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

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Introduction

Few data have been reported on the dependence of the electric conductivity of sodium silicate solution on temperature. In the present paper are given the electric conductivities measured at 5°, 15°, 25°, 35°, 45° and 60°C of sodium silicate solution of silica-alkali molar ratio ranging from 1 to 3.95 over a wide range of concentration.

From the results, temperature coefficients of the specific conductivity were computed and compared with those of simple strong electrolyte solutions. The equivalent conductivity was derived in the same way as reported in the preceding paper[1]. For the dilute solutions the applicability of Walden's rule, i. e., the independency of the product of equivalent conductivity and solvent viscosity on temperature was examined, and the ionic radius of silicate ion was estimated therefrom. Theoretical treatment of the equivalent conductivity for the 3.95 molar ratio solution was extended to those at other temperatures than 25°C, and it was confirmed that they could be explained theoretically at each temperature with the same assumption as previously described.

Meanwhile, hydroxyl ion concentration was checked at these temperatures for the sodium silicate solutions of three kinds of molar ratio to examine its contribution to their conductivities.

The independence of the conductivity on the viscosity of solution in the higher concentration range was emphasized, and this problem will be discussed in the succeeding paper.

Experimental

Materials. — The sodium silicate solutions were prepared by the same method as described previously[1]. The silica-alkali molar ratio of the solutions herein used were 1.00, 1.55, 2.13, 3.19, and 3.95.

Apparatus and Measurements.—Apparatus for the conductivity measurement was the same as previously reported. The six cells were used, the constants of which were 0.4850, 0.6568, 1.242, 1.380, 16.86 and 18.75. The measurements were made at a series of increasing temperatures from 5° to 60°C, without replacing the solution, except in the case where variation in conductivity with temperature was so much as to require the use of different cell constant. For a dilute solution having possibility of change in conductivity with time, the measurement at each temperature was made 30 minutes after preparation. However, the conductivity change with time was small as compared with the accuracy of this experiment, at most within ±0.5% during the first one hour after preparation. For each molar ratio solution density was measured at these temperatures over a wide range of concentration, using 25 cc. pycnometer. These values were needed for expressing concentration as normality.

Besides, pH was measured for three kinds of sodium silicate solution of molar ratio 1.00, 2.13, and 3.95, at temperatures 5°, 15°, 25°, 35 and 45°C. Beckman Model H-2 *p*H-Meter was used with Beckman type E glass electrode especially designed for the measurements in highly alkaline solution. It is questioned, however, whether the silicate solution does not give any detrimental effect on the glass electrode. To ascertain the reliability of the observed data *p*H values obtained

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[1] H. Ukihashi. This Bulletin, **29**, 537 (1956).

[2] R. W. Harman. *J. Phys. Chem.*, **30**, 1100 (1926).

at 25°C were compared with those obtained by Harman[2] with hydrogen electrode, and those measured by Küntzel et al.[3]. They were approximately in accord with each other within ±0.1, whereas no comparison was available for the values obtained at other temperatures than 25°C[4,5]. For pH measurement, a sample solution was put in 100 cc. polyethylene beaker and covered with vinyl plate with two holes for insertion of electrodes. The meter was frequently standardized with borax and soda buffer solution at each temperature.

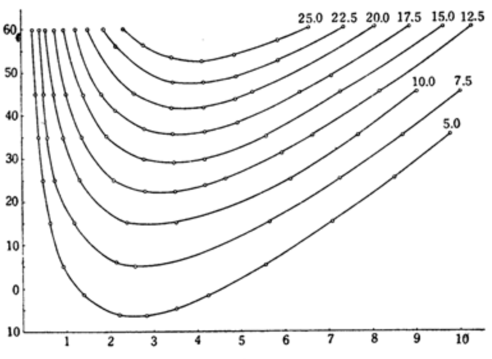

Fig. 1. Iso-conductivity curve of sodium metasilicate solution (numerals for each curve denote $\lambda \times 10^2$)

