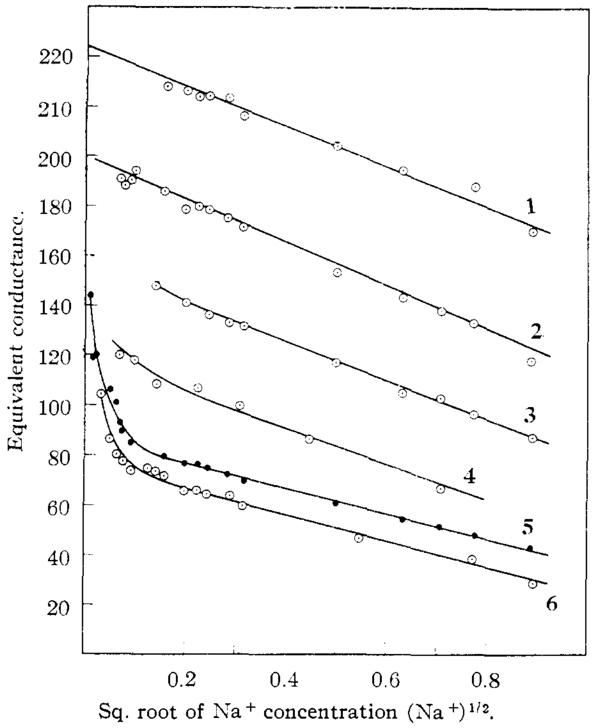

Fig. 2.—Relationships of the equivalent conductances with (Na$^+$)$^{1/2}$ of solutions of sodium hydroxide and sodium silicates of various mole ratios: (1) NaOH; (2) 1:0.5; (3) 1:1; (4) 1:1.5; (5) 1:2; (6) 1:3.

It is possible to calculate the equivalent conductance of $H_3SiO_4^-$ ions at infinite dilution by means of the equation

$$\lambda_{Na_2O\cdot nSiO_2} = \lambda_{Na^+} + (1 - x)\lambda_{H_3SiO_4} + x\lambda_{OH^-} \quad (11)$$

where x is the fraction of $H_3SiO_4^-$ ions hydrolyzed. The procedure consists in choosing linear portions of the curves in Fig. 2 at low concentrations where only Na$^+$, OH$^-$ and $H_3SiO_4^-$ ions are present (pH<11.8) and extrapolating these curves to zero concentrations. The intercept values are then considered the equivalent conductances at infinite dilution of mixtures of Na$^+$, $H_3SiO_4^-$ and OH$^-$ ions. Since λ_0 for Na$^+$ is 50.1 and for OH$^-$ is 198.6 at 25°[26] and the x values are known[9,13,27] in the region of concentrations considered, the λ_0 for $H_3SiO_4^-$ ions can be evaluated. In Table I the results are summarized.

TABLE I

THE EQUIVALENT CONDUCTANCE OF $H_3SiO_4^-$ IONS AT 25°

Na$_2$O: SiO$_2$ mole ratio	Λ_0, Na$_2$O: nSiO$_2$ 25°, ohms^{-1} cm.^{2}	χ I Hagg[9] 20°	χ II Harman[27] 25°	χ III Bacon and Wills[13] 20°	λ_0, $H_3SiO_4^-$, ohs^{-1} cm.^{2} I ref. 9	λ_0, $H_3SiO_4^-$, ohs^{-1} cm.^{2} II ref. 27	λ_0, $H_3SiO_4^-$, ohs^{-1} cm.^{2} III ref. 13	λ_0, H$_3$-SiO$_4^-$ Harman[15] (dil. soln.)
1:0.5	200	0.59	0.35	0.80	93	125	..	..
1:1	165	.38	.25	.50	65	87	32	60
1:1.5	127	.19	.12	.27	48	60	33	35
1:2	92	.040	.040	.06	35	35	32	43
1:3	83	.012	.011	.013	31	31	30	41

The table lists the various Na$_2$O:SiO$_2$ mole ratios, the Λ_0 or intercept values, average degrees of hydrolysis χ taken from several sources[9,13,27] and λ_0 values for silicate ions calculated on the basis of the various χ values. In the last column the λ_0 values for $H_3SiO_4^-$ ions reported by Harman are shown. Some difficulty was encountered in estimating χ, therefore both 20 and 25° data were used since χ does not change markedly with temperature.

The λ_0 value of 35 for the 1:2 mole ratio was considered most reliable because χ could be estimated accurately for this ratio. The difference between 31 and 35 in the 1:3 and 1:2 mole ratio solution is within experimental error, or as is more probably the case (Table II), there are a certain number of low molecular weight silicate aggregates present in the 1:3 solution. From the value 35 for λ_0 it should follow that $\lambda_{OH^-} - \lambda_{H_3SiO_4^-}$ at infinite dilution is about 160. Considering the large possible error in the extrapolation of the data using the relationship shown in eq. 10, which leads to a difference of about 145, we can conclude that the agreement is reasonable.

Transference Numbers.—A re-examination of the data of Harman[28] leads to quite interesting conclusions. Table II summarizes the results.

It was assumed that in these solutions only Na$^+$, OH$^-$ and $H_3SiO_4^-$ ions need be considered. By using the equation of Harman to calculate n_{SiO_2}, but assuming each SiO$_2$ is singly charged as $H_3SiO_4^-$ instead of doubly charged $H_2SiO_4^{=}$ ions as Harman did, the values of n_{SiO_2} were evaluated. Where the sums of n_{Na^+}, n_{OH^-} and n_{SiO_2} are greater than one, it is assumed that there is more than one SiO$_2$ per ion and in the last column of the table the values of N (no. of SiO$_2$ per ion) are listed.

