

The Thermodynamics of Aqueous Borate Solutions. II. Mixtures of Boric Acid with Calcium or Magnesium Borate and Chloride

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Potentials for the cell without liquid junction



with $M = Ca^{2+}$ or Mg^{2+} are reported over a range of ionic strength at 5, 15, 25, 35, 45, and 55°C. Parameters of Pitzer's ion interaction treatment are determined for $Ca(B(OH)_4)_2$ and $Mg(B(OH)_4)_2$ by fitting to the cell results. Apparent association of alkaline earth borates to form the monovalent species $CaB(OH)_4^-$ and $MgB(OH)_4^-$ makes it necessary to use the extended $\beta^{(2)}$ form of the ion interaction treatment to represent the potentials reported here. Trace activity coefficients of calcium and magnesium borates are tabulated at various temperatures and ionic strengths. The association constants for ion pair formation implied by the values of $\beta^{(2)}$ for these salts are compared with ion pair formation constants available in the literature.

KEY WORDS: Borates; thermodynamics; electrolytes; Harned cells.

1. INTRODUCTION

In our earlier work,⁽¹⁾ trace activity coefficients of sodium and potassium borates in chloride media were obtained from emf measurements. Borate containing systems of practical interest, including natural

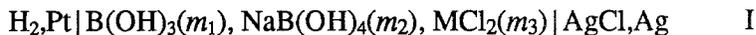
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waters, may include calcium and magnesium ions in solution. Hershey *et al.*⁽²⁾ have recently reported results of potentiometric titrations of boric acid in the presence of Ca^{2+} and Mg^{2+} . These authors have applied the ion interaction treatment of Pitzer,⁽³⁾ and have calculated trace activity coefficients for calcium and magnesium borates in chloride media at 25°. Here, emf measurements are reported for the cell



with $\text{M} = \text{Mg}^{2+}$ or Ca^{2+} and m is molality ($\text{mol}\cdot\text{kg}^{-1}$). Again in this study the total molality of boron has been restricted to low levels to minimize polyborate formation. Ion interaction parameters for $\text{Ca}(\text{B}(\text{OH})_4)_2$ and $\text{Mg}(\text{B}(\text{OH})_4)_2$ have been determined from these results as functions of temperature in the range from 5 to 55°. The extended form of the ion interaction treatment, developed to represent the thermodynamics of 2-2 and higher charge type electrolytes,⁽⁴⁾ was needed to represent the observed cell potentials. Comparison of association constants K for the formation of $\text{CaB}(\text{OH})_4^\ddagger$ and $\text{MgB}(\text{OH})_4^\ddagger$ calculated from the parameters of the extended ion interaction treatment with those obtained from other treatments show the same patterns as 2-2 charge type electrolytes, with the ion interaction treatment giving lower values of K . Trace activity coefficients of $\text{Mg}(\text{B}(\text{OH})_4)_2$ and $\text{Ca}(\text{B}(\text{OH})_4)_2$ in chloride media are tabulated at regular temperature intervals, and are compared with those calculated from the parameters given by Hershey *et al.*⁽²⁾

2. EXPERIMENTAL

Stock solutions of reagent grade (Fisher ACS Certified) magnesium chloride hexahydrate and calcium chloride dihydrate were analyzed gravimetrically as chloride to a precision of $\pm 0.01\%$. Boric acid (99.999%, Aldrich Gold Label) was used without further purification. Sodium hydroxide stock solutions were standardized by weight titration under CO_2 -free conditions to phenolphthalein end point using NBS reference primary standard potassium hydrogen phthalate. The experimental cell solutions were prepared by weight using appropriate amounts of standard hydroxide solution, magnesium or calcium chloride stock solution, solid boric acid, and doubly distilled water. All weighings were corrected to vacuum. Final molalities of the cell solutions have an uncertainty of $\pm 0.05\%$ due to weighing imprecision.