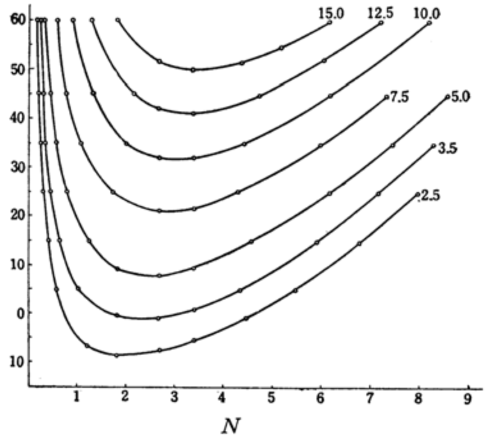

Fig. 2. Iso-conductivity curve of sodium silicate solution of molar ratio 1.55 (numerals for each curve denote $\lambda \times 10^2$)

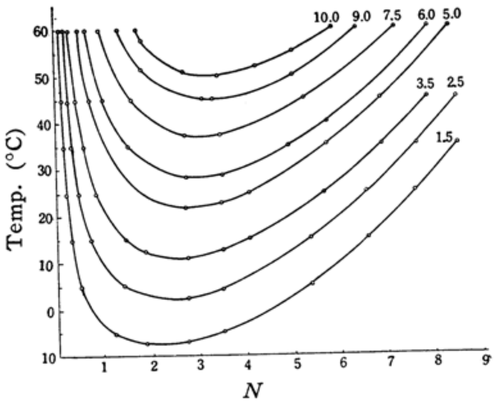

Fig. 3 Iso-conductivity curve of sodium silicate solution of molar ratio 2.13 (numerals for each curve denote $\lambda \times 10^2$)

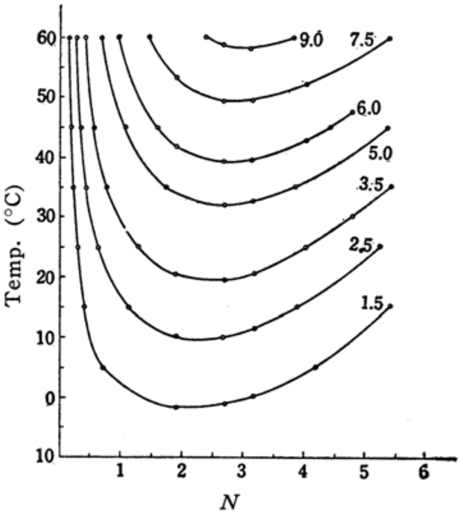

Fig. 4. Iso-conductivity curve of sodium silicate solution of molar ratio 3.19 (numerals for each curve denote $\lambda \times 10^2$)

Results and Discussion

In Fig. 1–5 contour maps are given, which express the specific conductivity as a function of temperature and concentration. Here points on each line have the same conductivity. These curves were drawn as follows. Points on temperature absissas of 5°, 15°, 25°, 35°, 45° and 60° were taken from the data on the curves expressing the relation between specific conductivity and concentration at respective temperatures. Other data were obtained by the inter- and extrapolation of the relation curves between conductivity and temperature at various concentrations.

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3) L. E. Küntzel, J. W. Hensley and L. R. Bacon, *Ind. Eng. Chem.*, **35**, 1286 (1943).

4) Schuffelen and Hulst[6], who measured the pH of some concentrated water glass, stated that glass electrode did not produce a satisfactory result, while Sb electrode did. On the other hand, Küntzel et al. measured the pH of dilute sodium silicate solution with both hydrogen and glass electrode, and found the differences between two values to be very small at room temperature but to increase as temperature increases. The pH values obtained by Schuffelen and Hulst are 0.3—0.5 smaller than those obtained by other workers cited herein.

5) Complete data of pH hereby measured will be reported in *Reports of the Research Laboratory, Asahi Glass Co.*

6) A. C. Schuffelen and L. J. N. van der Hulst, *C. A.* **36**, 3583, 5580 (1942).

