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ABSTRACT

Electrical conductance measurements of aqueous boric acid solutions (15-110 g/kg-H_2O ≡ 0.251 - 1.815 mol/kg-H_2O) were measured over the temperature range 25 to 75°C at saturation vapor pressures in glass cells with parallel platinum electrodes. Sixteen series of measurements were made involving three samples of boric acid from different sources. Conductance measurements were also made at 15.5 and 30.5 g/kg-H2O over the temperature range 100 to 350°C at 50°C intervals with a metallic cell fitted with concentric platinum electrodes. The specific conductances of $H_3BO_{3\,(aq)}$ were calculated after correction for the conductance of the solvent (water) and are tabulated in this report. At the specific conditions requested in the project description, namely a concentration of 110 g/kg-H_2O and 65°C, the specific conductance of boric acid is 293.2±1.8 microSiemens/cm based on duplicate measurements of four independent solutions.

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

Dilute aqueous boric acid solutions have been used as inhibitors to prevent intergranular stress corrosion cracking and intergranular attack, which are caused by alkaline contaminants, in nuclear steam generators.[1,2] Although aqueous boric acid solutions contain many species,[1-3] orthoboric acid (H_3BO_3 or $B(OH)_3$) is believed to be the only neutral stable species in aqueous solution.[1-3] The physical and chemical properties of H_3BO_3 have been studied by many research groups (ref. 1 and 2, and references therein). The electrical conductances of aqueous H_3BO_3 solutions at concentrations up to *ca.* 0.5 mol/kg-H_2O (30 g/kg-H_2O) have been measured by Kolthoff[4] and Thygesen[5] at 18°C and by Byrnes[1] at 100-315°C. However, these data are not available at concentrations > 0.5 mol/kg-H_2O and between 18 and 100°C. In this report measurements of the electrical conductance of aqueous H_3BO_3 solutions are presented at concentrations up to 110 g/kg-H_2O and temperatures from 25 to 75°C with glass cells and 100 to 350°C with a metallic cell. These tests were funded by the Department of Energy and the Princeton Plasma Physics Laboratory. The results will be utilized by the Tokamak Physics Experimental Project (TPX).

EXPERIMENTAL

Materials

Three sources of boric acid (US Borax, type D, GRAN SQ; Baker analyzed reagent, lot #39629; Aldrich, 99.999%, lot #05821CY) were used in this study. The stock solutions of boric acid (from 15 to 110 g/kg-H_2O) were prepared with conductivity water, which was obtained by bubbling argon through double-distilled, deionized water (4-stage Barnstead Nanopure system) for at least two hours before use. The specific conductance of this water was 7.8 x 10^{-7} Siemens/cm at 25°C and these values are listed in Table 1 for the range 25 to 75°C. All solutions were prepared by weight. The concentration of each stock solution was checked by removing water from weighed aliquots of the solution via rotor evaporation under vacuum at 30°C (this low temperature was chosen to prevent loss of H_3BO_3 due to sublimation) and dried over P_2O_5 under vacuum for at least seven days. The boric acid concentration of the solution was calculated from the mass of the anhydrous H_3BO_3 acid remaining. Solutions, which were supersaturated with respect to boric acid at 25°C, were first warmed and transferred to a closed container, then weighed after cooling and treated as above. The differences between replicate analyses were 0.01 to 0.15% for solutions up to 22 g/kg-H_2O, and 0.01 to 1.4% for the supersaturated solutions.

Experimental Equipment and Procedures

Low Temperature Cells: The electrical conductance of the aqueous H_3BO_3 solutions was measured at saturation vapor pressure in the temperature range 25-75°C using two cylindrical glass cells with parallel platinized-platinum electrodes. The cells were filled with the appropriate solution and immersed in a refrigerated ethylene glycol bath (Neslab PH1). The temperature was monitored with a primary standard platinum resistance thermometer (RTD) connected to a digital readout (Instrulab 4221) to within an accuracy of ±0.01°C.

