A Study on the Electric Conductivity of Sodium Silicate Aqueous Solution. III. On the Relationship between Conductance and Viscosity

By Hiroshi UKIHASHI

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Introduction

In the previous papers[1,2], the author has remarked that the electric conductivity of sodium silicate solution seemed independent of their viscosity at high concentration range. This has been suggested by the experimental facts that the change of viscosity with concentration varied widely among the solutions having different molar ratio around the concentration where maximum specific conductivity was shown, and that the equivalent conductivity computed theoretically, with viscosity correction, fell increasingly below the observed value above a definite concentration range.

Since conductance in electrolyte solution is a result of the movement of ions under an applied potential, and viscosity is the reciprocal of fluidity which expresses the rate of shear taking place with a definite velocity under unit force, they both can be treated as rate process. Then the comparative study of conductance and viscous flow in view of the theory of rate process is of much value on considering the structure of solution, as it gives some information concerning the bearings on the mechanisms of both phenomena.

In the present report the mechanism of conductance of concentrated sodium silicate solutions of various molar ratio has been discussed in comparison with that of viscous flow from the above mentioned standpoint, and an interpretation has been given for the structure of these solutions.

Experimental

Preparation of sample sodium silicate solutions, apparatus and methods used for the measurement of electric conductivity were described in the preceding paper. Sample solutions for the measurement of viscosity were the same as those for that of the conductance. Viscosity was measured by the capillary method, using Ubbelohde viscometers with varied capillary constants which were originally determined by the maker and calibrated in the author's laboratory, using glycerol solutions of varied concentrations as standards. Measurements were made at a series of increasing temperatures from 5 to 60°C. The relative viscosity was calculated by the usual formula,

$$\eta_{\mathrm{rel}} = \frac{t\ (\text{flow time of solution}) \cdot d\ (\text{density of solution})}{t_0\ (\text{flow time of water}) \cdot d_0\ (\text{density of water})}.$$

With the concentrated solutions, absolute viscosity was calculated directly by the formula $\eta/d = \mathrm{A}t$

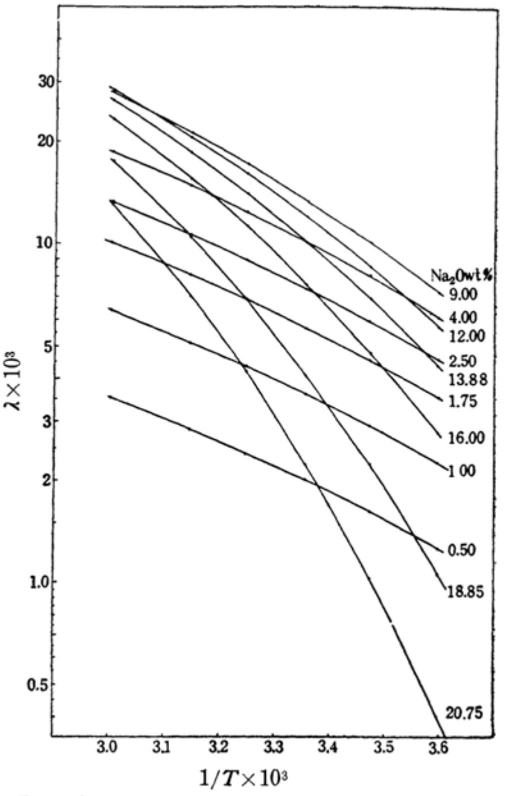

Fig. 1. Variation of the logarithm of specific conductivity with reciprocal of absolute temperature for the 1.00 molar ratio solutions.

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

[2] Idem., ibid, **30**, 414 (1957).

$-B/t$, where A is constant characteristic of capillary, and B constant for kinetic energy correction. It may be conceived that as the concentrated sodium silicate solutions, especially of high molar ratio, would show structural viscosity or thixotropy, the so-called one-point method for the measurement would not be adequate. However, since the present paper has been aimed at discussing primarily the mechanism of electric conductance of sodium silicate solution in relation to that of viscous flow, it would be permissible to set aside, for the present, the problem of exact viscous behavior of the concentrated solution and to leave it for later debate.