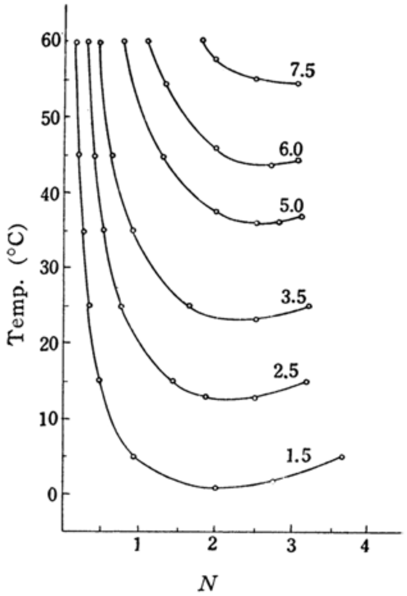

Fig. 5. Iso-conductivity curve of sodium silicate solutions of molar ratio 3.95 (numerals for each curve denote $\lambda \times 10^2$)

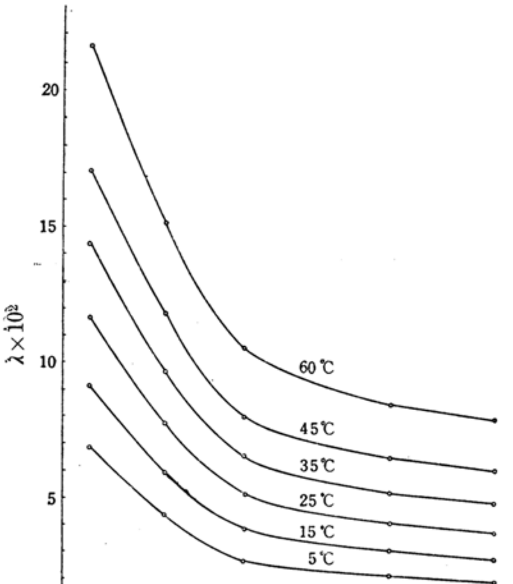

Fig. 6. Relationship between specific conductivity and molar ratio at Na_2O wt. % 5.00.

Here the concentration is indicated by normality of sodium ion content. As seen in these figures the change in specific conductivity with temperature increases as concentration increases in view of wide temperature range, but at a fixed temperature it has the maximum at a moderate concentration, where maximum specific conductivity is attained. As for the concentration dependence of specific conductivity, it increases as temperature rises up, and at a fixed temperature it becomes the minimum around a moderate concentration where specific conductivity shows the maximum. This concentration moves upwards with temperature increase. Fig. 6 shows the relationship between conductivity and molar ratio of sodium silicate solution at a fixed concentration. It is seen that decrease in conductivity with molar ratio gets more remarkable as temperature goes up, and yet all the curves have an obvious bend around molar ratio 2. In Fig. 7 the concentration showing maximum conductivity is plotted against the molar ratio of the solution. In this case no bend seems to appear. This fact should be expected, because the change in conductivity with molar ratio is due primarily to the difference of hydrolysis percentage in the solutions, while the concentration giving maximum specific conductivity may be attributed to the degree of compactness of the solute molecule in the solution and dependent on the molecular volume of sodium silicate molecule in respective molar ratio solution. If the latter is admitted, intermolecular distance at that concentration may have a linear relation with cubic root of molecular weight. This was the case as seen in Fig. 8, where two curves were drawn for both 5°C and 60°C. Here molecular weight was assumed as such

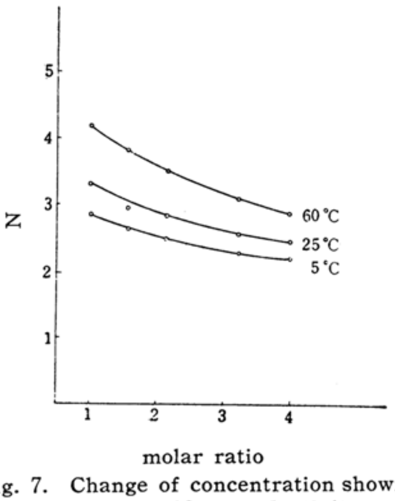

Fig. 7. Change of concentration showing maximum specific conductivity with molar ratio of sodium silicate solutions.

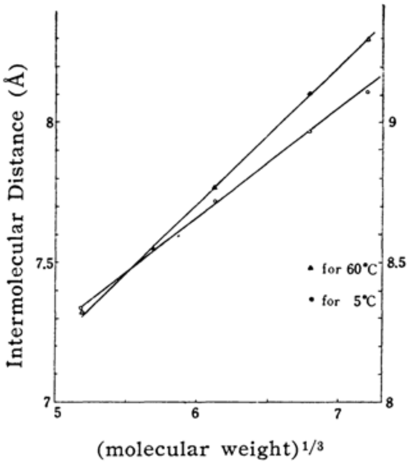

Fig. 8. Relationship between intermolecular distance at concentration showing maximum specific conductivity and cubic root of molecular weight of various sodium silicates.

expressed by the conventional formula.

