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Electrical Conductance of Molten Salt Systems: Ag_2O-B_2O_3 and Ag_2O-Na_2O-B_2O_3

Hiroshi KODAMA, Yoshihiro KIMURA, Toshio YOKOKAWA and Kichizo NIWA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The electrical resistance of the Ag_2O-B_2O_3 and Ag_2O-Na_2O-B_2O_3 systems has been measured in the approximate temperature range from 750 to 1000°C. The equivalent conductance at 900°C and the activation energy of the conductance for the Ag_2O-B_2O_3 system were calculated. They were then compared with the corresponding values of alkali borate melts. The results led to the conclusion that the silver ion is not bound to the oxygen ion in the melt, but behaves like Li^+, Na^+, and K^+ which are known to be monovalent network modifiers and to be free to move in the melt.

Various physico-chemical properties of alkali borate melts have been reported by several groups of workers.[1] Electrical conductance, one of them, has been measured by a few investigators.[2,3] Silver oxide, as well as alkali metal oxide, dissolves into molten boron trioxide at high temperatures to form a silver borate melt.[4,5] Therefore, it seemed of interest to study the silver borate melt from the kinetic point of view. Thus, a comparison of the electrical conductance of the melts, of both Ag_2O-B_2O_3 and Ag_2O-Na_2O-B_2O_3, with that of alkali borate melt will provide important knowledge concerning the conduction mechanism in the silver-containing melt. Two possible, contradictory

1) J. D. Mackenzie, "Modern Aspect of the Vitreous State," Vol. 1, 2, 3, Butterworths, London (1964).

2) J. Kinumaki and K. Sasaki, *Repts. Research Insts. Tohoku Univ., Ser. A*, **3**, 285 (1951).

3) L. Shartsis, W. Capps and S. Spinner, *J. Am. Ceram. Soc.*, **36**, 319 (1953).

4) G. M. Willis and F. L. Hennessy, *J. Metal,* 1367 (1953).

5) T. Maekawa, T. Yokokawa and K. Niwa, This Bulletin, **42**, 677 (1969).

results may be anticipated; One might expect to obtain data analogous to that on the conduction of the binary alkali borate melt, because the silver ion, which is considered to be the sole electric carrier, has the same charge as the sodium ion, and, moreover, their ionic radii are nearly the same. On the other hand, the silver ion might display, notwithstanding these similarities, quite a different behavior since the silver ion has a stronger covalency than the alkali metal ion.

This report will present data on the electrical conductance of the binary melt, Ag_2O-B_2O_3 as well as the ternary melt, Ag_2O-Na_2O-B_2O_3, in the approximate temperature range from 750 to 1000°C. Further, the equivalent conductance will be estimated for the binary melt with the aid of the density data.[6]

Experimental

Materials and Reagent. The silver borate melt was prepared in the following way. Anhydrous boron trioxide of a guaranteed reagent grade was put into a platinum crucible (34 mm in diameter and 38 mm high) and heated in an air atmosphere at about 1000°C for long enough for the water to be driven off from the oxide melt. Then, $AgNO_3$ of a guaranteed reagent grade was added in its melt. Silver nitrate decomposed with NO_2 fumes and reacted immediately with the molten boron trioxide to produce the silver borate. The melt of the required Ag_2O content was stirred sufficiently with a silver rod in order to achieve a uniform composition. The ternary melt, Ag_2O-Na_2O-B_2O_3, was made by adding $AgNO_3$ to the Na_2O-B_2O_3 binary melt which had been prepared by melting the required amounts of alkali carbonate and anhydrous boron trioxide in a platinum crucible. The samples were analyzed for B_2O_3 content by titration with a 0.1N NaOH aqueous solution and for Ag_2O content by titration with a KSCN solution.

Apparatus and Procedure. A diagramatic sketch of the apparatus for measuring electrical resistance is given in Fig. 1. A dipping electrode arrangement was used to measure the melt resistance. It consisted of a pair of parallel Pt wires. An alternating current signal was supplied to a Kohlrausch Bridge (Yokogawa Electric Works type K-1) by means of an Audio Frequency Oscillator (Trio Corporation Type AG-10). The output of the resistance bridge was fed into the vertical input of a cathoderay oscillograph (Daimatsu Electric Company Type LBO 3A). 20 mm of the electrodes were dipped into the melt in the cell, the immersion depth being fixed precisely by a device in the electrodes' connection with a cathetometer. Since the resistance was shown to be independent of the frequency between 1 and 10 kc, the measurements were made at 10 kc. The determination of the cell constant was made at 25°C by means of a 0.1N KCl solution.

