Study on the Electric Conductivity of Sodium Silicate Aqueous Solution. I.

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Introduction

The electric conductivity of sodium silicate solution has been only rarely reported, since Harman[1] measured it in 1925 in one of his consecutive experiments attempted for the electrochemical investigation of this solution. Though his experiment exceeds far beyond that previously reported by Kohlrausch[2], with repect to the range of molar ratio and concentration of solutions measured, it still lacks satisfactory abundance of data, especially for higher concentration. In the present study the measurement was made for the solution of molar ratio (SiO_2/Na_2O) 1.00, 1.52, 2.15, 3.02. and 3.95 at the concentration ranging from 0.001 N up to that, over which the solution hardly flows due to high viscosity, with reasonable numbers of measured points between both extreme concentrations. Where the ratio and concentration of the hereby measured silicate solutions corresponds to those measured by Harman, the two values were in good accordance.

The equivalent conductivity was derived from the specific conductivity, using the molecular weight as indicated by a formula. Thus far no theoretical treatment has been given for the conductivity of sodium silicate solution. Herein theoretical calculation was attempted for the equivalent conductivity of the molar ratio 3.95 silicate solution, and the results were found to be in good agreement with experimental data, if some supposition was admitted. In lower ratio solution, as hydrolysis takes place considerably, the results could not be dealt with theoretically, due to the complicated state of ions in solution.

Experimental

Materials.—Two methods were used for the preparation of pure sodium silicate solution. (1) First, sodium metasilicate crystal $Na_2(H_2SiO_4)\cdot 8H_2O$ was prepared by the following method from the original solution of molar ratio 3.0 and Na_2O concentration of 9%, then it was electrolyzed with mercury cathode to obtain the desired molar ratio. The original solution, of commerical grade produced by Asahi Glass Co., was diluted by the same volume of water, adding 2 volumes of NaOH solution of sp. gr. 1.26 and 2 volumes of ethyl alcohol. A small number of crystals were used as nuclei in order to hasten the crystallization which otherwise would have taken several days. After the crystals developed, they were filtered off by Buchner funnel, washed by 50% alcohol, drained off thoroughly, then resolved again into pure water. To the solution, containing about 20% sodium metasilicate, was added one tenth volume of NaOH solution (sp. gr. =1.26), ethyl alcohol and a bit of nuclei. The solution was kept cool in ice water under stirring. Then sodium metasilicate recrystallized out in a few hours. This was filtered off, washed, drained and dried completely in a vacuum desiccator. The stock solution was prepared by dissolving these crystals. In order to make higher molar ratio silicate solution, this stock solution, usually containing 20% metasilicates was electrolyzed with mercury cathode and rotating platinum plate anode. An electrolytic cell is shown in Fig. 1.

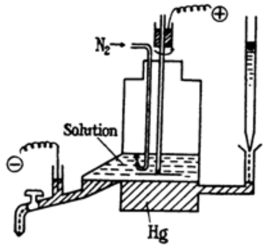

Fig. 1. Electrolytic cell.

The anode, a disk of 5 cm. diameter, was rotated with a velocity of 200 r. p. m. keeping 5 mm. away from the surface of mercury. The Na-amalgam produced was pushed out towards the outlet owing to the increased surface level caused by constantly supplied fresh mercury. During the electrolysis CO_2-free nitrogen gas was bubbled through the solution. In a run 150 cc. of solution was treated. The current density was kept at 0.8 amp. per sq. cm. Electrolysis was conducted for the time necessary for removing the definite amount of Na_2O to reach the degired molar ratio. (2) As it was time-consuming to make a concentrated solution of high molar ratio by the foregoing method, the following method of purification was substituted for it. The original various solutions, of commercial grade, were diluted to the concentration of about 3% Na_2O. After being filtered twice through hardened, alkali-proof filter paper, they were concentrated by vacuum evaporation. The

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[1] R.W. Harman, *J. Phys. Chem.*, **29**, 1155 (1925).

[2] F.W. Kohlrausch, *Z. Physik. Chem.*, **12**, 773 (1893).

products were quite transparent, though retaining their original yellowish colour. The silicate solutions of ratio 2 prepared by the two methods were compared with each other as to their conductivity. The results showed no significant differences between the two series of data. The stock solutions thus prepared were analysed respecting their SiO_2 and Na_2O content and the molar ratio was decided strictly. Besides, the CO_2 content was analysed for check because of its deleterious effects. The more dilute solutions were prepared by diluting the stock solution with pure water which was distilled twice using quartz apparatus. It has the conductivity of $1\sim2\times10^{-6}$ $\Omega^{-1}\,cm^{-1}$. Every solution was stored in a polyethylene bottle free from the atmosphere. All chemicals used were of reagent grade.