Results

Activation Energy of Conductance and Viscous Flow.—In Figs. 1 and 2, the logarithm of specific conductivity was plotted against the reciprocal of absolute temperature for the sodium silicate solutions of molar ratio 1.00 and 3.95. These figures illustrate the different behavior in most marked contrast at various concentrations. The similar curves for viscosity were shown in Figs. 3 and 4 for the corresponding solutions. Although both sets of curves have slight curvature[3)], they are regarded as showing approximately linear relationship over a narrow temperature range. The activation energies of conductance and viscous flow are expressed as $d\ln\lambda/d(1/T) = -E_\lambda/R$, and $d\ln\eta/d(1/T) = E_\eta/R$ respectively, where λ is specific conductivity, η viscosity, T absolute temperature, R gas constant, and E_λ and E_η activation energy of conductance and viscous flow. Their values at 25°C were calculated by the following equation, using those at 15°C and 35°C for λ_1, η_1, T_1 and λ_2, η_2, T_2 respectively.

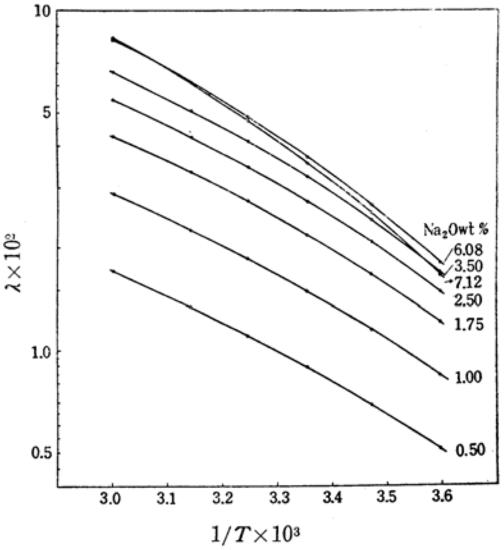

Fig. 2. Variation of the logarithm of specific conductivity with reciprocal of absolute temperature for the 3.95 molar ratio solutions.

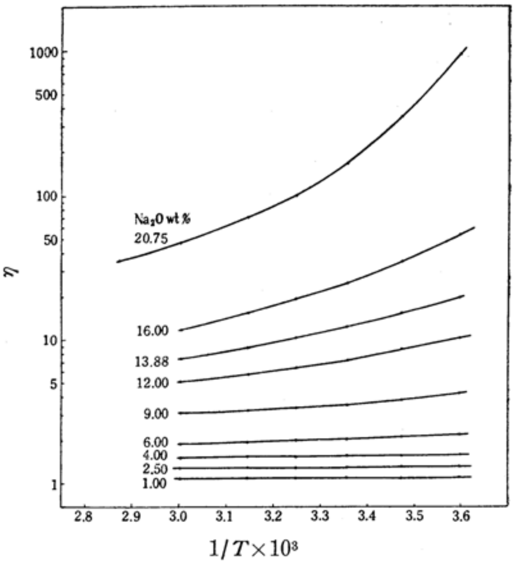

Fig. 3. Variation of the logarithm of viscosity with reciprocal of absolute temperature for the 1.00 molar ratio solutions.

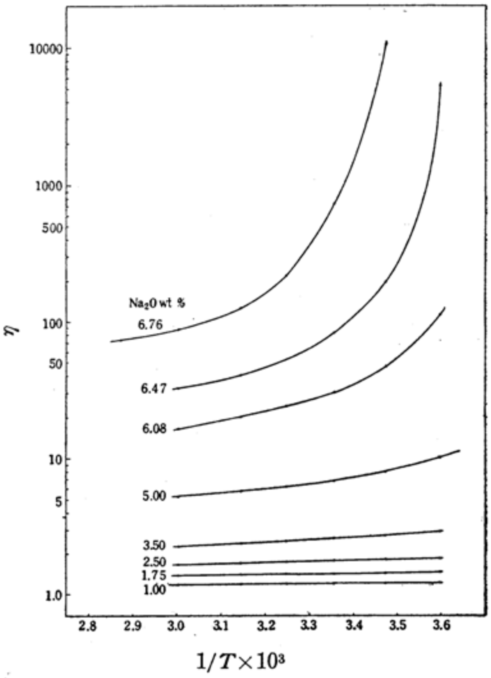

Fig. 4. Variation of the logarithm of viscosity with reciprocal of absolute temperature for the 3.95 molar ratio solutions.