The standard potential of the AgCl, Ag electrode was determined by measuring potentials of the cell



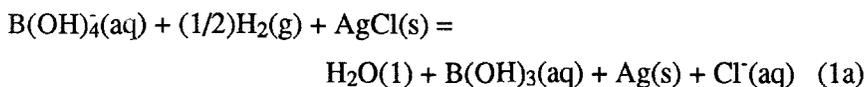
using established procedure.⁽⁵⁻⁷⁾ The electrode potentials were 0.23438, 0.22882, 0.22259, 0.21590, 0.20860, and 0.20081 V at 5, 15, 25, 35, 45, and 55°. Potentials were measured with a digital multimeter (Keithley Model 191); cell temperatures were measured to $\pm 0.01^\circ$ with a Hewlett-Packard quartz thermometer. Details of electrode preparation, temperature control, hydrogen purification, and cell design have been reported previously.⁽⁸⁻¹⁰⁾

Cell potentials were first measured at 10° intervals from 25 to 5°. The cells were then returned to 25° and potentials measured from 25 to 55°; a final measurement was always made at 25°. Agreement of duplicate measurements at 25° was within ± 0.05 mV.

3. RESULTS

Cell potentials, stoichiometric molalities, and experimental temperatures and pressures are given in Tables I and II. Values listed are not corrected to unit hydrogen fugacity. The vapor pressure of water over the cells was calculated for each measurement using solution osmotic coefficients obtained from the interaction-model treatment described below and the equation of state for water of Haar *et al.*,⁽¹¹⁾ with the hydrogen fugacity assumed equal to its partial pressure. The precision of the measurements, based on reproducibility of a given experiment and experience with these cells, is estimated to be ± 0.3 mV.

The reaction in cell I is



and the cell potential is given by

$$E = E^\circ(\text{AgCl}, \text{Ag}) = (RT/F) \{ \ln K_1 - (1/2) \ln [f(\text{H}_2)/p_o] + \ln(a_w) + \ln(m_{\text{HB}} m_{\text{Cl}} / m_{\text{B}} m_o) + \ln(\gamma_{\text{HB}} \gamma_{\text{Cl}} / \gamma_{\text{B}}) \} \quad (1b)$$

where K_1 is the ionization constant of boric acid, $f(\text{H}_2)$ is the hydrogen fugacity, a_w is the activity of water, and the subscripts HB and B denote boric acid and borate. The quantities p_o and m_o are 101.3 kPa and 1.0 mol·kg⁻¹, respectively. Other symbols have their usual meanings, with values of R and F taken from Cohen and Taylor.⁽¹²⁾ Values of K_1 were calculated from the equation given by Manov *et al.*⁽¹³⁾

In terms of Pitzer's ion interaction treatment⁽³⁾ as developed for

Table I. Potentials for Cell I with $M = \text{Mg}^{2+}$ and Solution Molalities $m_1[\text{B}(\text{OH})_3]$, $m_2[\text{NaB}(\text{OH})_4]$ and $m_3(\text{MgCl}_2)$