The cell constants of the two glass cells were determined to be 0.180 and 0.407 cm^{-1} by measuring the conductances of 0.001, 0.002, and 0.005 demal (mol/kg-solution) KCl (Baker, Ultrapure, 99.999%) solutions at 25.00±0.01°C. The cell constant of a high-temperature cell (0.09 cm^{-1}) was determined using 0.001 and 0.005 demal KCl standard solutions at 25.00±0.01°C. The mean values of the cell constant were calculated based on the specific conductances of the KCl solutions reported from 0 to 50°C. (6,7)

High Temperature Cells: These cells have been described in detail previously. (8) The stainless steel (Udimet 700), cylindrical high-pressure vessel encompasses a 75% platinum - 25% iridium alloy liner, which serves as the outer electrode in a concentric electrode configuration. The sample chamber, whose length is defined by two thick-walled, close-fitting platinum - iridium tubes inserted into each end of the liner, is 6.35 cm long and has a volume of 1.03 cm^3. The inner surface of the liner is platinized in this center region. The inner electrode consists of a thin platinum wire welded to a 1/16 in. od platinum - iridium cylinder that is also coated with platinum black. The wire is double-insulated by a non-porous sintered Al_2O_3 tube encased in a ZrO_2 tube. The platinum wire is welded to the Al_2O_3 and ZrO_2 tubes by high temperature ceramic material. The conductance measurements at elevated temperatures were performed as follows. The clean conductance cell and the separator vessel (8) (sample reservoir) were flushed with Ar and rinsed three times with sample solution. The reservoir was then filled with solution, sealed under argon, and solution was forced through the cell, which was closed by a high pressure valve before turning on the furnace. The performance of the actual conductance measurements are described below.

General: The solution in the cell was equilibrated at the desired temperature for an hour, whereupon the conductance was measured with Wayne Kerr 6425 Component Analyzer at eight frequencies in the range 0.5-10 kHz. The conductance at infinite frequency was computed using a standard second-order polynomial regression (conductance vs. square root of frequency). The reproducibility of the conductance measurements was generally better than ±0.1%. The resistances of the lead wires were compensated for prior to each measurement. The bridge was calibrated periodically against NIST-certified resistances and capacitances.

The specific conductance (κ) was calculated from equation (1).

$$\kappa = aC \tag{1}$$

where a is the cell constant (cm^{-1}) and C is the conductance of solution in microSiemens at infinite frequency.

RESULTS

Low Temperature Results: The electrical conductances of aqueous H_3BO_3 solutions (15-110 g/kg-H_2O) were measured from 25-75°C at saturation vapor pressure. In Table 1 are listed the specific conductances of the water used to make up the stock solutions and the H_3BO_3 solutions at 25-75°C, where the latter were corrected for the conductivity of the solvent (water). Figure 1a-b illustrates that the specific conductances of 0.25 and 0.5 mol/kg-H_2O (15-30 g/kg-H_2O) of all three H_3BO_3 solutions are in good agreement with each other. This is particularly significant in view of the fact that these solutions are relatively poor conductors and hence trace impurities of electrolytes in the solid boric acid samples could significantly elevate the conductance.

The specific conductance of $H_3BO_{3(aq)}$ increases with increasing concentration and increasing temperature over the range 25 to 75°C. Specific conductances of 0.25 and 0.50 mol/kg-H_2O H_3BO_3 solutions measured at 18°C in a water bath by Kolthoff[4] and Thygesen,[5] and the solid lines for 0.25 and 0.50 mol/kg-H_2O H_3BO_3 estimated from Figure III-3 in ref. 1, are included in Figure 1a-b for comparison. It can be seen that the present results are in reasonable agreement with the corresponding data reported in the literature. Note that the curves representing the data of Byrnes[1] were obtained by digitizing the plots shown in Figure III-3 of that article, as the actual values on which these plots were based are not published. Furthermore, as stated by Byrnes, these curves were not corrected for the conductance of water, which accounts for them being higher than the other results, although Byrnes apparently used the results of Kolthoff[4] and Thygesen[5] to constrain these fitted curves at 18°C, because his measurements terminated at 100°C.

Figure 2 presents the plots of the specific conductance of H_3BO_3 solutions at all concentrations (15 to 110g/kg-H_2O) as a function of temperature. Figure 2 also shows that at constant concentration, the specific conductance increases only slightly with increasing temperature from 25 to 75°C. However, this figure illustrates that the conductivity of the water itself is a very substantial contribution to the measured conductances, particularly at the lowest concentrations, e.g., 15.5 g/kg-H_2O.