Apparatus for the Conductivity Measurement.—Conductivity was measured by Wheatstone bridge, using cathode ray oscillograph as detector. The bridge consisted of shielded variable resistance boxes, of which two had 10,000 Ω, and one 100,000 Ω. A variable condenser was set up parallel with the latter one. The measurement was made at 1000 cycles. A variable audiofrequency oscillator served as current source. The constants of four conductivity cells used were 1.242, 1.380, 0.4850 and 0.6568. The former two had platinized electrodes and they were used for the concentrated silicate solutions, the latter two, used for the dilute solution had non-platinized electrodes. The inner surface of the cell was coated with epoxy resin film to protect the glass wall from corrosion by the alkaline solution. The temperature was controlled to ±0.01° at 25°C, employing a double thermostat with sensitive regulator operated by electronics circuit.

Measurement.—Measurement was made at twenty-four hours after new dilute solution had been prepared, except for a very dilute solution, where it was made at thirty minutes after the preparation. The variation of conductivity with time was small enough to allow the later theoretical consideration without correction, even with very dilute solutions. The data were reproduced within ±0.2% except for a very dilute solution. The cell constant was checked frequently with 0.01 N or 0.1 N KCl standard solution. Even after the most concentrated silicate solution was measured, the constant did not change appreciably, if washed carefully.

Results

The specific conductivity λ for various molar ratio sodium silicate solutions is shown in Fig. 2 and Fig. 3. The concentration is indicated by Na_2O weight percent. The conductivity increases with increasing concentration until it attains its maximum, then begins to decrease. This tendency of conductivity curve is not very different from what is seen with common low molecular electrolyte solution. As shown here, all the curves seem to have much the same form regardless of molar ratio of sodium silicate solution, although the change of conductivity becomes greater as the molar ratio of solution decreases. It is noteworthy that the form of conductivity curves, having similarity among different molar solutions, appears to have little dependence on

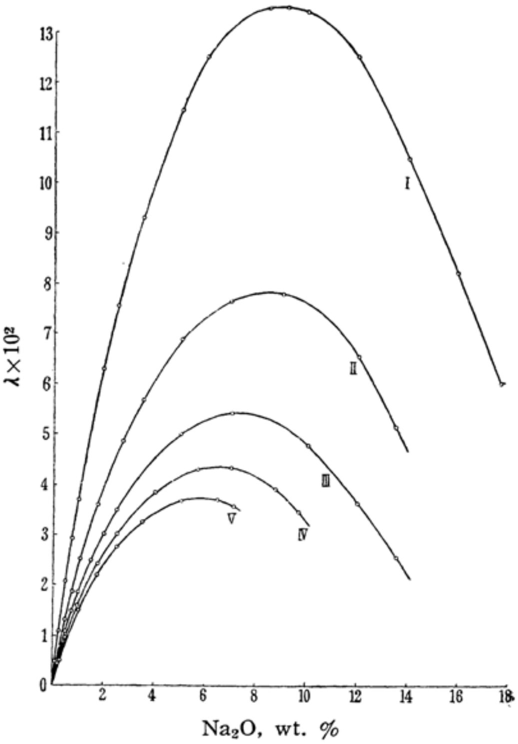

Fig. 2. Variation of specific conductivity of sodium silicate solutions with concentration at 25°C.

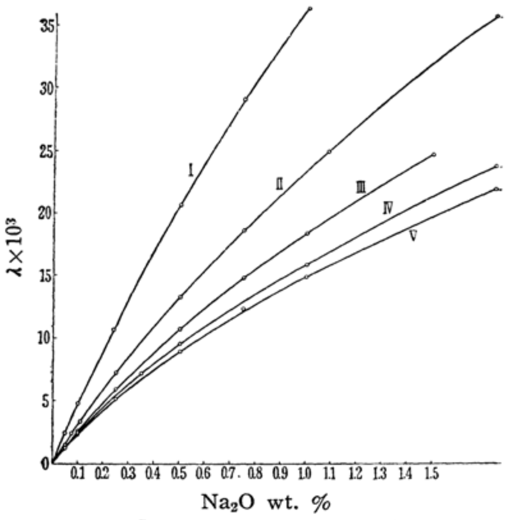

Fig. 3. Specific conductivity of sodium silicate solutions for lower concentration range at 25°C. Molar ratio, I 1.00; II 1.52; III 2.15; IV 3.02; V 3.95.

their viscosity. For instance the solution of molar ratio 3.95 has the maximum specific conductivity at the concentration of 6%, and at 7% it has a slightly lower, but still high conductivity. However, viscosity increases surprisingly between the two concentrations (0.25 poise at 6%, more than 1000 poise at 7%). On the other hand, for the solution of molar ratio 2.15, viscosity changes slowly from 0.032 poise at the concentration where maximum conductivity is shown, to 1.03 poise at as high as 13%. Also there is only a little increase of viscosity for the metasilicate solution over the measured concentration range, though specific conductivity varies very widely.