The temperature coefficient of specific conductivity, as expressed by a and b in the following equation were calculated by the least square method and tabulated in Table 1.

$$\lambda=\lambda_0+aT+bT^2$$

λ_0 is the specific conductivity at 0°C. The table indicates that the first order temperature coefficient has the maximum values in a moderate concentration, while the second order temperature coefficient continues to increase with concentration. This means that the higher the temperature, the larger the temperature coefficient of the more concentrated solution becomes. In Fig. 9 $d\lambda/dT$ at 25°C was plotted against concentration of various sodium silicate solutions together with those of simple strong electrolyte solutions, the latter being quoted from "Landolt und Börnstein Tabellen" with adequate unit conversion.

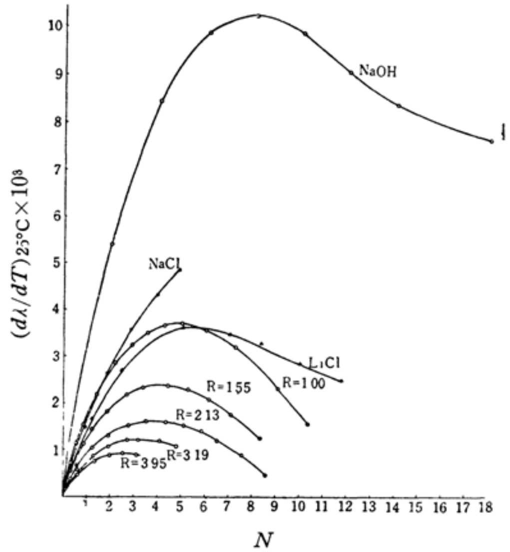

Fig. 9. The change of temperature coefficient of specific conductivity.

TABLE I

TEMPERATURE COEFFICIENT OF SPECIFIC CONDUCTIVITY OF VARIOUS MOLAR RATIO SODIUM SILICATE SOLUTIONS

Na$_2$O wt% Molar Ratio		1.00	2.50	5.00	7.50	9.00	10.50	12.00	16.00
1.00	$\lambda_0\times10^2$	1.96	3.93	5.78	6.20	5.93	5.31	4.50	2.03
	a $\times10^4$	6.36	13.10	20.25	25.21	26.01	25.73	23.82	13.32
	b $\times10^6$	1.74	4.36	9.18	14.53	18.29	22.19	26.77	37.35
1.55	$\lambda_0\times10^2$	1.35	2.60	3.57	3.55	3.21	2.60	1.97	(15.00) 0.84
	a $\times10^4$	4.79	9.31	14.43	16.28	16.03	14.90	12.54	5.05
	b $\times10^6$	1.63	4.14	7.82	12.15	15.06	17.78	20.56	25.25
2.13	$\lambda_0\times10^2$	0.874	1.59	2.16	2.15	1.89	1.49	1.03	0.332
	a $\times10^4$	3.50	6.77	9.98	11.10	10.72	9.06	6.94	4.72
	b $\times10^6$	1.69	3.52	6.25	9.08	11.06	13.40	15.25	17.53
3.20	$\lambda_0\times10^2$	0.739	1.30	1.64	1.47	1.15	(10.13) 0.861		
	a $\times10^4$	2.95	5.71	8.23	8.34	7.14	5.58		
	b $\times10^6$	1.49	2.90	5.08	7.89	9.70	11.03		
3.95	$\lambda_0\times10^2$	0.688	1.16	1.41	(6.47) 1.36				
	a $\times10^4$	2.93	5.78	7.86	8.03				
	b $\times10^6$	1.19	2.34	4.64	5.83				

The figure shows that the temperature coefficient of specific conductivity of sodium silicate solution is rather small as compared with simple strong electrolyte solutions, and the decrease in temperature coefficient with concentration in the higher concentration range is more marked than that of those solutions. This might lead to a suggestion that the temperature coefficient of mobility of silicate ion is small and its trend of making a kind of configuration in the solution is greater than that with simple strong electrolyte.