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3) Log $\eta-1/T$ curves for the highly concentrated solutions may no more be postulated as showing linearity. There must be appreciable change of structure with temperature, which results in the marked variation of E_η with temperature.

$$\frac{R(\ln\lambda_2-\ln\lambda_1)}{(1/T_1-/1T_2)}=E_\lambda,\quad \frac{R(\ln\eta_1-\ln\eta_2)}{(1/T_1-1/T_2)}=E_\eta.$$

In Fig. 5 and 6, the results were plotted against the concentration for all systems studied. It is visualized that for the higher molar ratio solutions the increase of E_λ with concentration is small over an entire concentration range measured, while that of E_η appeared to become remarkably large at high concentration, and that for the lower molar ratio solutions both E_λ and E_η increase with similar manner up to the value several times as large as those in dilute concentration. For the convenience of discussion, the data of E_λ and E_η for the solutions of molar ratio 1.00 and 3.95, as extreme examples, are tabulated in Table I. It seems at first sight rather curious that for the 1.00 molar ratio solution E_λ is smaller than E_η even at dilute concentration range. This may be ascribed to the OH ion contribution to the conductivity as described in the previous report. Conductance by OH ion in aqueous solution requires much smaller activation energy (3.4 kcal.) as compared with usual ionic conductance owing to its special conduction mechanism, which is successfully accounted for as a prototropic process where the proton is transferred from a water molecule to an hydroxyl ion.

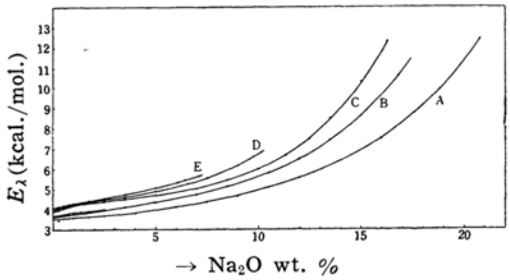

Fig. 5. Variation of the activation energy of conductance with concentration for the sodium silicate solutions of molar ratio.
A: 1.00, B: 1.55, C: 2.13,
D: 3.19 and E: 3.95

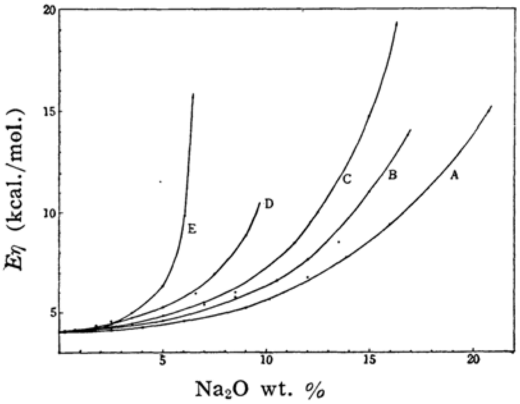

Fig. 6. Variation of the activation energy of viscous flow with concentration for the sodium silicate solutions of molar ratio.
A: 1.00, B: 1.55, C: 2.13,
D: 3.19 and E: 3.95

TABLE I

M. R.=1.00			M. R.=3.95		
C (Mol./l.)	E_λ	E_η	C (Mol./l.)	E_λ	E_η
0.08	3.52	4.04	0.08	4.14	4.11
0.16	3.57	4.13	0.16	4.23	4.11
0.42	3.69	4.11	0.30	4.40	4.28
0.69	3.84	4.25	0.44	4.54	4.40
1.09	4.11	4.56	0.64	4.74	4.97
1.74	4.68	5.20	0.98	5.04	6.31
2.47	5.54	6.70	1.25	5.32	9.78
2.97	6.31	7.67	1.35	5.43	15.61
3.58	7.48	9.37	1.44	5.55	179.8
5.15	12.37	14.90	1.53	5.64	

