[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ARKANSAS]

The Effect of Solutes on the Properties and Structure of Liquid Boric Oxide

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Measurements of the viscosity, density and dielectric constant of boric oxide and its solutions have been made between 500 and 800°, and the results are interpreted in terms of a network model for the liquid.

Introduction

The publication of Zachariasen's paper[1] on the nature of glasses and the structural requirements for glass formation permitted increased understanding of the physical properties of glasses. Since boric oxide has a low glass transition temperature it has received considerable attention, and the work of Warren,[2] which gives direct evidence as to the correctness of the coördination predicted by Zachariasen, provides a basis for correlation of the properties of boric oxide glass. More recently the study by Richter and co-workers,[3] although it proposes a refinement that shows the structural relationship between boric oxide glass and crystal, also confirms Zachariasen's hypothesis. In addition, the persuasive evidence[4] for a shift from three- to four-coördination in binary boric oxide glasses invites the conviction that the structure of boric oxide glass is well understood.

Following the structure determination for crystalline boric oxide by Berger[5] there remains only the question as to the extent and nature of structure in liquid boric oxide. Although it seems attractive to interpret the behavior of liquid boric oxide in terms of the glass-like structure there has been some inclination[6] to reject the existence of the network structure in favor of a molecular unit, B_4O_6, in both glass and liquid. Under the circumstances there is need for a direct investigation of the liquid structure by X-ray diffraction. The authors nevertheless wish to present some other experimental results which seem most reasonably interpreted by the network model for the liquid.

Experimental

Measurement of Viscosity.—All viscosity measurements were made with a Model HBF Brookfield Viscometer. The easy operation of this device allowed use of a simple apparatus, which was as follows. A 600-ml. Griffin type beaker of stainless steel was used as the container. The beaker was placed in a Lindberg crucible furnace whose top was drilled with two holes, one of which carried chromel-alumel thermocouple leads in a stainless steel well, the other permitting the entry of a stirrer or the viscometer shaft. A 600-g. load of Eastman Kodak Co. (DPI) boric oxide was placed in the beaker and heated to 900° to remove residual water. When solute was added, the mixture was stirred thoroughly and then allowed to stand so that air bubbles might escape. The stirrer was withdrawn and replaced by the viscometer spindle. The taking of measurements began when the temperature and viscometer readings were constant with time. It is estimated that viscosities could be determined to within 30 poises and temperatures to within 3°. Obtaining the same viscosity with different shear rates indicated the Newtonian behavior of boric oxide.

Measurement of Density.—Densities of boric oxide and its solutions were measured in the same furnace. A buoyancy method was used and the suspension wire for the gold sphere passed through the opening used previously for the viscometer spindle. Eastman Kodak Co. (DPI) boric oxide was used in most of the experiments although several were made with Baker and Adamson boric oxide. Both products contain substantial amounts of water and, as before, heating to 900° for a long period of time (about 48 hours) was used to reduce water content to a minimum. Corrections were made for the thermal expansion of the gold ball and for the effect of the surface tension on the suspension wire. Because of severe damping of balance motion equilibrium weighings of the ball were impossible and an extrapolation to zero rate of plots of load *versus* rate of balance movement was used to obtain the apparent weight of the ball in the solution. The estimated absolute error in the density determinations is 0.005 g./cm.^{3}.

Measurement of Dielectric Constant.—A cell containing eleven rigidly mounted nickel plates was used for the measurement of the dielectric constant. A stainless steel beaker was used as a container and the plate assembly was immersed in the molten boric oxide. A chromel-alumel thermocouple placed near the plates was used to measure temperature. Capacitance measurements were made with a General Radio 716C bridge and a Dumont oscilloscope (304-H CRO) as a null detector. During measurements the heating furnace was disconnected from the line. The cell's capacitance in air was 30.5 $\mu\mu$f, and it was calibrated with C.P. benzene distilled from phosphorus pentoxide. That the results were not affected by the metal container was shown by agreement with measurements made in a Vycor beaker. The dielectric behavior of boric oxide and the characteristics of the

TABLE I

VISCOSITY DATA (INTERPOLATED)