Fig. 4 shows the change of specific conductivity with molar ratio of silicate solution of the definite Na_2O content. The variation of conductivity with the ratio appears to be sharp around molar ratio 2. This would be explained by the fact that hydrolysis increases rapidly as the molar ratio of solution falls below 2, and OH ion with exceptionally high mobility comes to contribute to the conductivity.

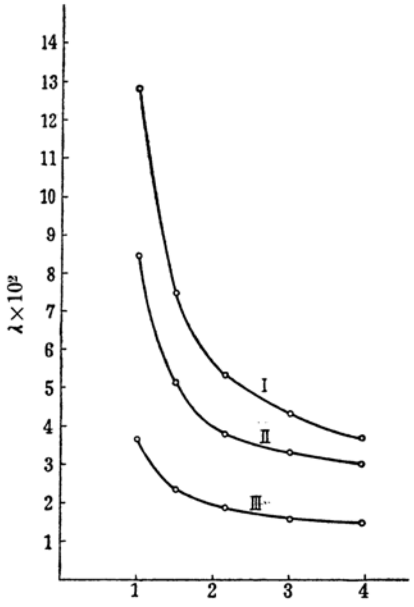

Fig. 4. Relationship between specific conductivity and molar ratio. Na_2O wt. %, I 6.50; II 3.00; III 1.00.

Equivalent conductivity Λ was calculated from the following equation.

$$\Lambda=1000\lambda\cdot N/A\cdot d=1000\lambda/C$$

A represents the solid content (g.) per 1000 g. solution, d, the density of solution, N, normal weight, and C, normality. For the estimation of normality, expressed with regard to Na gram equivalent per 1000 cc. of solution, molecular composition such as Na_2SiO_3, $Na_2O\cdot2SiO_2$, $Na_2O\cdot3SiO_2$, etc. was employed. Thus, for example, 1 N solution of 2.15 molar solution contains 1/2 ($Na_2O\cdot2.15\,SiO_2$) expressed in grams, in 1000 cc. solution. Fig. 5 shows Λ vs. C curves for various silicate solutions. The fact that curves in Fig. 5 show no breaking point would evict any idea of discontinuous change of molecular constitution, e. g. micelle formation, over the whole range of concentration. At the extreme dilution it appear that equivalent conductivity tends to go up irregularly high, so that it is difficult to extrapolate them to zero concentration. It may have been caused partly by hydrolysis effect[3].

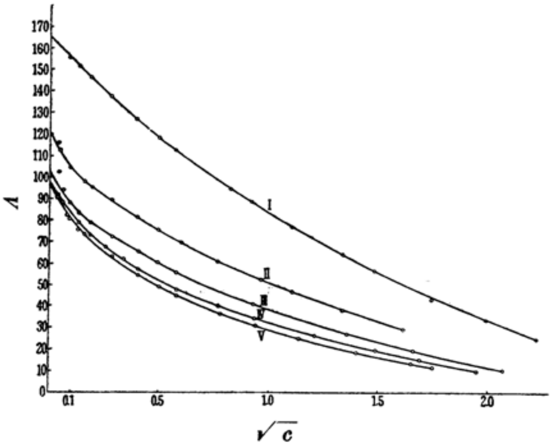

Fig. 5. Variation of the equivalent conductivity of various sodium silicate solutions with square root of concentration. Molar ratio, I 1.00; II 1.52; III 2.15; IV 3.02; V 3.95.

Nevertheless, limiting equivalent conductivity was estimated by the extrapolation of curves on Fig. 5. The extrapolation would have eliminated the effect of hydrolysis which increased rapidly below the concentration of 0.005 N. Thus obtained values for silicate solution of molar ratio 1.00, 1.52, 2.15, 3.02 and 3.95 were 165, 120, 103, 98, and 96 respectively. Since the limiting equivalent conductivity of sodium ion is 50.1, that of silicate ion seems to be fairly high, almost comparable with that of sodium ion, taking into consideration the fact that the contribution of OH ion is very small for the higher molar ratio solution[4].

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3) Harman[5] calculated hydrolysis percentage for various molar ratio solutions from the pH values, showing that it increases rapidly in the extreme dilution for the lower ratio solution.