The Product of Equivalent Conductivity and Solution Viscosity.—According to Eyring⁴⁾, activation free energy of viscous flow ΔF_η is expressed as

$$\eta=hN/V\exp(\Delta F_\eta/RT) \tag{1}$$

while equivalent conductivity Λ, as a result of theoretical treatment of rate process, may be expressed in terms of activation free energy of conductance ΔF_λ as follows⁵⁾,

$$\Lambda=\frac{V^{2/3}\Sigma Z_iF^2\cdot10^7}{hN}\exp(-\Delta F_\Lambda/RT) \tag{2}$$

where h denotes Planck's constant, N Avogadro number, V molal volume of moving unit, F the Faraday, and z charge valence.

If approximation can be made that the ΔF_η has the same value as ΔF_Λ and that volume of moving unit is similar in both cases the product $\Lambda\eta$ becomes

$$\Lambda\eta=\Sigma z_iF^2\cdot10^7/V^{1/3} \tag{3}$$

Equation (3) implies that $\Lambda\eta$ is constant irrespective of variation of temperature and concentration, if the viscous flow and electric conduction occur by the same mechanism, and the volume of the moving unit is alike in both cases, and that its value should be the order of unity. Though this relationship has been derived only by the formal treatment of the theory of rate process basing on drastic assumption, it would be interesting to see how it can be applied for the sodium silicate solution. Fig. 7 exhibits the dependence of $\Lambda\eta$ on concentration, again for the molar ratio 1.00 and 3.95 solutions. The figure

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4) S. Glasstone, K. J. Laidler and H. Eyring, "The theory of rate process", McGraw-Hill Book Co., New York, N. Y., 1941, First Edition.

5) This formula was derived for a single ion as follows, $\Lambda=uF$, u is a mobility of ion under unit potential and related to diffusion coefficient D_i as $u=D_ize/kT$. Then $\Lambda=D_izF^2/RT$. From the reaction rate theory $D_i=\kappa\cdot V^{2/3}/N$, where κ is the specific rate constant, expressed as $\kappa=kT/h\exp(-\Delta F/RT)$, hence, Λ is given as

$$\Lambda=V^{2/3}z\cdot F^2\times10^7/h\exp(-\Delta F/RT)$$

Therefore, strictly, D_i should be the sum of that for each component ion, and herein the sum of averages was taken.

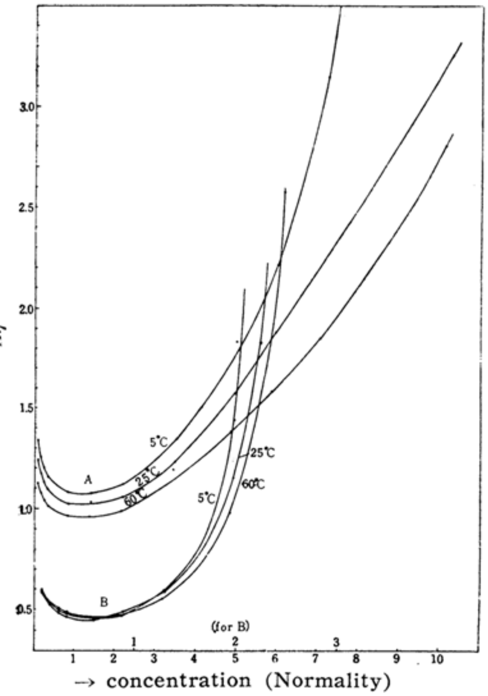

Fig. 7. Variation of the product of equivalent conductivity and viscosity with concentration for the sodium silicate solutions of molar ratio.
A: 1.00 B: 3.95