	Mole %	600°	650°	700°	750°
	0.0	2400[a]	1100	600	370
Li_2CO_3	1.0	1680	650	320	160
	3.0	..	580	240	120
	6.0	1500	500	170	80
Na_2CO_3	1.0	1750	670	280	180
	3.0	1650	650	280	150
	6.0	1700	700	280	180
K_2CO_3	1.0	1300	540	280	180
	3.0	1000	360	160	96
	6.0	1600	440	160	96
Rb_2CO_3	1.0	920	440	240	160
	3.0	840	320	140	80
Cs_2CO_3	1.0	1400	600	300	200
	3.0	1000	400	180	140
NaCl	1.0	2100	920	480	300
	2.0	2000	860	400	240
NaF	2.7	1800	700	320	160
	6.4	1400	500	220	105
	12.1	2400	720	240	80
	18.9	3600	800	240	120
Na_3AlF_6	1.6	1080	440	240	140
	3.2	480	180	100	72
$Na_2B_4O_7$	1.5	..	820	350	200
	3.0	..	800	350	200

[a] Viscosity in poises.

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(1) W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932).

(2) B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

(3) H. Richter, G. Breitling and F. Herre, *Naturwiss.*, **40**, 482 (1953); *Z. Naturforschung*, **9a**, 390 (1954).

(4) J. Biscoe and B. E. Warren, *J. Am. Ceram. Soc.*, **21**, 287 (1938); R. L. Green, *ibid.*, **25**, 83 (1942).

(5) S. V. Berger, *Acta Chem. Scand.*, **7**, 611 (1953).

(6) K. Fajans and S. W. Barber, THIS JOURNAL, **74**, 2761 (1952).

bridge made it impossible to obtain data outside the range 1 kilocycle to 1 megacycle.

Results and Discussion

The data obtained are presented in Tables I, II and III, and in Figs. 1-6. In addition pertinent thermodynamic data are set forth in Table IV.

TABLE II

DENSITY DATA (INTERPOLATED), G./CM.^{3}

Mole % NaF	600°	700°	800°
0.0	1.586	1.567	1.548
2.69	1.620	1.600	1.579
7.65	1.710	1.685	1.659
12.4	1.782	1.752	1.720

TABLE III

DIELECTRIC DATA FOR BORIC OXIDE

	10^3/sec.	5×10^3/sec.	10^4/sec.	10^6/sec.
25°	4.15[a]	3.46	3.32	3.18
	0.33	0.10	0.07	0.02
240°	3.42	3.30	3.24	3.16
	0.04	0.03	0.02	0.01
355°	3.66	3.40	..	3.19
	0.10	0.05	..	0.02
410°	5.54	3.64	..	3.28
	0.05	0.13	..	0.04
445°	20.0	7.28	4.67	3.45
	..	0.80	0.44	0.09
	5×10^4/sec.	8×10^4/sec.	2×10^5/sec.	5×10^5/sec.
570°	26.7	26.3	5.68	4.24
	2.3	2.3	0.74	0.37

[a] The upper number is ϵ' in the expression for the complex dielectric constant, $\epsilon^* = \epsilon' - i\epsilon''$. The lower number is tan $\delta = \epsilon''/\epsilon'$.

TABLE IV

THERMODYNAMIC DATA FOR BORIC OXIDE, B_2O_3

	Fusion ($c \rightarrow 1$)	Vaporization ($1 \rightarrow v$)	
T, °C.	450[a]	2240[b]	1860[c]
ΔH kcal./mole	5.3	78	66
ΔS, e.u./mole	7.3	31.2	32.2

[a] National Bureau of Standards, Circular 500. [b] Estimated from vapor pressure data of J. R. Soulen, P. Sthapitanonda and J. L. Margrave, *J. Phys. Chem.*, **59**, 132 (1955). [c] Estimated from vapor pressure data of S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, **18**, 82 (1935).

Viscosity.—The activation energy ($= RT \ln \eta/A$) for viscous flow of pure boric oxide in the temperature region examined in this work is about 34 kcal. per mole as compared to 61 kcal. per mole found below 450° by Parks and Spaght.[7] The alkali metal carbonates are assumed to decompose to the corresponding oxide but there does not seem to be a regular trend, according to cation, in the effectiveness of the initial lowering of viscosity. On the other hand the effectiveness of anions is, in decreasing order, fluoride, oxide and chloride. Passage of viscosity isotherms through minima appears typical and is shown in Fig. 2 for sodium fluoride solutions. At the temperatures considered the higher valence oxides, CaO, MgO, Al_2O_3, SnO_2, Sb_2O_5, TiO_2 and Fe_2O_3, and aluminum fluoride have inappreciable solubilities (<0.5 mole %) and the effect on viscosity was not determined for these substances, although at higher temperatures (>1000°) more concentrated solutions are obtainable.[8] Even though aluminum fluoride is practically insoluble it is of interest that cryolite, Na_3AlF_6, has a substantial solubility.