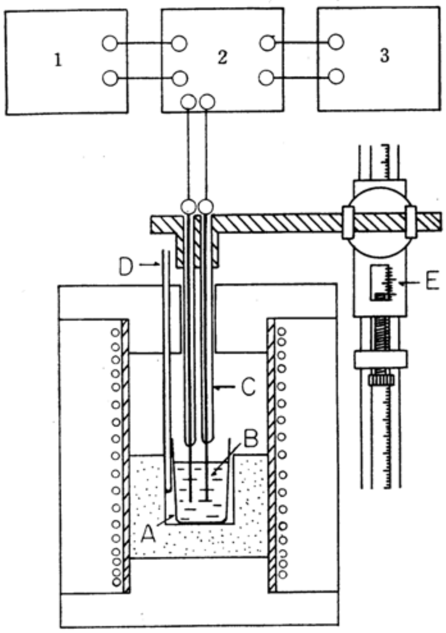

Fig. 1. Apparatus for measurement of electrical resistance.
A: Pt-crucible, B: Pt-electrode, C: electrode-holder (quartz tube), D: thermocouple-sheath, E: cathetometer.
1: Oscillograph, 2: Kohlrausch Bridge, 3: Oscillator

Results and Discussion

Binary Liquid, Ag_2O-B_2O_3. For each melt, the electrical resistance values were obtained at about every 20°C. Figure 2 shows a plot of the logarithmic specific conductance (κ) against the functions of the reciprocal absolute temperature

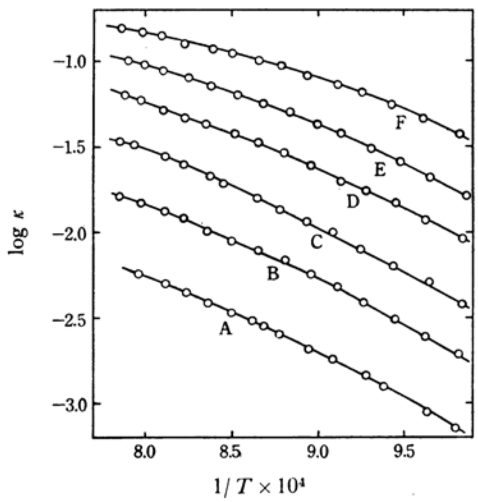

Fig. 2. Relation between specific conductance and temperature for silver borate melts.
A: 3.49 mol% Ag_2O B: 5.32 mol% Ag_2O
C: 8.35 mol% Ag_2O D: 11.74 mol% Ag_2O
E: 15.86 mol% Ag_2O F: 20.44 mol% Ag_2O

6) Y. Ono *et al.*, Unpublished.

$(1/T)$. These conductance-temperature relations are analogous to those of the sodium borate melt in magnitude as well as in the temperature coefficient, which had been measured by Shartsis.[3] Since an alkali borate melt is an ionic conductor, the present results suggest that the silver borate melt is also an ionic conductor.

It is clear in Fig. 2 that the graphs can be represented by curves rather than straight lines. A recent investigation[7] has established that the temperature dependence of the conductance at low temperatures can be described rather accurately by a modified form of the Arrhenius equation;

$$\Lambda = AT^{-1/2}\exp\left(\frac{-k}{T-T_0}\right)$$

where Λ is the equivalent conductance and where A, k, and T_0 are constants. This empirical equation has been supported by the theoretical treatment, too.[8,9] In the present investigation, $\log \Lambda + 1/2 \log T$ was tentatively plotted as a function of $\log (1/T—T_0)$ with various values of T_0. Although this procedure gave a better linear relation than the graphs in Fig. 2, a definite value of T_0 could not be evaluated from the data on the temperature range covered. Thus, the further consideration of T_0 was abandoned in the present study. The activation energy of the conductance was, therefore, estimated with an Arrhenius-type equation for the higher temperature range. The activation energy is shown in Fig. 3 as a function of the silver oxide concentration. In Fig. 3 the decrease in the activation energy with the increase in the amount of silver oxide is interpreted as the effect of the silver oxide's modification of the borate network structure as well as the effect of the change

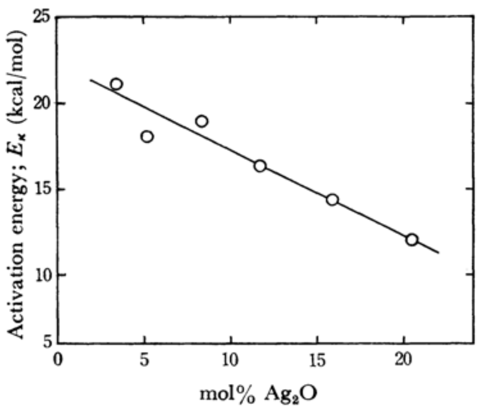

Fig. 3. Relation between activation energy and composition of silver borate melts at 900°C.