shows that $\Lambda\eta$ decreases a little in dilute concentration region and becomes constant over a certain range, then begins to increase above the value marked at start point up to a remarkably large one. The initial decreasing part of $\Lambda\eta$ curves is thought to have been brought about by the increase in molal volume with concentration as expected from the equation (3). Also, the smaller value of $\Lambda\eta$ for the high molar ratio solution may well be ascribed to the larger molal volume of the solution, as compared with the lower molar ratio ones, while the increase in $\Lambda\eta$ with concentration which takes place above a certain concentration, would predict that the change in activation free energy with concentration become different between conductance and viscous flow. All these trends seem quite similar to those found with simple strong electrolytes[6] except the fact that the degree of rise in $\Lambda\eta$ with concentration approaches a much larger value than the degree for those solutions. It is noticeable, however, that within the moderate concentration range the value of $\Lambda\eta$ spreads for all the systems only in narrow range, viz. between about 0.5 and 1.0, thus well satisfying the requirement of equation (3). As for the variation of $\Lambda\eta$ with temperature, that of the higher molar ratio solution seems independent of temperature as expected from the equation (3) except at higher concentration range. That $\Lambda\eta$ for the 1.00 molar ratio solution decreases with temperature even at low concentration range can be well attributed to the effect of OH ion, $\Lambda\eta$ of which, as stated in the previous paper, decreases with temperature rise even at infinite dilution.

Thus it may be understood that as a whole, the tendency of curves in Fig. 7 shows no speciality which distinguishes them from those for the simple electrolyte solutions. Merely the concentration above which $\Lambda\eta$ begins to increase markedly lies in lower range than with those solutions. From the comparative study on Fig. 5, 6, and Table I it is found that the concentration, where $E\eta$ exceeds E_λ is almost the same as the abovementioned concentration read in Fig. 7. They were about 1.45, 1.05 and 0.95 N for the solutions of molar ratio 2.13, 3.19 and 3.95 respectively. The value for the last one may be favorably compared with 0.8-0.9 N, above which the equivalent conductivities theoretically computed no longer agree with those observed experimentally and tend to fall increasingly below the latter. For the lower molar ratio solutions two curves in Fig. 5 and 6 never cross, and the similar curves to that in Fig. 7 indicate that the concerned concentration for molar ratio 1.00 and 1.55 are about 2.15 and 1.85 N respectively. It is interesting to compare these values with 5 to 6 N for $NaClO_4$, NaSCN, and NaI, which were recently reported by Miller.

Discussion

The Structure of Concentrated Sodium Silicate Solutions as Interpreted by the Mechanisms of Conductance and Viscous Flow.—The foregoing results revealed that the mechanisms of conductance and viscous flow become different above a definite concentration range for all the systems studied. Herein, discussion has been made as to the actual behavior of the solutions in this concentration region.

Despite the theoretical incompleteness, it is widely accepted that the concentrated electrolyte solutions may be closely modeled after molten salts in view of the fact that they retain short range local order in component distribution, taking quasi-crystalline structure, where anion is most likely considered to play the predominant roll, due to its superiority in ion size to cation. In such a state, cation takes over progressively of the conduction. Thus, the flow of solution begins to be disturbed more and more by anion arrangement, consequently to need larger activation energy, while conductance is still performed in increasing proportion by cation so that its activation energy does not vary very much. Since the silicate ions, as already reported, are much larger than the sodium ion, particularly in the

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[6] M. L. Miller, *J. Phys. Chem.*, **60**, 186 (1956).

high molar ratio solutions, it would be quite reasonable to expect that this quasicrystalline structure may be established even at lower concentration with a greater degree, as compared with simple strong electrolyte solutions. Then, with the higher molar ratio sodium silicate solution, as concentration increases above a certain limit, one silicate ion begins to get contact with another so as either to get combined by hydrogen bond or mechanically tangled, thus leading to the establishment of even rigid structure due to a kind of net work at comparatively low concentration, such as to allow the sodium ion to pass freely through its meshes. This situation is best represented in the 3.95 molar ratio solution which has at 2.88 N viscosity of 650 c.p., E_η of 180 kcal., and yet E_λ of only 5.5 kcal., and at 3.07 N E_λ of 5.64 kcal. and viscosity more than 10,000 c.p.. On the other hand, a lower molar ratio solution contains rather small silicate ions together with considerable amount of OH ions, therefore it cannot afford to form net work structure, thus the rigid state as seen in the higher molar ratio one may not be yielded even at strikingly high concentration where solutions are packed so closely that sodium ion itself can no longer move with ease. Hence, E_λ reaches much larger values than with the high molar ratio solutions, while increase of E_η is not so great as with these ones, being parallel with that of E_λ over a wide concentration range. For the comparison of the behavior of various molar ratio solutions, in Fig. 8, the viscosity of solutions at a concentration where maximum specific conductivity was shown, and in Fig. 9, the equivalent conductivity together with E_λ at a concentration where the solutions exhibit the same viscosity, were plotted against the molar ratio. It is recognized that the higher molar ratio solutions have the greater equivalent conductivity than with the lower molar ratio ones if compared on the same level of high viscosity.