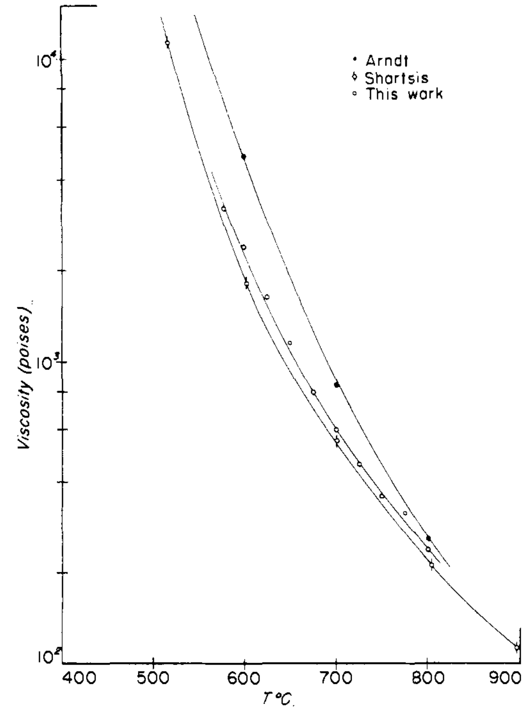

Fig. 1.—Viscosity of pure boric oxide *versus* temperature. The data of previous workers are shown for comparison (K. Arndt, *Z. Elektrochem.*, **34**, 578 (1907), ref. 12). From left to right curve: ϕ, Shartsis, *et al.*; O, this work; ●, Arndt.

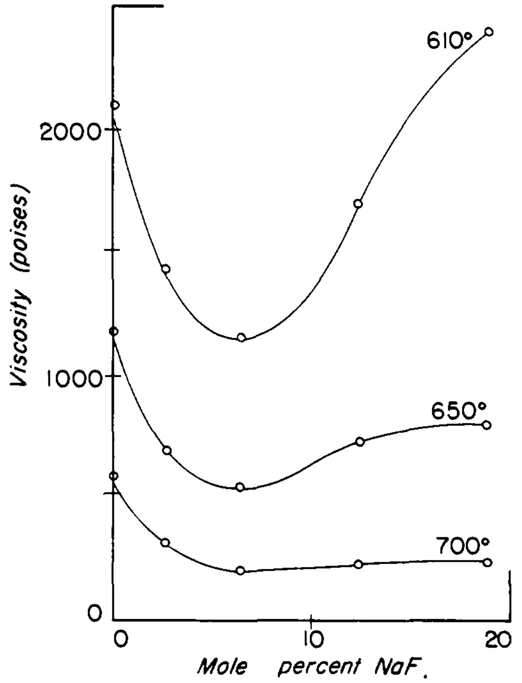

Fig. 2.—Viscosity isotherms for boric oxide solutions of sodium fluoride.

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[7] G. S. Parks and M. E. Spaght, *Physics*, **6**, 69 (1935).

[8] M. Foex, *Compt. rend.*, **206**, 349 (1938).

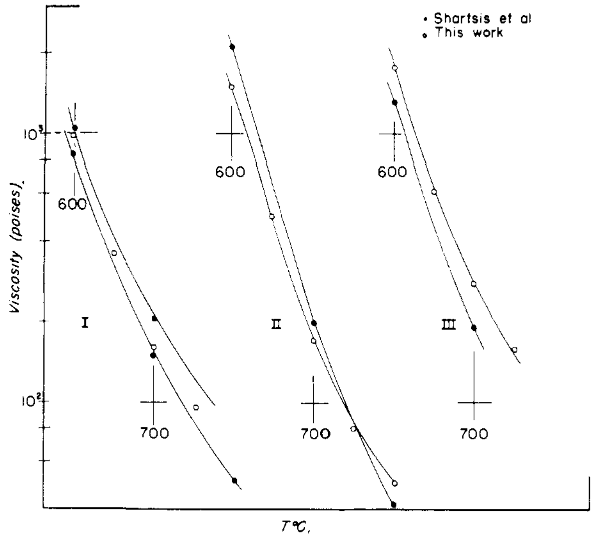

Fig. 3.—Curves I show viscosity of 3.0 mole % K_2CO_3 (this work) and of 2.1 and 3.9 mole % K_2O solution (ref. 12). Curves II show viscosity of 6.0 mole % solution of Li_2CO_3 (this work) and 6.3 mole % solution of Li_2O (ref. 12). Curves III show viscosity of 6.0 mole % solution of Na_2CO_3 (this work) and 6.2 mole % solution of Na_2O (ref. 12).