Run 1								
$10^2 m_1$	2.5198	2.3647	2.4965	2.5645	2.6033	2.5219	2.4553	2.5365
$10^2 m_2$	2.5001	2.4228	2.4998	2.4997	2.4994	2.4852	2.5003	2.5026
$10^2 m_3$	0.7999	1.5507	2.3950	3.2991	3.9998	4.9704	6.0008	7.0070
$p = 96.60 \text{ kPa}^a$	$E \text{ (mV)}$							
5°	847.34	831.82	819.46	809.20	803.33	797.15	792.70	786.73
15°	858.32	842.60	829.39	819.07	812.68	806.77	801.91	795.28
25°	869.13	852.30	838.71	828.73	821.83	815.25	810.28	803.76
35°	879.27	861.94	847.49	837.41	830.08	823.47	818.16	810.90
45°	888.97	870.87	855.93	845.43	837.82	831.05	825.40	818.33
55°	898.04	879.19	863.33	852.80	844.90	837.64	831.88	824.59
Run 2								
$10^2 m_1$	1.9857	2.0422	2.0424	2.0058	2.0134	2.0470	1.9733	2.0156
$10^2 m_2$	1.9643	1.9977	2.0247	2.0013	2.0449	2.0003	2.0001	1.9880
$10^2 m_3$	8.0220	10.009	13.162	16.011	23.512	27.001	30.004	32.787
$p = 96.87 \text{ kPa}$	$E \text{ (mV)}$							
5°	783.66	776.19	767.18	760.12	745.58	738.58	735.06	730.37
15°	791.41	784.10	774.53	768.04	752.29	745.34	741.62	736.87
25°	799.46	791.69	781.90	774.55	758.53	751.83	747.98	743.10
35°	806.81	798.81	788.67	780.73	765.08	757.61	753.81	748.81
45°	814.32	805.04	794.73	787.16	779.42	762.68	758.80	753.00
55°	819.03	810.53	799.60	792.26	773.64	766.84	762.80	757.81
Run 3								
$10^2 m_1$	2.4549	2.3064	2.2338	2.0333	1.8060	1.6554	1.5046	1.3542
$10^2 m_2$	2.4205	2.2900	2.1856	1.9777	1.7720	1.6068	1.5155	1.3656
$10 m_3$	3.8729	4.4799	4.9657	5.9330	6.8901	7.6589	8.0838	8.7799
$p = 97.03 \text{ kPa}$	$E \text{ (mV)}$							
5°	722.41	715.24	710.08	699.90	691.15	684.45	681.53	676.17
15°	728.73	721.42	716.16	705.81	696.86	690.02	687.06	681.60
25°	734.20	727.21	721.87	711.26	702.00	695.00	692.05	686.50
35°	739.67	732.56	727.12	716.22	706.73	699.70	696.78	690.96
45°	744.23	737.10	731.42	720.33	710.68	703.37	700.44	694.48
55°	748.35	740.70	734.90	723.52	713.58	705.88	702.91	696.74
Run 4								
$10^2 m_1$	2.2413	2.0166	1.8222	1.6057	1.4077	1.2536	1.0684	
$10^2 m_2$	2.2019	1.9908	1.7989	1.6022	1.4012	1.2323	1.0000	
$10^2 m_3$	4.0037	4.9762	5.9971	7.0091	7.9944	9.2425	9.9995	

^a Average ambient pressure over cells.

Table I. Continued.

$p = 96.63 \text{ kPa}$				$E \text{ (mV)}$			
5°	805.02	798.15	792.40	787.26	--	777.55	773.63
15°	--	806.34	800.45	795.30	790.70	785.13	781.02
25°	821.84	814.58	808.42	803.19	798.30	794.23	788.05
35°	830.42	823.41	816.14	810.62	--	801.17	796.43
45°	838.06	830.35	823.25	817.57	811.96	807.55	802.56
55°	844.61	836.17	829.64	823.72	818.20	813.13	806.69

^a Average ambient pressure over cells.

mixed electrolytes by Pitzer and Kim,⁽¹⁴⁾ the logarithm of the activity coefficient ratio of Eq. (1b) is given by

$$\begin{aligned} \ln(\gamma_{\text{HB}}\gamma_{\text{Cl}}/\gamma_{\text{B}}) = & \ln \gamma_{\text{HB}} + 2m_{\text{M}}(B_{\text{MCl}} - B_{\text{MB}}) + 2m_{\text{Na}}(B_{\text{NaCl}} - B_{\text{NaB}}) \\ & + 2m_{\text{M}}(\Sigma mz)(C_{\text{MCl}} - C_{\text{MB}}) + 2m_{\text{Na}}(\Sigma mz)(C_{\text{NaCl}} - C_{\text{NaB}}) \\ & + 2\theta_{\text{B,Cl}}(m_{\text{B}} - m_{\text{Cl}}) + m_{\text{M}}m_{\text{Na}}(\Psi_{\text{M,Na,Cl}} - \Psi_{\text{M,Na,B}}) \\ & + (m_{\text{B}} - m_{\text{Cl}})(m_{\text{M}}\Psi_{\text{M,B,Cl}} + m_{\text{Na}}\Psi_{\text{Na,B,Cl}}) \end{aligned} \quad (2)$$

with $M = \text{Ca}^{2+}$ or Mg^{2+} ; Σmz is a sum over all cations or anions. In Eq. (2), the small molality of hydroxide ion in these solutions due to the equilibrium



is not included in the calculation. The correction to the final concentrations of boric acid and borate ion is less than 1% in the buffer ratio for the boron molalities considered here, but has been included for all experiments.