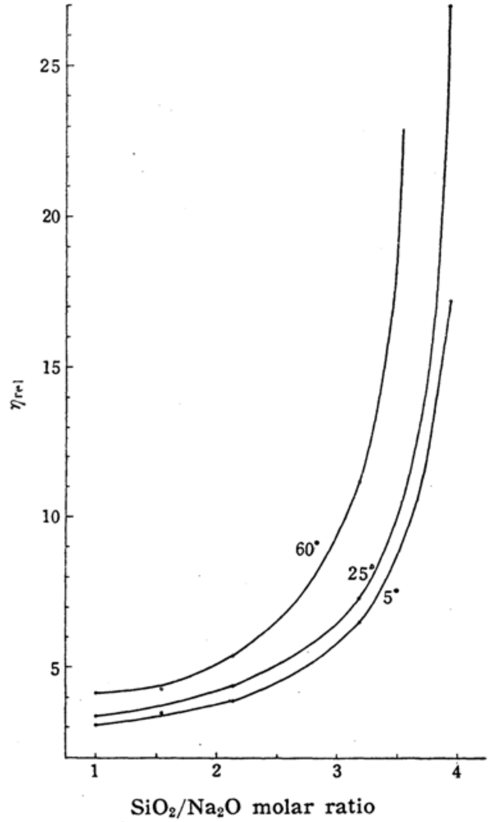

Fig. 8. Viscosity change with molar ratio of sodium silicate solutions at the concentration where maximum specific conductivity is given.

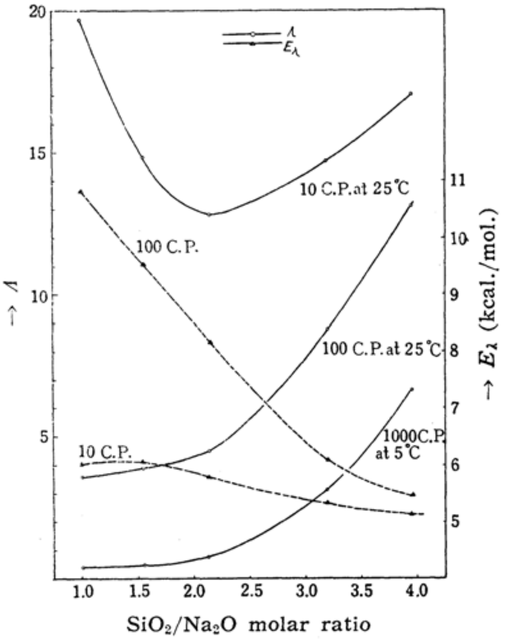

Fig. 9. Iso-viscosity curves 1. Equivalent conductivity 2. Activation energy of conductance—molar ratio relationships.

It would be worth while to estimate the average interionic distance at the highest concentration measured of the molar ratio 1.00 and 3.95 solutions. Assuming the existence of three mole ions in one mole solution, they are calculated as 4.75 Å and 7.11 Å for 10.3 N of the 1.00 molar ratio solution and 3.07 N of the 3.95 molar ratio one.

When the values computed previously of the diameter of corresponding silicate ion, i.e., 7.2 Å and 9.2 Å, are subtracted from the values of three times the foregoing data, there remain 7 Å and 12 Å for two sodium ions in respective solutions. Since the diameter of hydrated sodium ion is supposed to be about 2.5 Å–3.0 Å it is seen that little space is left for the free passage of sodium ion in the former solution, whilst there are still available spaces for the movement of sodium ion in the latter solution. Further, this condition may well be understood if the E_λ of the concentrated sodium silicate solution is compared with those observed for the molten alkali silicates the latter being 10–11 kcal. for all the liquid of silica-alkali weight ratio of 1.5–3.0, according to O'M Bockris et al.[7]. This value of E_λ for molten silicates is much larger than 5.64 kcal. for the 3.95 molar ratio solution at 3.08 N, but lower than 12.4 kcal. for the 1.00 molar ratio one at 10.3 N. Considering these figures and the fact that E_λ is about 5 kcal. for the simple strong electrolyte solutions at 10 N, water in the highly concentrated solution of lower molar ratio seems no longer to be regarded as the solvent but only as a part of kinetic entity as hydration sheath, whereas it is still available as a solvent for the higher molar ratio solution at high concentration, such as to form rigid structure.