In order to calculate the specific conductance of a boric acid solution at 65°C and a concentration of 110 g/kg-H_2O, four pairs of values were taken from Table 1 from each of the last four series from 110.00 to 112.2 g/kg-H_2O measured at 65.00±0.01°C. These values were each divided by the boric acid concentration listed for each pair, which is equivalent to estimating molar conductance in these different units, whereupon the average was estimated and the standard deviation of the mean, and the resulting average value was then multiplied by the desired concentration of 110.00 g/kg-H_2O to give **293.2±1.8 microSiemens/cm**. Interestingly, in the measured temperature range of 55 to 75°C, the specific conductance of these highly concentrated solutions proved to be temperature independent within the uncertainty and reproducibility of the measurements. Indeed the mean value of the 15 measurements listed in Table 1 at 110.00±0.03 g/kg-H_2O from 54.99 to 75.00°C is **293.4±1.8 microSiemens/cm**.

The upper limit for the safe operation of these glass cells is 75°C due to the fragility of the platinum to glass seals of the wire feed-throughs. The lower temperature limit was imposed by the insolubility of boric acid at these high concentrations below 55°C.

High Temperature Results: The results with the high temperature cell are always inherently less precise than for the traditional glass cells discussed above for reasons of less precise temperature control, less rigid electrode configuration, and surface contamination from the metal surfaces. In the present study, the latter condition was exasperated by the low conductivity of the solutions with respect to water, which in turn has a higher conductivity for this reason. Therefore, three series of measurements were made at each concentration of 0.25 and 0.50 mol/kg-H_2O at 50°C intervals from 100 to 350°C at saturation vapor pressure. It was noted that in each case the measurement became somewhat unstable at the maximum in conductances observed at *ca.* 150°C.

The specific conductances for each concentration and temperature were averaged in the manner described above and these average values are listed in Table 2, together with the corresponding values for water and the average of the low temperature measurements. The specific conductances are also shown in Figure 3 at each concentration, where it is immediately apparent that both sets of data pass through a maximum and fall to very low values at high temperatures.

The complete temperature dependencies of the specific conductances of boric acid solutions at the two concentrations are shown in Figure 4 together with the "uncorrected", "digitized" curves taken from Byrnes.[1] For the reasons stated previously, the comparison can only be qualitative without access to the original data of Byrnes. I t is noteworthy that the specific conductance for $KCl_{(aq)}$ reported at 100 and 200°C are in very good agreement with measurements made in this laboratory (e.g., for a 0.0015 mol/kg-H2O KOH solution κ is 0.745 and 1.119 (cf. 0.77 and 1.1 [1]) microSiemens/cm, respectively, largely because the contribution of the water is minor in such highly conducting solutions.

The initial increase in conductivity is typical of electrolytes in general due to the increased mobility of the ions as the dielectric constant of the solvent decreases. Presumably, the conductance decreases at higher temperatures as boric acid becomes weaker, or more strongly associated, as do all acids and bases in aqueous solution. The speciation of boric acid solutions can be modeled over this temperature range based on earlier potentiometric work carried out in this laboratory.[9] In addition, it must be remembered, that additional quantities of lithium hydroxide may markedly increase the observed conductivities of these solutions.

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Table 1. Specific Conductance ($\mu S \cdot cm^{-1}$) of Aqueous Boric Acid Solutions at Temperature 25-75°C[1,2]

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
0.0		25.00	0.78
		50.00	1.30
		55.00	1.45
		65.00	1.80
		75.00	2.20
0.2507[a]	15.50	24.99	8.48
		24.99	8.46
		50.00	11.07
		49.99	10.97
		65.00	12.22
		65.00	12.32
		75.01	12.99
		75.01	12.99
0.2505[a]	15.49	25.00	8.48
		25.00	8.48
		25.00	8.48
		50.01	11.04
		50.01	11.06
		50.00	11.06
		65.02	12.24
		65.00	12.24
		64.99	12.23
		75.00	12.82