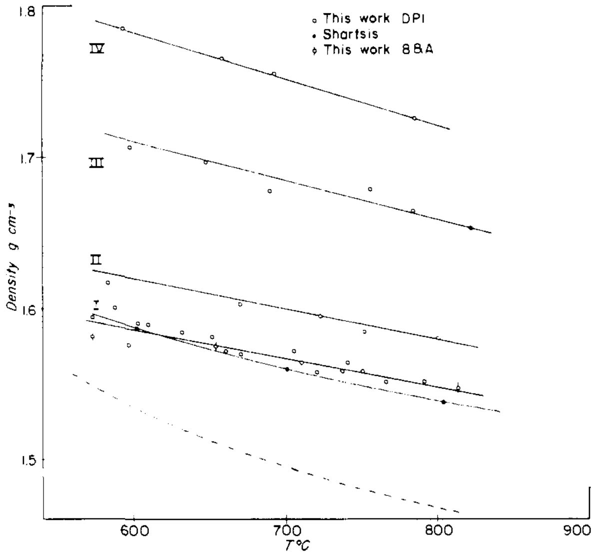

Fig. 4.—Densities of pure boric oxide and sodium fluoride solutions. Curves I compare the density of pure boric oxide obtained in this work and by the National Bureau of Standards.[9] The dotted curve represents the density for pure boric oxide obtained by Parks and Spaght (M. E. Spaght and G. S. Parks, *J. Phys. Chem.*, **38**, 103 (1934)). Curves II, III and IV give densities of 2.69, 7.65 and 12.4 mole % solutions, respectively, of sodium fluoride in boric oxide.

Density.—The data obtained for pure boric oxide differ by, at most, 0.5% from those of Shartsis, Capps and Spinner,[9] and the addition of sodium fluoride produces a marked reduction in molal volume as does sodium oxide.[9] Sodium fluoride is, however, not quite as effective in reducing the molal volume as sodium oxide, which is clear from the estimated partial molal volumes in dilute solution at 600° of −20 and −40 cm.³, respectively. The smaller viscosity of sodium fluoride solutions as compared to sodium oxide solutions is largely a result of the density difference. Although the density data are not precise enough to permit a careful determination of partial molal volumes it seems that in dilute solution the partial molal volume of boric oxide is little different from its molal volume. In the vicinity of about 10 mole % boric oxide's

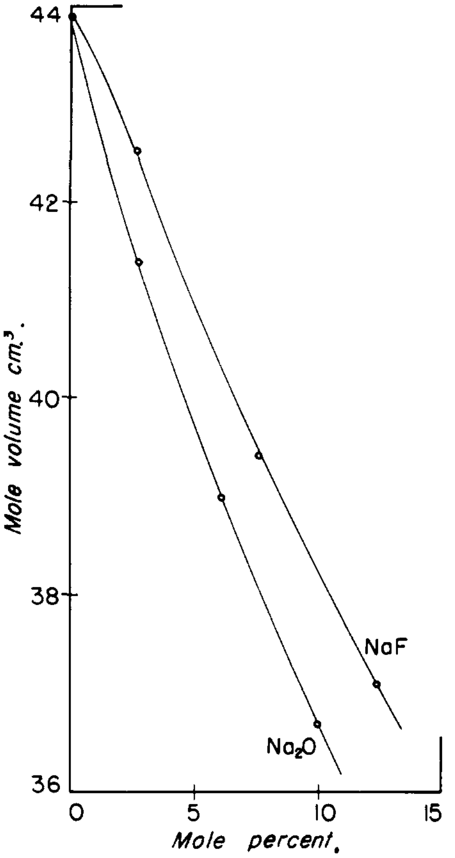

Fig. 5.—Molal volume of boric oxide solutions. The data for sodium fluoride were obtained in this work, and those for sodium oxide by Shartsis and co-workers.[12]