The equivalent conductivity Λ at various temperatures were plotted against the square root of concentration. Fig. 10, 11 and 12 show those obtained for the silicate solutions of molar ratio 1, 2.13 and 3.95.

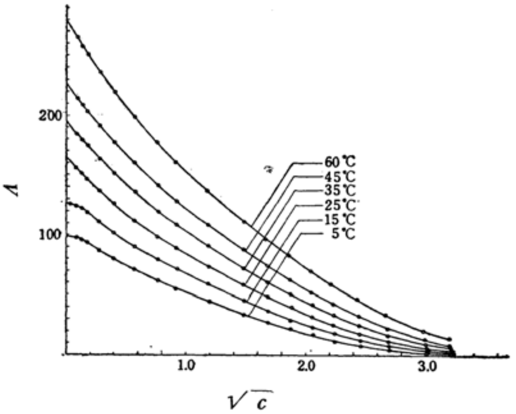

Fig. 10. Variation of the equivalent conductivity of sodium metasilicate solution with square root of concentration at various temperatures.

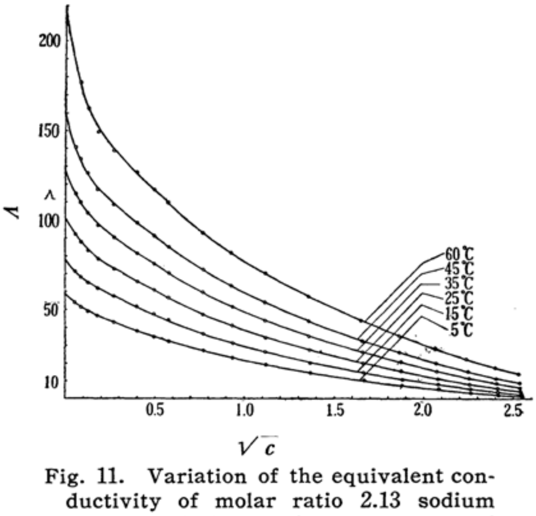

Fig. 11. Variation of the equivalent conductivity of molar ratio 2.13 sodium silicate solution with square root of concentration at various temperatures.

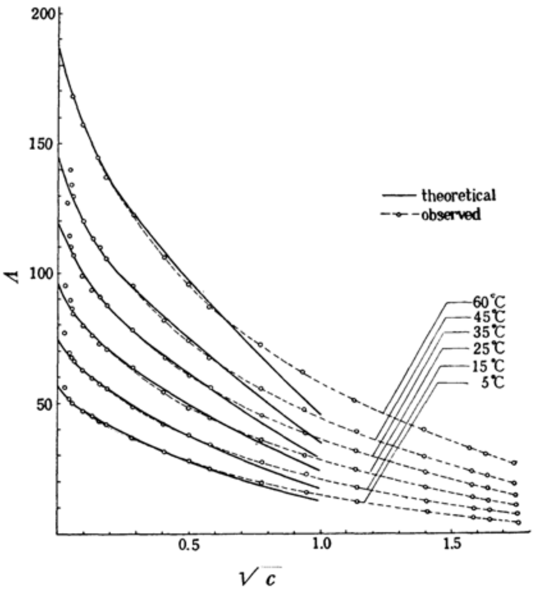

Fig. 12. Comparison of the equivalent conductivity of molar ratio 3.95 sodium silicate solution with those calculated from the theoretical equation at various temperatures.

The limiting equivalent conductivity Λ_0 was estimated by the extrapolation of curves to infinite dilute concentration. They are tabulated in Table II, together with the product of Λ_0 and solvent viscosity η_0. In Fig. 13 $\Lambda\eta$, including $\Lambda_0\eta_0$, are plotted against temperature for dilute solutions of these three kinds of molar ratio. It is seen that while Walden's rule is fully applicable to the 3.95 molar ratio solution, $\Lambda\eta$ for metasilicate solution decreases markedly with increase in temperature, and that for the 2.13 molar ratio solution increases slightly with it. These facts may be explained by considering the contribution of OH^- ion in the solutions to the equivalent conductivity.