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
		75.00	12.83
		75.00	12.81
0.2519[b]	15.58	25.00	7.89
		25.00	7.89
		25.00	7.89
		50.02	10.58
		50.01	10.58
		50.00	10.58
		65.01	11.91
		65.02	11.91
		65.00	11.98
		75.00	12.77
		74.99	12.67
0.2538[c]	15.69	25.00	8.47
		24.99	8.48
		50.01	10.90
		50.02	10.90
		65.00	11.95
		65.01	11.97
		75.00	12.49
		75.00	12.48
		75.00	12.49
0.3535[a]	21.86	25.00	13.54
		25.00	13.551
		50.00	16.83

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
		50.00	16.84
		65.00	18.22
		65.01	18.21
		65.01	18.22
		75.01	18.98
		75.00	18.98
0.3630[c]	22.44	25.01	15.28
		25.00	15.28
		50.00	19.33
		50.01	19.33
		50.00	19.32
		65.01	21.21
		65.01	21.21
		75.01	22.21
0.5093[a]	30.53	24.99	25.68
		24.99	25.67
		25.00	25.68
		50.00	30.26
		50.00	30.28
		65.00	32.32
		65.00	32.38
		75.00	33.32
		75.01	33.29
0.5088[a]	30.50	25.01	24.82
		25.00	24.97

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
		50.04	29.03
		50.04	29.06
		65.02	31.80
		65.02	31.85
		65.03	31.85
		75.01	33.32
		75.01	33.28
		75.01	33.30
0.5117[b]	31.64	25.01	23.89
		25.01	23.89
		50.00	28.48
		49.99	28.44
		50.00	28.56
		65.03	31.31
		65.02	31.29
		65.01	31.30
		75.01	32.59
		75.00	32.59
0.5156[c]	31.88	24.99	25.84
		25.00	25.84
		24.99	25.83
		50.01	30.28
		50.00	30.27
		49.99	30.28
		65.00	31.74

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
		65.00	31.75
		75.00	32.52
		74.99	32.53
0.8728[a]	53.97	50.01	82.97
		49.99	82.97
		54.99	83.74
		55.01	83.75
		65.01	84.67
		65.00	84.67
		74.99	84.79
		75.00	84.66
0.9292[c]	54.45	49.93	86.33
		49.96	86.49
		55.00	87.09
		55.00	87.10
		55.01	87.10
		64.99	87.86
		64.99	87.86
		65.01	87.86
		75.00	87.57
		74.99	87.56
		75.00	87.58
1.779[a]	110.00	55.02	293.29
		54.99	292.37
		55.01	291.98

Molality	g/kg-H_2O	Temp. (°C)	Specific Conductance[2]
		65.00	290.34
		65.00	290.43
		75.00	295.95
		74.98	295.90
1.771[a]	109.97	55.00	294.15
		55.00	294.14
		55.00	294.10
		65.01	294.68
		65.01	294.75
		65.01	294.65
		75.00	292.17
		75.00	292.21
1.805[a]	111.58	50.00	294.04
		55.01	296.59
		55.01	296.75
		65.01	297.90
		65.01	297.78
		74.99	295.52
1.815[c]	112.20	55.03	299.35
		55.02	299.28
		55.01	298.97
		65.01	299.91
		65.01	299.87
		75.00	303.22
		75.00	302.86

[1] Measured with glass cell; values of solution specific conductances were corrected for water.
[2] μS: microSiemens/cm
[a] US Borax Type D.
[b] Baker analyzed reagent.
[c] Aldrich 99.999%.

Table 2. Specific Conductance (μS/cm) of Aqueous Boric Acid Solutions at 25-350°C

Temp.(°C)	H_2O	0.25 mol/kg-H2O[a]	0.50 mol/kg-H2O[a]
25	0.78	8.42±0.06	25.11±0.09
50	1.30	10.9±0.1	29.5±0.2
65	1.45	12.0±0.2	31.1±0.6
75	1.80	12.6±0.3	31.9±0.7
100	31.6	13.8±0.4	31.8±0.9
150	71.9	14.7±0.4	32.1±1.0
200	82.2	14.4±0.4	29.7±1.3
250	81.0	12.3±0.6	24.7±1.7
300	80.1	8.9±0.5	17.1±2.5
350	78.5	4.3±0.8	6.1±2.1

[a] Corrected for water conductance.

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