4) According to Harman's data hydrolysis % of $Na_2O\cdot4SiO_2$ solution at 0.01N is 1.5% which contributes only 2 to its limiting equivalent conductivity.

Discussion

It is well accepted that a molecule of sodium metasilicate[5,7] consists of $Na_2(H_2SiO_4)$ which dissociates in solution into four kinds of ion, i.e. Na^+, $H_3SiO_4^-$, $H_2SiO_4^{--}$ and OH^-. Here OH^- ion is brought about by hydrolysis which takes place in two steps,

$$H_2SiO_4^{--} + H_2O \rightleftarrows H_3SiO_4^- + OH^-$$
$$H_3SiO_4^- + H_2O \rightleftarrows H_4SiO_4 + OH^-$$

As for the silicate solutions having other molar ratio than 1, there is not yet a definite theory as to the kinds and behaviors of ions present in solution. However, the light scattering experiments[8] revealed that in these solutions molecules were still not of large size as with organic high molecular compound, but at most, of several hundreds in molecular weight. This fact was also well explained by viscometric study[8,9]. Furthermore there are other indications[7,10] showing that the existence of molecular-type compounds such as expressed by $Na_2O \cdot 2SiO_2$, $Na_2O \cdot 3SiO_2$, etc.[11] in solution may not be highly inadequate. First of all, assuming this is the case, it was attempted to see whether the equivalent conductance could be explained by theory. For this purpose the silicate solution of molar ratio 3.95 was sampled, because its negligible hydrolysis made it possible to consider the existence of only two kinds of ion, i.e. two sodium ions and one silicate ion. Secondly it was assumed that the silicate ion possessed two minus charges as a result of dissociation of two sodium ion. The theoretical treatment was based on Falkenhagen's equation which was the recent theoretical extension of the theory of Onsager to include the effect of definite ionic size and has been proved to show excellent agreement with experimental data for 1:1 type electrolyte solution[12].

Wishow and Stokes[13] showed furthermore, that Falkenhagen's equation stands good for 1:1 electrolyte solution up to surprisingly high concentration if applied with the correction for bulk viscosity. For unsymmetrical electrolytes, the apparent defect of the theory, caused by the unsatisfactory convergence of electrophoretic terms may be eliminated, if a large effective ionic diameter can be assigned to them. With these facts, it would be interesting to attempt here the comparison of the experimental data with those derived from the theory, though electrolyte was assumed hereby to be 1:2 type instead of 1:1.

Falkenhagen's expression for the equivalent conductivity of single electrolyte solution is written as follows:

$$\Lambda=\left\{\Lambda^0-\frac{1.546\times10^{-7}}{6\pi\eta}(|z_1|+|z_2|)\frac{\kappa}{1+\kappa a}\right\}$$
$$\times\left(1+\frac{\Delta X}{X}\right)$$

$$\kappa=\left(\frac{8\pi Ne^2}{1000\varepsilon KT}\right)^{1/2}\sqrt{I}$$

e: electronic charge
N: Avogadro's number
η: viscosity of solvent
z_1, z_2: valencies of cations and anions respectively
I: ionic strength
K: Boltzmann's constant
T: absolute temperature
ε: dielectric constant of solvent
a: mean ionic diameter

The second term on the right hand expresses the electrophoretic effect on conductivity. The last term $\Delta X/X$ expresses the relaxation field and is shown as[14]

$$\frac{\Delta X}{X}=\frac{z_1z_2e^2}{3\varepsilon KT}\cdot\frac{q}{1-q}\cdot\frac{\kappa}{\kappa a(1+\kappa a)}[e^{\kappa a(1-\sqrt{q})}-1]$$

q is defined by

$$q=\frac{|z_1z_2|}{|z_1|+|z_2|}\cdot\frac{\lambda_1^0+\lambda_2^0}{|z_2|\lambda_1^0+|z_1|\lambda_2^0}$$
$$=\frac{|z_1z_2|}{(|z_1|+|z_2|)(|z_2|t_1^0+|z_1|t_2^0)}$$

t_1, t_2 and λ_1^0, λ_2^0 denote transport number and equivalent conductivity of cation and anion respectively at infinite dilution. Here the Eigen and Wicke distribution function was replaced by the Boltzmann distribution function.

Inserting the values of constants the equation reduces to

$$\Lambda=\left(\Lambda^0-\frac{156.5}{1+0.568\mathring{a}\sqrt{c}}\right)$$
$$\times\left(1-\frac{0.721\sqrt{c}}{1+0.568\mathring{a}\sqrt{c}}\cdot F\right)$$

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5) R.W. Harman, *J. Phys. Chem.*, **30**, 1100 (1926).