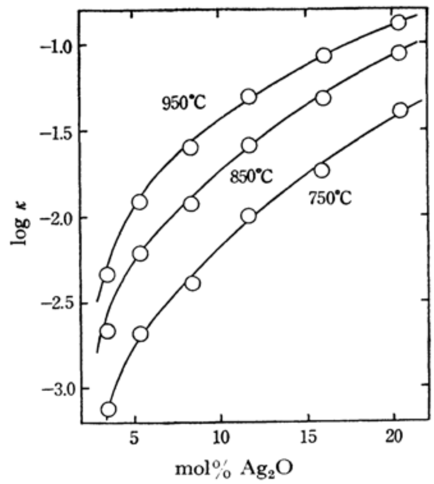

Fig. 4. Relation between specific conductance and composition of silver borate melts.

in thermal expansibility with the change in composition. The value of the activation energy for silver borate and the rate of its decrease are similar to those for alkali metal borates. In Fig. 4 $\log \kappa$ is plotted agnist the silver oxide contents. The conduction-composition isotherms show that the addition of silver oxide increases the conductance of the liquid. An increase similar to this has already been found in the case of alkali metal oxides (see also Fig. 9). For a discussion of the mehcanism of conductance, it is necessary to employ a equivalent conductance which is independent of the ionic concentration per unit of volume. For a system in which the conductance is due to a single ionic species, the equivalent conductance is given by:

$$\Lambda = \frac{100\,kM}{\rho\, nzx}$$

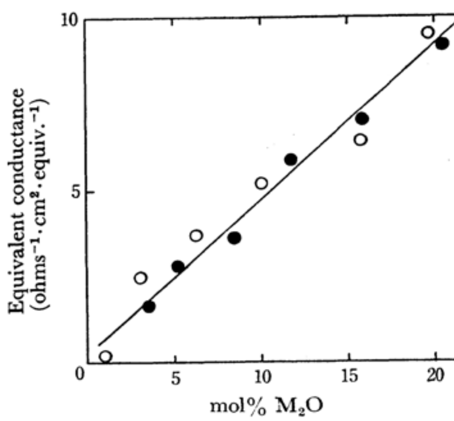

Fig. 5. Equivalent conductance isotherms for silver borate melt and sodium borate melt as functions of composition at 900°C.

● M=Ag ○ M=Na

7) C. A. Angell, *J. Phys. Chem.*, **70**, 2793 (1966).
8) G. Adam and J. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).
9) P. B. Macedo and T. A. Litovitz, *ibid.*, **42**, 245 (1964).

where ρ is the density of the melt; n, the wt% of the melta oxide; M, the molecular weight of M_xO_y; z, the charge on M, and x, the number of M atoms per molecule of M_xO_y. In the present case, since only the silver ion contributes to the conductance, this equation is valid. Making use of the density data of Ono *et al.*,[6] the equivalent conductance was then calculated from the above equation.

Figure 5 shows the equivalent conductance isotherm for 900°C as a function of the concentration of silver oxide (with the concentrations ranging from zero to 20 mol%), as well as the corresponding value of sodium borate, determined by Shartsis *et al.* From this agreement of the concentration dependence of the two borates, it is evident that the gradual increase in the equivalent conductance with the increase in the silver oxide contents can be interpreted in terms of the "network-destruction effect."

Ternary Melts; Ag_2O-Na_2O-B_2O_3. As has been stated previously, silver oxide was added to

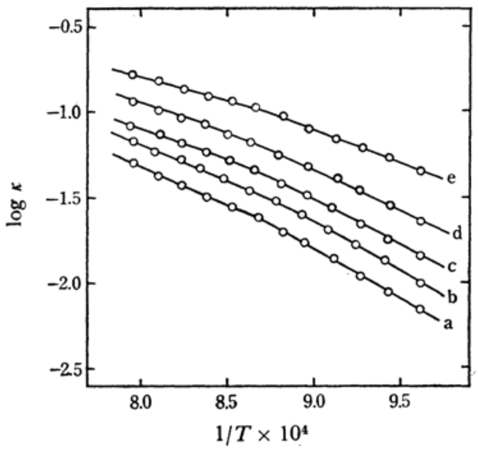

Fig. 6. Relation between specific conductance and temperature for Ag_2O-Na_2O-B_2O_3 system (series A, having a molar ratio $Na_2O/B_2O_3=3.97$).
a : 7.03 mol% Ag_2O b : 9.02 mol% Ag_2O
c : 10.42 mol% Ag_2O d : 13.42 mol% Ag_2O
e : 17.24 mol% Ag_2O