TABLE II

LIMITING EQUIVALENT CONDUCTIVITY AND ITS PRODUCT WITH VISCOSITY OF SOLVENT

M.R.	1.00		2.13		3.95	
Temp.	Λ_0	$\Lambda_0\eta_0$	Λ_0	$\Lambda_0\eta_0$	Λ_0	$\Lambda_0\eta_0$
5°C	98	149	59	90	56	85
15°C	128	145	79	90	74	84.4
25°C	165	148	102	91.5	96	85.8
35°C	194	140	128	92.5	119	85.9
45°C	227	136	158	94.6	144	86.2
60°C	282	132	210	98.5	186	87.2

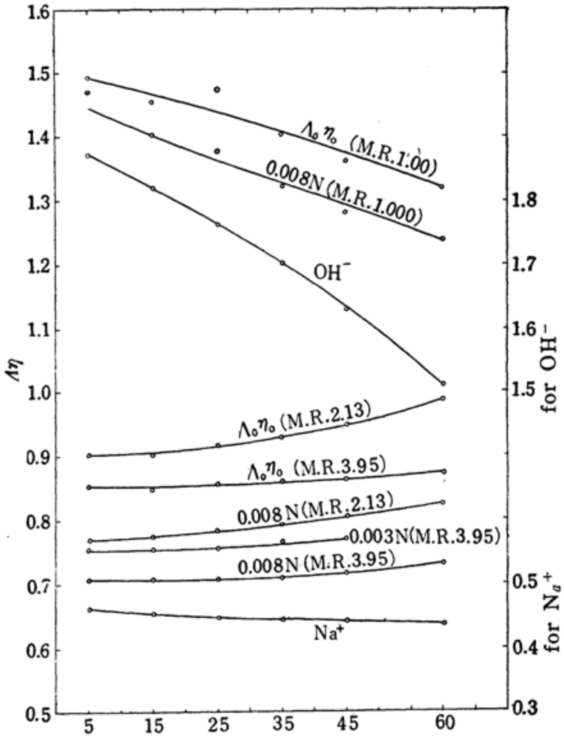

Fig. 13. Variation of $\Lambda\eta$ with temperature for extreme, and infinite dilute sodium silicate solutions and for Na^+ and OH^- ion at infinite dilution

In order to examine this, OH^- ion concentration at various temperatures was calculated from *p*H values, and hydrolysis percentages were derived from them⁷⁾. They were 23, 26, 28, 26 and 26% at 5°, 15°, 25°, 35° and 45°C for 0.008 N metasilicate solution, 1.4, 2.8, 3.2, 3.9 and 4.2% at above respective temperatures for the 2.13 molar ratio solution. For the 3.95 molar ratio solution they were negligibly small, i. e. varies only from 0.7% to 1.9% at 0.008 N between 5° and 45°C. Thus it is well understood that for the metasilicate solution, the decreasing tendency with temperature of $\Lambda_0\eta_0$ of OH^- ion, which is shown also in Fig. 13 along with that of Na^+ ion, appears to give a prominent effect on its $\Lambda\eta$ while the constancy of $\Lambda\eta$ of the 3.95 molar ratio solution is well satisfied. For the 2.13 molar ratio solution Λ increase with temperature is affected by the change in OH^- ion concentration with temperature, so that $\Lambda\eta$ becomes larger than in the case where the composition of the solution holds constant.

$\Lambda_0\eta_0$ for an ion is related to the ionic radius r as shown by the equation $r=0.820|z|/\Lambda_0\eta_0$ where r is expressed by Ångstrom and $|z|$ denotes the charge valency. Since this relation was derived from Stokes' law $r=1/(6\pi\eta u)$, where ionic mobility u is related to the limiting equivalent conductivity by $6.47\times10^6\Lambda_0/|z|$, it is applicable only to the ion of symmetrical shape. Therefore, though this treatment may be merely a rough approximation, it would be of some value to estimate the radius of silicate ion by this equation. Λ_0 of silicate ion in the solution of molar ratio 1.00, 2.13 and 3.95 were computed from their limiting equivalent conductivity as follows,