It is not possible to determine both the activity coefficient of boric acid and the interaction parameters for the magnesium or calcium borate salts from the results of Tables I and II. In the case of the sodium and potassium borate systems the activity coefficient of boric acid was assumed to be

$$\ln \gamma_{\text{HB}} = m_{\text{HB}} \delta_{\text{HB}} + I \lambda_{\text{HB,MX}} \quad (4)$$

where the $\lambda_{\text{HB,MX}}$ parameters appropriate for NaCl(aq) and KCl(aq) media are calculated from the parameters given by Felmy and Weare.⁽¹⁶⁾ It is not possible to use this procedure in the present case, as Felmy and Weare assumed that the species in solution was the monovalent cation

Table II. Potentials for Cell I with $M = \text{Ca}^{2+}$ and Solution Molalities $m_1[\text{B}(\text{OH})_3]$, $m_2[\text{NaB}(\text{OH})_4]$, $m_3(\text{CaCl}_2)$

Run 1								
$10^2 m_1$	2.3967	2.4091	2.0973	1.9135	1.5687	1.3991	1.2274	1.0101
$10^2 m_2$	2.4000	2.1977	2.0000	1.7999	1.6001	1.4000	1.2000	0.9999
$10^2 m_3$	2.9193	3.8732	4.8983	5.8450	6.7886	7.7918	8.7585	9.7476
$p = 96.58 \text{ kPa}$	$E \text{ (mV)}$							
5°	812.63	800.16	794.42	788.74	785.18	779.25	774.75	771.47
15°	821.73	808.99	802.88	797.06	793.30	787.84	782.87	778.92
25°	830.05	817.79	811.02	804.65	801.29	795.58	790.18	786.29
35°	838.64	825.16	818.42	812.25	808.50	802.35	796.92	792.99
45°	846.54	832.65	825.66	819.10	815.13	809.14	803.32	799.14
55°	853.61	839.87	832.23	825.44	821.19	814.90	809.27	804.77
Run 2								
$10^2 m_1$	1.9673	2.0404	2.0488	2.0258	2.0614	2.0245	1.9522	2.0307
$10^2 m_2$	1.9999	2.0002	2.0000	1.9978	1.9982	1.9999	1.9353	2.0000
$10^2 m_3$	7.4030	9.2956	13.899	18.468	23.116	25.452	27.880	32.422
$p = 96.42 \text{ kPa}$	$E \text{ (mV)}$							
5°	781.93	773.11	758.17	747.79	737.55	733.89	729.92	723.81
15°	790.55	780.49	765.84	754.41	744.05	740.76	736.54	729.02
25°	798.29	787.94	772.89	761.09	749.85	745.79	742.01	--
35°	804.94	794.84	778.64	766.75	755.50	751.54	747.57	739.97
45°	811.56	801.29	784.20	772.20	760.99	756.54	752.15	744.76
55°	817.14	806.00	789.39	776.80	763.48	759.50	755.71	748.19
Run 3								
$10^2 m_1$	2.0942	2.4511	2.1678	2.0362	1.8175	1.5545	2.1341	1.2528
$10^2 m_2$	2.5001	2.2978	2.1997	1.9994	1.7998	1.6000	1.4998	1.2998
$10 m_3$	4.1019	4.6275	5.1248	6.1539	7.1817	8.2046	8.7183	9.2320
$p = 96.57 \text{ kPa}$	$E \text{ (mV)}$							
5°	717.43	706.05	702.50	691.66	682.85	674.55	661.54	666.81
15°	724.08	711.80	708.08	696.92	687.83	679.58	666.00	671.22
25°	729.35	716.92	713.14	701.68	692.34	684.18	670.05	675.46
35°	734.32	721.38	717.50	705.81	696.34	--	673.21	678.72
45°	738.66	725.43	721.30	709.43	699.79	690.81	676.50	681.74
55°	741.67	728.47	723.48	712.01	702.33	693.00	678.39	683.94

MB^+ ($M = \text{Ca}$ or Mg), and determined interaction parameters of this ion with other ions in the system. Millero⁽¹⁵⁾ has used an expression linear in ionic strength to represent $\ln \gamma_{\text{HB}}$; Hershey *et al.*⁽²⁾ have extended this

expression to include a term in I^2 . In the case of sodium or potassium borate, the coefficient of the ionic strength dependence used by Millero has the opposite sign from that calculated from the parameters of Felmy and Weare. As these ionic strength coefficients are small, and the molality of boric acid is low in all solutions considered here, the activity coefficient of undissociated boric acid is assumed to be unity in this analysis. The use of other values of the activity coefficient, through assumption of a dependence on ionic strength, only changes the values of the ion interaction parameters obtained in the analysis. The quality of fit of the data is independent of the choice of boric acid activity coefficients.