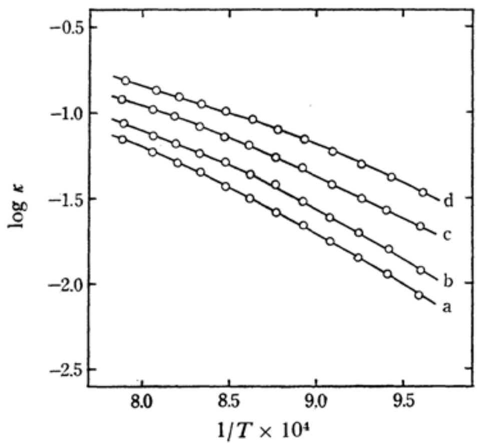

Fig. 7. Relation between specific conductance and temperature for Ag_2O-Na_2O-B_2O_3 system (series B, having molar ratio $Na_2O/B_2O_3=7.91$).
a : 2.63 mol% Ag_2O b : 5.33 mol% Ag_2O
c : 8.90 mol% Ag_2O d : 11.61 mol% Ag_2O

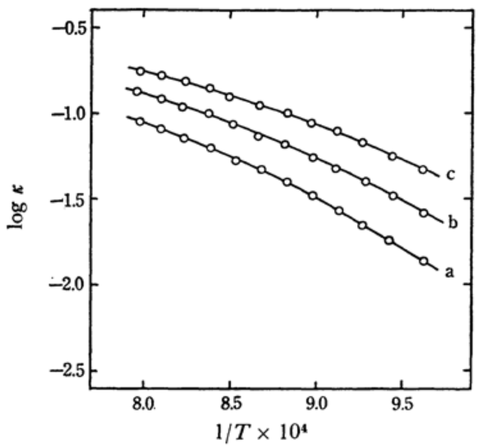

Fig. 8. Relation between specific conductance and temperature for Ag_2O-Na_2O-B_2O_3 system (series C, having a molar ratio $Na_2O/B_2O_3=18.96$).
a : 1.95 mol% Ag_2O b : 6.07 mol% Ag_2O
c : 10.66 mol% Ag_2O

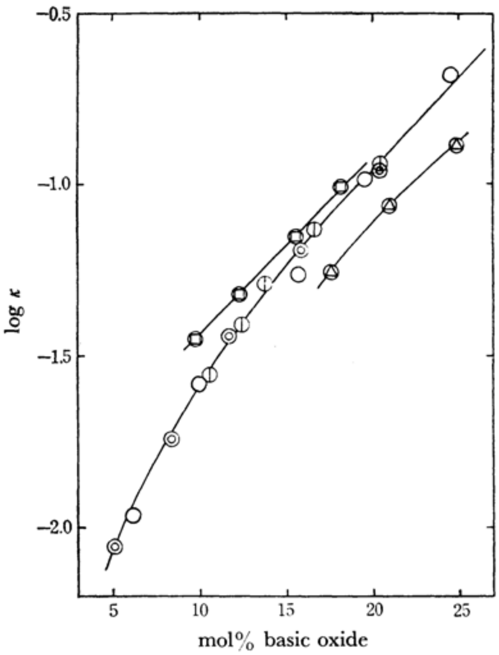

Fig. 9. Relation between specific conductance and basic oxide compositions, which are given by mol% of Ag_2O or Na_2O for the binary borate and by their sum for the ternary systems.
○, Na_2O–B_2O_3; ◎, Ag_2O–B_2O_3; ⦶, series A; ⊟, series B; △, series C

a Na_2O-B_2O_3 binary system, and the resistance was then measured for the region from 750 to 1000°C. This procedure was repeated several times. The starting compositions for binary systems were 3.97 (Series A), 7.91 (Series B), and 18.96 (Series C) at the molar ratio of Na_2O/B_2O_3. Plots of log κ against the functions of $1/T$ are shown in Figs. 6, 7, and 8. In Fig. 9 the log κ isotherms of both binary and ternary systems at 900°C are plotted as a function of the sum of the mole percents of Na_2O and Ag_2O. This figure shows that the data of Series A coincide with those of Na_2O-B_2O_3 or Ag_2O-B_2O_3, while Series B and C show some deviation. Considering the effect of the molar volume, this shows that the conductance is nearly additive with respect to silver and sodium ions. It may be concluded from the results of this conductance investigation that, when silver oxide dissolves in borate melt, silver oxide dissociated almost perfectly in silver- and oxygen-ions; that is, silver oxide acts as a network modifier of boric oxide and the silver ion shows a conductance behavior very similar to that of potassium, sodium, and lithium ions.