From a knowledge of n_{SiO_2} in experiments 5 and 6, it was possible by means of the equivalent conductance data to evaluate λ_0 for $H_3SiO_4^-$ as 34 and 33, which is in good agreement with the quantities calculated from conductance results (Table I).

Conclusions

The results of the present study show fairly conclusively that in solutions of sodium silicate with SiO$_2$:Na$_2$O mole ratios up to 3:1 and above pH 10.5[15] a considerable number of experimental data can be explained without postulating the existence of polymeric particles or aggregates of monosilicic acid [Si(OH)$_4$]$_n$.

For the most part the diffusion experiments of Ganguly[29] support this theory. Cryoscopic measurements on sodium silicate solutions[9,30] indicate decreasing effects with increase in SiO$_2$:Na$_2$O ratio. Unfortunately, the results are often confusing and disagreements between authors[9,30] are found which perhaps show the experimental difficulties involved in these experiments. Although light-scattering measurements are reported[11] to *indicate* that the molecular weights of the silicate polyanions in Na$_2$O:nSiO$_2$ solutions with mole ratios between 1:0.5 and 1:3.75 increase from 60 to 400, the authors emphasize that these quantities are not absolute. It should be noted

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TABLE II

TRANSFERENCE NUMBERS

Expt. no.[28]	Mole ratio	(Na+)	pH	n_{Na^+}	$1 - n_{Na^+}$	n_{SiO_2}	n_{OH^-}	Hydrolysis,[25] %	N (no. of SiO_2/ion)
4	1:2	1.0	12.12	0.42	0.58	0.45	0.13	1.38	1
5	1:2	0.5	11.96	.34	.66	.33	.33	1.88	1
6	1:2	0.1	11.46	.45	.55	.47	.08	2.85	1
7	1:3	1.0	11.29	.40	.60	.68	..	0.192	1.1
8	1:3	0.5	11.27	.45	.55	.78	..	.36	1.4
9	1:4	1.0	10.86	.53	.47	1.17	..	.071	2.2
10	1:4	0.1	10.75	.44	.56	1.23	..	.57	2.2

that in the dilute solutions of sodium silicate used in light-scattering measurements, it is probable that all the silicate species are in solution as monomeric silicic acid.[24,31]

The silica in solutions appears to be colloidal under two conditions. In alkaline solutions above pH 10.6 low molecular weight silicate species are brought into solution by peptization.[31] Also in concentrated solutions of silicic acid the monosilicic acid behaves as if it were aggregated into $[Si(OH)_4]_n$ particles where n is probably a small number.[15]

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CHICAGO, ILLINOIS

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The Synthesis and Properties of Zirconium Disulfide[1]

BY ABRAHAM CLEARFIELD

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Historic methods for preparing zirconium disulfide were re-examined and new and refined methods for obtaining a pure product have been developed. The reaction of carbon disulfide with zirconia yields a mixture of zirconium disulfide and zirconium sulfoxide, ZrOS, in the temperature range 850–1200°. Above 1200° only zirconium disulfide is obtained. This has been correlated with the presence of different forms of zirconia in the two temperature ranges. The air oxidation of the disulfide was examined by means of differential thermograms and high temperature X-ray diffraction patterns.

Published information on the sulfides of zirconium is meager and much of what is reported is conflicting. Therefore, a study of the zirconium–sulfur system was undertaken. The present paper describes the synthesis and some properties of zirconium disulfide.

Zirconium disulfide has been synthesized by a variety of methods. Frémy[2] claimed to have prepared it by the action of carbon disulfide on zirconia at red heat. No analysis was given and it is questionable that his product was oxygen-free. A number of workers obtained zirconium disulfide by combination of the elements.[3–5] Of these only Biltz[3] used reasonably pure metal. Biltz and his co-workers also treated zirconium tetrachloride with hydrogen sulfide in a heated tube. They derived a pure product only after reheating the initially obtained material in a hydrogen sulfide atmosphere. Paykull[6] had been unsuccessful with this reaction because he did not rigidly exclude oxygen. VanArkel and DeBoer[7] passed zirconium tetrachloride and sulfur vapors over a hot wire and obtained pure zirconium disulfide but in poor yield. Finally, Hägg and Schönberg[8] reported its preparation by the action of hydrogen sulfide on zirconium metal in the temperature range 550–900°.

Experimental

Materials.—Pure zirconium dioxide was prepared by addition of glycolic acid (3 moles) to a solution of zirconyl chloride (1 mole) and calcining the precipitated triglycolatozirconic acid at 900–1000°. A typical sample contained 0.001% Al, 0.002% Ba, 0.02% Ca, 0.002% Cu, 0.001% Fe, 2% Hf, 0.01% Mg, 0.002% Na, 0.01% Si, 0.002% Ti. Zirconium tetrachloride was resublimed from a fused salt ($KCl-ZrCl_4$) melt as described by Horrigan.[9] The zirconium metal powder was Titanium Alloy P grade (–200 mesh) and contained 1–2% oxygen. Zirconium Hydride was obtained from Metal Hydrides, Inc. Traces of oxygen were removed from argon (originally 99.9% pure) by bubbling it through alkaline pyrogallol and drying by passage through tubes containing P_2O_5. Gaseous impurities in tank hydrogen sulfide (99.8% pure) were minimized by inverting the tank and drawing off liquid H_2S. Reagent grade carbon disulfide was used without further purification.

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