To represent the potentials reported here, it is necessary to extend the functional form of the ionic strength dependence of the second virial coefficients to include the $\beta^{(2)}$ parameter first used by Pitzer and Mayorga⁽⁴⁾ to treat the properties of 2-2 charge type electrolytes. Thus

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}h_1(I) + \beta_{MX}^{(2)}h_2(I) \quad (5)$$

$$\text{where } h_j(I) = (2/\alpha_j^2 I) [1 - (1 + \alpha_j \sqrt{I}) \exp(-\alpha_j \sqrt{I})] \quad (6)$$

with $j = 1$ or 2 . The activity coefficient third virial parameter C_{MX} is related to the corresponding parameter for the osmotic coefficient through

$$C_{MX} = C_{MX}^0 / 2 \sqrt{|z_{MX} z_X|} \quad (7)$$

The values of α to be used in Eq. (6) are specific to the type of electrolyte. For the mixed systems considered here, $\beta^{(2)} = 0$ in all cases except the calcium or magnesium borates. When $\beta^{(2)} = 0$, $\alpha_1 = 2.0$; this is the value of α usually used with simple electrolytes and mixtures.^(14,17) Pitzer and Mayorga⁽⁴⁾ used $\alpha_1 = 1.4$ ($\text{kg}\cdot\text{mol}^{-1}$)^{1/2} and $\alpha_2 = 12.0$ ($\text{kg}\cdot\text{mol}^{-1}$)^{1/2} for 2-2 electrolytes at 25°. Significantly larger values of $\alpha_1 = 2.0$ and $\alpha_2 = 50$ were used by Pitzer and Silvester in their correlation of data on 3-2 and higher charge type electrolytes.⁽¹⁸⁾ Thus, values of α_2 lower than 12 and α_1 in the range of 1.4 to 2.0 are appropriate for the present case. We have chosen $\alpha_1 = 1.4$ and $\alpha_2 = 6.0$ on the basis of a series of fits with different values of these parameters.

Only the pure electrolyte interaction parameters of Eq. (2) for calcium and magnesium borates were determined from the data in Tables I and II. Values of pure electrolyte parameters for calcium and magnesium chloride at 25° were taken from Pitzer and Mayorga.⁽¹⁷⁾ Temperature coefficients for these parameters were taken from Silvester and Pitzer.⁽¹⁹⁾ Interaction parameters and temperature coefficients for sodium

borate and sodium chloride, and the mixed-electrolyte parameters $\theta_{B,Cl}$ and $\psi_{Na,B,Cl}$, are from our earlier work.⁽¹⁾ The mixing parameters ${}^s\theta_{Mg,Na}$, ${}^s\theta_{Ca,Na}$, $\psi_{Mg,Na,Cl}$ and $\psi_{Ca,Na,Cl}$ have been given by Pitzer.⁽²⁰⁾ The higher order electrostatic effects for mixed unsymmetrical electrolytes have been included in these calculations. The other mixing parameters involving borate ion could not be determined unambiguously from the results reported here and have been set to zero. The interaction parameters $\beta^{(0)}$ and $\beta^{(1)}$ were assumed to vary linearly with the temperature difference ($T - 298.15$ K). The $\beta^{(2)}$ coefficients were given a quadratic temperature dependence of the form $(T - 303.15 \text{ K})^2$. Six adjustable parameters, included $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and their temperature coefficients, have been determined for $Mg(B(OH)_4)_2$ and $Ca(B(OH)_4)_2$; these values are listed in Table III. Fits of the data were not improved by including third virial coefficients C^ϕ for either system. Standard errors of fit were 0.65 mV for the magnesium system and 0.55 mV for the calcium system. The values of the interaction parameters are dependent on the assumed value of the boric acid activity coefficient. Thus the parameters of Table III should be used with the present assignment $\gamma_{HB} = 1$, as discussed above.