The Application of Absolute Reaction Rate Theory to the Conductance of the Concentrated Sodium Silicate Solutions of Molar Ratio 3.95—Now that it seems reasonable to presume that only sodium ion carries electricity under an electric field in the concentrated sodium silicate solutions of high molar ratio, the calculation was attempted in the following of the energy barrier, namely, activation free energy of conductance ΔF_Λ on the basis of the absolute reaction theory. Since it is impossible to calculate the height of the energy barrier by means of quantum mechanics in such a complicated system, this height was determined from the experimental conductivity according to the method employed by Eyring in case of the proton transfer in aqueous solution.

When a field having an effective potential gradient Φ is applied, the specific reaction rate at an angle θ to the direction of the field is given by $\kappa = kT/h \exp[-(\Delta F - \delta F)/RT]$ where δF is defined by $\delta F = \Phi \cos\theta \times d \times 23060$, d being half the distance between the initial and the final state along the reaction coordinate. Since the distance travelled by an ion in the direction of the applied field is $2d\cos\theta$, the velocity of an ion in cm/sec, v, is:

$$v = 2d\cdot\cos\theta\cdot kT/h\cdot\exp(-\Delta F/RT)\cdot\exp(a\cdot\cos\theta)$$

where $a \equiv \Phi\cdot d \times 23060/RT$.

This equation applies to motion in one direction only and to obtain the distance moved in the direction of the field it is necessary to take the average over all angles,

$$v = 2d\,kT/h\,\exp(-\Delta F/RT) \times \frac{\int_0^\pi \exp(a\cdot\cos\theta)\cdot\cos\theta\cdot\sin\theta\cdot d\theta}{\int_0^\pi \sin\theta\cdot d\theta}$$

as the quantity a is very small, so that it is possible to write $\exp(a\cdot\cos\theta) = 1 + a\cdot\cos\theta$, and hence

$$v = 2d\cdot kT/h\cdot\exp(-\Delta F/RT)\cdot a/3.$$

As $\Lambda = vF$ then

$$\Lambda = 2/3\cdot dF\cdot a\cdot kT/h\cdot\exp(-\Delta F/RT). \qquad (4)$$

The effective potential gradient in the liquid Φ has been suggested to be placed equal to $(\varepsilon+2)/3$ for an applied potential gradient of 1 V/cm, where ε is the dielectric constant of the solution. Difficulty arises, however, in knowing the dielectric constant of the solution. Hasted, Ritson and Collie[8] derived for this the equation $\varepsilon = \varepsilon_w + 2\bar{\delta}C$, where ε_w is the dielectric constant of solvent water, $\bar{\delta}$ half the molar depression of dielectric constant of water by electrolyte. This linear relationship is said to hold up to 2 N concentration. Though no data are available for the silicate ion, ε was calculated using this equation with the assumption that $\bar{\delta} = 10$ for sodium silicate, a comparable value to those for NaOH and Na_2SO_4, considering the extent of hydration. As to $2d$, i.e. the distance travelled by an ion in the conduction process in overcoming one potential energy barrier, it may be taken either as the average dimensions of water molecule or as that of SiO_4 tetrahydra, the former being 3.1 Å, the latter 3.2 Å. Therefore $d = 1.6$ Å was used reasonably. The equation (4), then, is expressed as:

$$\Lambda = 3.98\times10^3\times\exp(-\Delta F/RT)$$
$$= 3.98\times10^3\times\exp(-\Delta H/RT)\exp(T\Delta S/R)$$

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[7] J. O'M. Bockris, J. A. Kitchener, S. Ignatowitcz and J. M. Tomlinson, *Trans. Farad. Soc.*, **48**, 75 (1952).