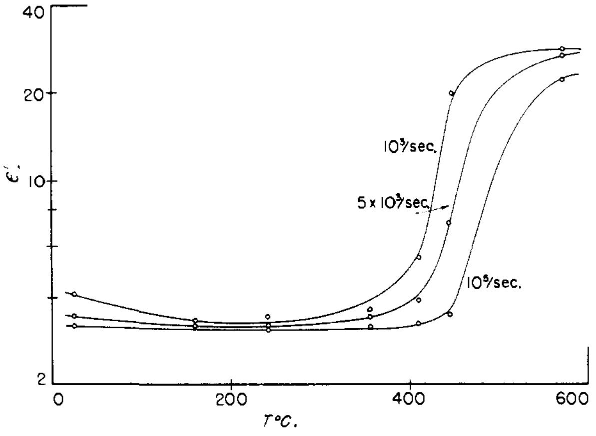

Fig. 6.—Dielectric constant for boric oxide *versus* temperature.

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(9) L. Shartsis, W. Capps and S. Spinner, *J. Am. Ceram. Soc.*, **36**, 35 (1953).

partial molal volume in both sodium oxide and sodium fluoride solution begins to decrease.[10]

Dielectric Constant.—Previous measurements[11] of the low frequency dielectric constant of boric oxide give a value of about 3.5. As shown in Fig. 6 the dielectric constant rises rapidly from this value between 400 and 500°. Except for the slight but reproducible minimum in the low temperature range the data can be fitted with the Debye equation and yield a dipole moment of about 3.5 debyes. The rapid increase of loss, especially due to increased conductivity, makes extension of measurements to higher temperatures very difficult.

Consideration of the relatively low entropy of fusion of crystalline boric oxide and the relatively high entropy of vaporization leads one to believe that the liquid has considerable structure. Indeed the low enthalpy of fusion is inconsistent with the breaking of boron–oxygen bonds on a large scale and rather suggests a configurational change accomplished without such breakage.

Since at low temperatures the activation energy for viscous flow is practically the same as the enthalpy of vaporization it can be assumed that the shearing stress must break boron–oxygen bonds for flow to occur. On the other hand, when thermal agitation has degraded the structure by breaking bonds, the activation energy for flow decreases by about one-half and is probably associated with hole-formation by a smaller structural unit. In effect, the boric oxide can be considered as a polymer, the size of whose structural unit decreases with increasing temperature, beginning at the lowest temperature at which the glass is known to exist. If this were not so, the viscosity would be expected to be much smaller at low temperatures than it actually is.

The effect of solutes on viscosity is similar to the effect of increasing the temperature. Thus when sodium fluoride or sodium oxide is added to boric oxide the initial decrease in viscosity can be attributed to the breaking of B–O–B linkages in the network of BO_3 triangles and the gaining of singly bonded anions, B–O X–B. That a bond breakage and formation is involved in viscosity reduction seems consistent with the fact that the order of effectiveness of chloride, oxide and fluoride in lowering viscosity is in the order of increasing electronegativity.

In one important respect, however, addition of solute differs from increasing the temperature. Addition of both sodium fluoride and sodium oxide gives an enormous decrease in molal volume. This is undoubtedly a result of the packing around the sodium ions of structural units whose valency is unsaturated because of anion addition. Since the addition of fluoride results in one unsaturation, whereas the addition of oxide gives two, the volume contraction in the fluoride solutions is less pronounced than in the oxide solutions.

The remarkable increase in density, accompanied by a decrease in viscosity, only seems compatible with the collapse of a large, open network into smaller structural units which are at the same time more mobile and more efficiently packed. Upon addition of more solute the subsequent transition from three- to four-coördination and the coupling of tetrahedral units permits the density to continue to increase although the viscosity increases. Eventually at sufficiently high concentrations the viscosity may be expected to pass through a maximum since there will be enough anions to reduce the need for sharing of tetrahedron corners. This is found to be the case in sodium oxide solutions,[12] but devitrification prohibited extension of measurements into this concentration range for sodium fluoride solutions.

The dielectric behavior of pure boric oxide shows an increasing relaxation loss with increasing temperature. Such behavior is clearly inconsistent with a change from a molecular liquid at low temperatures to a strongly coördinated one at high temperature.

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[10] *Cf.* G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 38.

[11] S. B. Thomas, *J. Phys. Chem.*, **35**, 2103 (1931); N. P. Begerodicki and V. N. Malysev, *Zhur. tekh. Fiz.*, **5**, 612 (1935).

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