4. DISCUSSION

The use of the $\beta^{(2)}$ extended form to describe the properties of 2-1 charge type electrolytes near ambient temperature is unusual. Partial support for our use of this extended form comes from noting the unusually large negative values of $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ obtained for calcium and magnesium borates by Hershey *et al.*⁽²⁾ Their values of $\beta_{MgB}^{(1)} = -4.98$ and $\beta_{CaB}^{(1)} = -4.49$ are strikingly different from values for other 2-1 charge type electrolytes,⁽¹⁷⁾ including the qualitatively similar magnesium and calcium bicarbonates.⁽²¹⁾ Their values of $\beta^{(0)}$ for these salts are also negative. The second virial parameter B_{MX} represents an average two-body short range interaction between solute ions. A large negative value of B_{MX} indicates a significant attractive interaction. This attractive interaction may also be described with an explicit equilibrium constant for the ion pairing reaction. An approximate relation between the $\beta^{(2)}$ parameter and the ion pair equilibrium constant is⁽⁴⁾

$$K = -2\beta^{(2)} \quad (8)$$

In an alternative treatment of their results, Hershey *et al.* calculated ion pairing equilibrium constants for the formation of $CaB(OH)_4^\ddagger$ and $MgB(OH)_4^\ddagger$ and obtained values of 52 and 28, respectively, at 25°.

Table III. Ion Interaction Parameters for Magnesium and Calcium Borates

Parameter ^a	Mg(B(OH) ₄) ₂	Ca(B(OH) ₄) ₂
	$\beta^{(0)}$	
a	-0.6230	-0.4462
$10^3 b$	6.496	5.393
	$\beta^{(1)}$	
a	0.2515	-0.8680
$10^3 b$	-17.13	-18.20
	$\beta^{(2)}$	
a	-11.47	-15.88
$10^3 c$	-3.240	-2.858

$${}^a P_i = a_i + b_i(T-298.15) + c_i(T-303.15)^2$$

A similar treatment has been used by Felmy and Weare⁽¹⁶⁾ in modeling solubility data in aqueous borate solutions containing calcium and magnesium. Association constants at 25° of 31 and 22 for calcium and magnesium borates are obtained from Eq. (8) and the parameters of Table III. These values agree only qualitatively with those of Hershey *et al.* and Reardon.⁽²²⁾ This comparison is similar to the case of the bivalent metal sulfates. Ion pairing constants calculated at 25° from $\beta^{(2)}$ values⁽⁴⁾ are significantly lower than constants calculated from an explicit ion pairing treatment,⁽²³⁾ but trends in the values for different electrolytes are similar. This comparison demonstrates that the calculated values of K are strongly influenced by the treatment of activity coefficients in a given formalism.

The complications introduced due to formation of polynuclear borate anions at higher total boron concentrations have been discussed previously.^(1,24) The maximum total boron molality has been limited to 0.05 to minimize polyborate formation. Given this relatively low total boron concentration, the quantities of most direct practical application which may be calculated from the results reported here are the trace activity coefficients of calcium and magnesium borates in chloride media. For mixed (sodium + calcium) or (sodium + magnesium) chloride media the trace activity coefficients are given by

$$\ln \gamma_{MB_2}^H = 2f^\gamma + (2/3)m_{Cl}[B_{MCl} + (\Sigma mz)C_{MCl} + 2\theta_{B,Cl}]$$

Table IV. Trace Activity Coefficients of Calcium and Magnesium Borates in Mixed Chloride Media (m_{Mg} or $m_{Ca} = 0.05$)