[8] J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

TABLE II

C (Mol./l.)	Λ	ΔF (kcal.)	ΔH (kcal.)	ΔS (e.u.)	η	ΔF_η (kcal.)	ΔH_η (kcal.)	ΔS_η (e.u.)
1.53	11.64	5.12	5.70	1.9				
1.44	12.72	5.09	5.59	1.7	650.1	6.17	179.8	583
1.35	13.60	5.07	5.53	1.5	74.11	4.88	15.61	36.0
1.25	14.81	5.04	5.38	1.1	27.52	4.29	9.78	18.4
0.983					6.22	3.40	6.31	9.77
0.646					2.36	2.80	4.97	7.28
0.443					1.60	2.56	4.40	6.19

ΔH is heat of activation and may be taken approximately as equal to the experimental activation energy E_Λ[9], and ΔS the activation entropy. In table II the results of calculation for ΔF and ΔS are shown along with the experimentally observed Λ and ΔH for the 3.95 molar ratio solution at several high concentrations. Also the same terms for viscous flow were computed from the equation (1), using the average molar volume over all the solute ions and solvent one, as V.

It is visualized that the activation free energy of conduction is almost the same as the activation energy which was obtained experimentally; that is, the entropy in the activated state is only slightly larger than in the equilibrium state, while the activation entropy of viscous flow increases rapidly with concentration. This implies that in order to cause the viscous flow some short range local order should be broken down; on the other hand, for the conduction process it is scarcely necessary to disrupt this structural order. Thus, the entropy behavior may be interpreted as the evidence of the occurrence of this local order which does not disturb the passage of sodium ion under electric field. Consequently this confirms the foregoing discussion.

Conclusion

The activation energies of conductance and viscous flow, E_λ and E_η, were computed from the experimental results of temperature dependence of conductivity and viscosity for the sodium silicate solutions of various molar ratio. And it was found that as concentration increases above a definite range, E_η becomes progressively larger than E_λ, to the greater extent with the higher molar ratio solutions, and that the product of equivalent conductivity and viscosity may be regarded almost as independent of concentration and temperature below a definite concentration range, above which it increases rapidly. This critical concentration range for the 3.95 molar ratio solution approximately coincides with that, below which the equivalent conductivities theoretically computed agree with those experimentally observed.

These results were considered to show that in the concentrated sodium silicate solutions, short range local order comes to be established so as to make a quasi-crystalline structure in which silicate ions take a predominant role. This tendency is greater for the higher molar ratio solution, where the arrangement of silicate ions proceeds until it yields even rigid net work structure, while sodium ion can still freely pass through the meshes.

Assuming this model for the concentrated sodium silicate solution of molar ratio 3.95, the activation free energy and entropy were calculated from the conductivity at high concentration region, using the absolute reaction rate theory. The results also confirmed the above interpretation.

Thus, it may be concluded that the electric conductance behavior of the sodium silicate solutions could be explained by regarding them as a kind of strong electrolyte solution over an entire range of concentraion, since within the moderate concentration range the conductivity could be theoretically accounted for, and even at the higher concentration, as described above its behavior would not be different essentially from those seen with simple strong electrolyte solutions, if the difference of anion size and extent of hydration is considered.

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Research Laboratory Asahi Glass
Co. Ltd. Tsurumi, Yokohama

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[9] E_Λ may be related to E_λ as follows, since $\Lambda=1000/(u\rho/M)$, where w is weight of solute per 1000 g solution, ρ density of solution, M molecular weight of solute. Then, $d\ln\Lambda/d(1/T)=d\ln\lambda/d(1/T)-d\ln\rho/d(1/T)$, $-E_\Lambda/R=-E_\lambda/R+T^2/\rho\cdot d\rho/dT$. If ρ is expressed as $\rho=\rho_0[1+\alpha(T-T_0)]^{-1}$, then, $E_\Lambda=E_\lambda+RT^2[1-\alpha(T-T_0)]$. As α is the order of 0.01%, the difference between E_Λ and E_λ is not large.