6) E. Thilo and W. Miedreich, *Z. anorg. allgem. Chem.*, **267**, 76 (1951).

7) P.P. Roller and G. Erwin, *J. Am. Chem. Soc.*, **62**, 461 (1940).

8) P. Debye and P.V. Nauman, *J. Phys. Chem.*, **55**, 1 (1951).

9) H. Ukihashi, *Reports of the Research Laboratory, Asahi Glass Co.*, Vol. II, No. 1, 48 (1952).

10) R.W. Harman, *J. Phys. Chem.*, **30**, 359 (1926).

11) The foregoing molecular formulae are stoichiometrically satisfied by writing as $Na_2O \cdot 2SiO_2 \cdot 2H_2O$, $Na_2O \cdot 3SiO_2 \cdot 3H_2O$, etc.

12) R.A. Robinson and R.H. Stokes, *J. Am. Chem. Soc.*, **76**, 1991 (1954).

13) B.F. Wishaw and R.H. Stokes, *J. Am. Chem. Soc.*, **76**, 2065 (1954).

14) R.H. Stokes, *J. Am. Chem. Soc.*, **76**, 1988 (1954).

$$F=(e^{\kappa a(1-\sqrt{q})}-1)/\kappa a(1-\sqrt{q}),$$
$$\kappa a=0.568\mathring{a}\sqrt{c}$$

$\mathring{a}$: mean ionic diameter expressed in Ångstrom

In order to calculate the equivalent conductivity of sodium silicate solution according to this equation it is important to assign the most probable value to $\mathring{a}$ and q. Here, t_1 was assumed to be equal to t_2, thus $t_1=t_2=0.5$. This assumption would not be so far away from the truth, as judged from the value of limiting equivalent conductivity and also the result obtained by Harman[10] regarding the transport number of sodium silicate solution[15]. For evaluating $\mathring{a}$, calculations were made on the equation by inserting to it various values of $\mathring{a}$, and the results were plotted on Fig. 6. It seems that the use of the value 7 Å. of $\mathring{a}$ on the calculation fits best for the agreement between experimental and theoretical curve. This value appears rather small. However, if attention is turned to the fact that at the concentration where the viscosity of sodium silicate solution abruptly increases to a remarkable degree, the distance between solute molecules was approximately 10 Å.[8,9], it would be allowable value, considering the hydration effect in the above case, along with such a discrepancy between the value of $\mathring{a}$ required theoretically and estimated from ionic radii, as usually encountered in the case of unsymmetrical electrolyte solution.

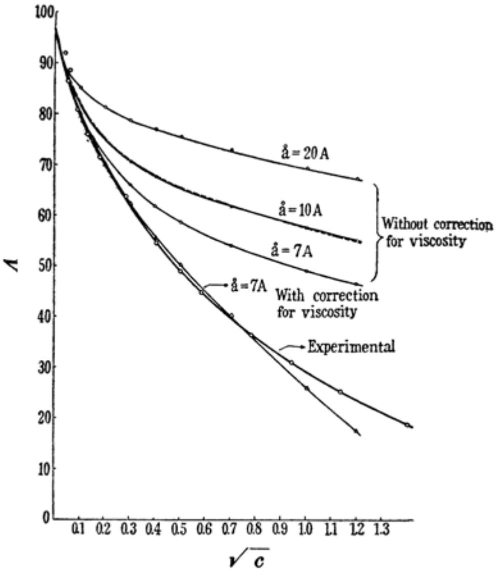

Fig. 6. Comparison of the equivalent conductivity of sodium silicate solution of molar ratio 3.95 with those calculated from the theoretical equation.

Since sodium silicate solution bears high viscosity owing to its hydration as with lithium chloride solution[13], the correction for the bulk viscosity would be necessary. For this purpose, Falkenhagen's equation has to be divided by relative viscosity of solution. After this was done, the agreement was further improved up to the higher concentration, about 0.8 N (2% of Na_2O concentration). Above that, the viscosity correction increases rapidly so that the theoretical line fall increasingly below the experimental values.

Thus, it is possible to explain the conductivity of sodium silicate solution, within the moderate concentration range, on the basis that its molecule essentially be small, and silica ion be polymerized to such an extent as expressed by its formula, even if it might be supposed to contain some aggregated molecules in the higher concentration. This fact is well consistent with the results obtained by both viscometric and light-scattering investigation.

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[15] A little difference in this value does not affect sensitively on the result of calculation. In Fig. 6 a curve is drawn which was obtained by using the values $t_1=0.6$, $t_2=0.4$ as a comparison.