I	5°	15°	25°	35°	45°	55°
$\gamma_{CaB_2}^H$ in (NaCl + CaCl ₂) media						
0.15	0.376	0.378	0.376	0.370	0.360	0.347
0.65	0.326	0.324	0.320	0.315	0.309	0.300
1.15	0.285	0.285	0.284	0.283	0.280	0.276
1.65	0.256	0.259	0.260	0.261	0.261	0.260
2.15	0.236	0.240	0.243	0.245	0.247	0.248
2.65	0.222	0.226	0.230	0.233	0.235	0.237
3.15	0.213	0.216	0.219	0.222	0.224	0.226
$\gamma_{MgB_2}^H$ in (NaCl + MgCl ₂) media						
0.15	0.421	0.425	0.423	0.417	0.405	0.390
0.65	0.351	0.349	0.345	0.339	0.331	0.322
1.15	0.307	0.307	0.306	0.303	0.299	0.294
1.65	0.279	0.280	0.281	0.281	0.281	0.279
2.15	0.260	0.263	0.265	0.266	0.267	0.267
2.65	0.247	0.250	0.253	0.255	0.256	0.257
3.15	0.240	0.242	0.244	0.245	0.246	0.247

$$\begin{aligned}
 &+ (4/3) \{ m_{Na} [B_{NaB} + (\sum m z) C_{NaB} + \theta_{M,Na} / 2] + m_M [B_{MB} \\
 &+ (\sum m z) C_{MB}] \} + m_{Na} m_{Cl} \{ 2B_{NaCl}' + [4C_{NaCl} + \psi_{M,Na,Cl} \\
 &+ 2\psi_{Na,Cl,B}] / 3 \} + m_M m_{Cl} \{ 2B_{MCl}' + [4C_{MCl} + 2\psi_{M,B,Cl}] / 3 \} \\
 &+ m_M m_{Na} [2\psi_{Na,M,B} / 3 + 2\theta_{Na,M}'] \quad (9)
 \end{aligned}$$

The limiting law function f^Y is

$$f^Y = -A_\phi [\sqrt{I} / (1 + b\sqrt{I}) + (2/b) \ln(1 + b\sqrt{I})] \quad (10)$$

where $b = 1.2$ (kg·mol⁻¹)^{1/2} and A_ϕ is the limiting slope for the osmotic coefficient taken from Bradley and Pitzer.⁽²⁵⁾ B' is the ionic strength derivative of the corresponding B ; noting that the B' quantities of Eqn.(9) apply to solutes for which $\beta^{(2)} = 0$,

$$B_{NX}' = (2\beta_{NX}^{(1)} / \alpha^2 I^2) [-1 + (1 + \alpha\sqrt{I} + \alpha^2 I / 2) \exp(-\alpha\sqrt{I})] \quad (11)$$

with $\alpha = 2.0$ (kg·mol⁻¹)^{1/2}.

While Eq. (9) is applicable to mixed media over the entire cation fraction range, many systems of interest will have relatively low cation fractions of calcium or magnesium. Trace activity coefficients of calcium or magnesium borates calculated from Eq. (9) are listed in Table IV for solutions with calcium or magnesium ion molality held at 0.05*m* and with sodium chloride from 0.5 to 3.0*m*. These concentrations correspond to the experimental conditions studied at 25° by Hershey *et al.*⁽²⁾ Trace activity coefficients at 25° listed in Table IV differ significantly at high ionic strengths from these calculated with the interaction parameters given by Hershey *et al.* These differences are due to the neglect of mixing terms involving borate ions in the work of Hershey *et al.* and the different values of the activity coefficient of undissociated boric acid. Values of the apparent ionization constant pK^* for boric acid may also be calculated in this medium using the two sets of interaction parameters. Differences in pK^* range up to about 0.04 units in each case. While these differences are relatively large, they are comparable with differences cited by Hershey *et al.* between their results and those of other workers, and indicates the uncertainty in quantities calculated from various fits of the available experimental results for these multicomponent systems. It should also be noted that these conditions (high Na^+ , low Ca^{2+} or Mg^{+2} concentrations) are significantly different from those studied experimentally in this work. Coupling of parameters and the inability to determine values of some mixing terms increases uncertainty in calculated quantities far from experimental conditions.

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CORRECTIONS TO THE PREVIOUS WORK

Our earlier work⁽¹⁾ includes errors which require correction. One coauthor, John Connole, was omitted from the author list on the title page, although his name appears on subsequent pages. In Table III, the factors for the parameters of the C^ϕ term should be 10^3 , 10^4 , and 10^6 for

a_i , b_i , and c_i . The bottom block in Table IV refers to KB in KCl media, not KCl in NaCl as shown. Copies of the work including these corrections are available from the authors.

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