$$\Lambda_{0(\text{sil.})}=(\Lambda_0-\Lambda_{0(\text{Na}^+)}-C_{\text{OH}}\Lambda_{0(\text{OH}^-)})/C_{\text{sil.}}$$

where C_{OH} and $C_{\text{sil.}}$ are OH^- ion and silicate ion concentration at infinite dilution. It seems difficult, however, to get the hydrolysis percentage at infinite dilution by the extrapolation of a curve plotted against concentration, and further more, unstable *p*H values observed in this dilute region do not enable one to get hydrolysis percentage. Meanwhile, the limiting equivalent conductivity was obtained by extrapolation of curve by neglecting the abruptly increased value observed in this extreme dilution. Thus replacement of the hydrolysis percentage at 0.008 N for that at infinite dilution will be tentatively justified. The concentration of silicate ion at infinite dilution was assumed to be $(1-X)$ N, where X denoted degree of hydrolysis. As a result, $r=4.0$ Å was obtained for both 2.13 and 3.95 molar ratio solutions, and $r=2.24$ Å for metasilicate solution. However, it is recognized that the Stokes' law radius is known to require the correction if applied for the smaller radius than 5 Å, due to the deviation of numerical constant from 6π. After the above-mentioned radii were multiplied by the correction factor⁸⁾ they become 4.56 Å and 3.63 Å. These values, despite a result of rather drastic estimation and resultant failure to distinguish between the radii of silicate ions in the 2.13 and 3.95 molar ratio solutions, their order seems quite reasonable as compared with data regarding the size of sodium silicate molecule

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7) Because of lack of extreme accuracy in the measurement hereby used, pH value ±0.1 would be within the error. This led to a considerable inconsistency of data of hydrolysis percentage especially for the solution having high OH^- ion concentration, such as sodium silicate solution.

8) This correction factor was cited from, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London (1955), p. 119.

reported elsewhere.

In the preceding paper the change in equivalent conductivity with concentration has been computed for the 3.95 molar ratio solution at 25°C, on the basis of Falkenhagen's equation,

$$\Lambda=\left(\Lambda_0-\frac{41.25(|z_1|+|z_2|)\sqrt{I}}{\eta(\varepsilon T)^{1/2}(1+\kappa a)}\right)\times$$

$$\left(1-\frac{2.801\times10^6|z_1z_2|q}{(\varepsilon T)^{3/2}(1+\sqrt{q})}\cdot\frac{e^{\kappa a(1-\sqrt{q})}-1}{\kappa a(1-\sqrt{q})}\cdot\frac{\sqrt{I}}{(1+\kappa a)}\right)$$

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

where notation is the same as used before.

This computation was extended for the equivalent conductivities measured at other temperatures, 7 Å for the mean ionic diameter a being used as in the previous treatment. The results were corrected for the solution viscosity and plotted in Fig. 12. The accordance of observed values with those theoretically computed is quite satisfactory as far as the concentration 0.8–0.9 N is reached. This consistent agreement at any temperature of theoretical and observed data shows that the change with temperature of equivalent conductivity—square root of concentration curve is explained only in terms of temperature change and consequent change of dielectric constant and viscosity of solvent, and that the change of composition of solution need not be considered; this change may occur, if any, on the part of silicate ion or molecule therein, because pH measurements indicated that OH^- ion concentration did not vary appreciably over the temperature range measured. Also it is recognized that the assumption, which has been set upon computing equivalent conductivity at 25°C on the basis of Falkenhagen's equation, was proved sufficient at any other temperature for the explanation of them.

Above the concentration 0.8–0.9 N, the theoretical values fall increasingly below the observed one. This was caused by the fact that the viscosity increase outgrew more and more the conductivity decrease, as concentration increased. On the other hand it has been already noticed that at the concentration where specific conductivity became maximum the viscosity of the solution varied strikingly according to the molar ratio of the solution and it appeared to have little effect on the specific conductivity at this concentration range. These facts suggest that the higher the concentration, the larger difference between the mechanisms of conductance and viscosity may appear. The correlation of conductivity and viscosity of the sodium silicate solution would be a very interesting subject, further study of which may throw some light upon the investigation of the structure of the concentrated solution. It will be dealt with in the succeeding paper.

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