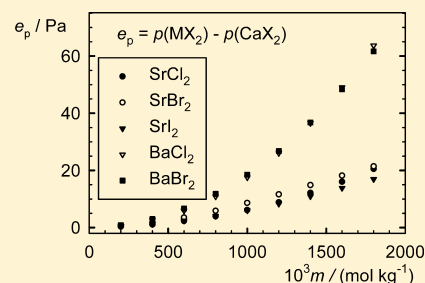


Traceable Activity and Osmotic Coefficients in Pure Aqueous Solutions of Alkaline Earth Metal Bromides and Iodides at 25 °C

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ABSTRACT: Two- and three-parameter Hückel equations have been determined for the mean activity coefficients of the electrolyte and for the osmotic coefficients of water in pure aqueous solutions of bromides and iodides of alkaline earth metals. The electrolyte parameters of the former equation are the ion-size parameter (B) and the hydration number parameter (b_1), and they can be used at least up to an ionic strength ($=I_m$) of 2.0 mol·kg⁻¹. The latter equation is an extended Hückel equation, and it contains a quadratic term in the molality when compared to the usual Hückel equation. The coefficient of this term is parameter b_2 , and this equation can be used in more concentrated solutions up to an I_m value of about 6 mol·kg⁻¹. All parameter values for the Hückel equations of MgBr₂ and MgI₂ were determined from the isopiestic data of Robinson and Stokes (Robinson, R. A.; Stokes, R. H. *Trans. Faraday Soc.* **1940**, 36, 733–734). All parameters for the other alkaline earth bromides and iodides were obtained from other referenced sources (Robinson, R. A. *Trans. Faraday Soc.* **1941**, 37, 82–84; **1942**, 38, 445–446). These salts were measured in those studies against KCl solutions. In these estimations, the previously determined parameters for the Hückel and extended Hückel equations were used for the KCl solutions, see (Partanen, J. I.; Covington, A. K. *J. Chem. Eng. Data* **2009**, 54, 208–219). The resulting parameter values were successfully tested with the cell potential, vapor pressure, and isopiestic data existing in the literature for solutions of these salts. Reliable activity and osmotic coefficients for alkaline earth bromide and iodide solutions can, therefore, be calculated by using the new Hückel equations, and these values are tabulated here at rounded molalities. The activity and osmotic coefficients obtained from these equations were compared to the values suggested by Robinson and Stokes (*Electrolyte Solutions*, 2nd ed.; Butterworths Scientific Publications: London, 1959, App. 8.10), to those calculated by using the Pitzer equations with the parameter values of Pitzer and Mayorga (Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, 77, 2300–2308), and to those calculated by using the extended Hückel equations of Goldberg and Nuttall (Goldberg, R. N.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1978**, 7, 263–310).



■ INTRODUCTION

In 1949, Stokes^{1,2} presented tables for activity and osmotic coefficients of 2:1 and 1:2 electrolytes in aqueous solutions at 25 °C, and these tables have been later widely accepted. The values of the activity quantities of MgBr₂ and MgI₂ solutions in these tables have been based on the isopiestic data measured by Robinson and Stokes³ and Stokes¹ against KCl and CaCl₂ reference solutions, respectively. For MgBr₂ solutions, values are given up to the saturated molality of 5.63 mol·kg⁻¹ and for MgI₂ solutions up to 5.0 mol·kg⁻¹. The values in the tables for CaBr₂ solutions were based on the isopiestic data of Robinson⁴ against KCl solutions and on those of Robinson and McCoach⁵ against CaCl₂ and H₂SO₄ solutions and values are given up to 8.0 mol·kg⁻¹. In ref 4, Robinson also determined the activity values for CaI₂, SrBr₂, SrI₂, and BaI₂ solutions and in ref 6 for BaBr₂ solutions. For all of these salts, values are given in the tables² up to 2.0 mol·kg⁻¹. Pitzer and Mayorga used these thermodynamic data² when they determined the parameters of the Pitzer equation for alkaline earth bromides and iodides in their well-known articles.^{7,8}

In the same way as in refs 9 to 12 for CaCl₂, MgCl₂, SrCl₂, and BaCl₂ solutions, it is reported now that reliable activity and osmotic coefficients for alkaline earth metal bromide and iodide

solutions (denoted here as MBr₂ and MI₂ solutions where M refers to alkaline earth metal) at 25 °C can be obtained up to an ionic strength ($=I_m$) of 2.0 mol·kg⁻¹ using the Hückel equation with two parameters (B and b_1) depending the electrolyte. B and b_1 for dilute MBr₂ and MI₂ solutions were now obtained from the same data as those used by Robinson and Stokes² for their tables. For MgBr₂ and MgI₂ solutions, however, only the data from ref 3 were used as well as for CaBr₂ solutions only the data from ref 4. The resulting parameters were tested with the data used in the parameter estimation and the BaBr₂ parameters also with the electrochemical data of Gelbach and Huppke.¹³

Additionally, it is shown here as in refs 9 to 12 for the alkaline earth metal chloride solutions that the Hückel equation can be extended using a quadratic term in the molality, and the resulting equation applies in the best cases up to I_m of 9 mol·kg⁻¹. The coefficient multiplying the quantity m^2 in this term is b_2 . The parameters in this extended Hückel equation of MBr₂ and MI₂ solutions were obtained and tested now in the following way (principally it is the same as that used in refs 9 to 12): The same

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Table 1. Parameter Values of the Equations of Goldberg and Nuttall³¹ (see eqs 7 and 8) for Alkaline Earth Metal Bromides and Iodides at 25 °C

	(B*) ^a	10 ³ C	10 ³ D	10 ³ E	10 ³ F	10 ³ G	10 ⁶ H	(m _{max} /m°) ^b
MgBr ₂	1.665	611.4	109.54	−7.902				5.61 ^c
MgI ₂	1.731	740.88	134.56	−9.497				5.01
CaBr ₂	1.794	324.4	208.63	−56.619	12.1565	−1.29303	48.494	7.660 ^c
CaI ₂	1.766	594.6	92.89					1.915
SrBr ₂	1.780	255.4	149.6	−14.62				2.123
SrI ₂	1.916	420.6	161.6	−16.23				1.970
BaBr ₂	1.513	342.8	28.70					2.321
BaI ₂	1.807	513.5	62.96					1.998

^aThe unit is (mol·kg^{−1})^{−1/2}. ^bThe maximum molality to which the equations apply (m° = 1 mol·kg^{−1}). ^cThe molality of the saturated solution.

Table 2. Parameter Values Recommended by Pitzer and Mayorga⁸ for the Pitzer Equations (see eqs 9 to 12) of Alkaline Earth Metal Bromides and Iodides at 25 °C

	β ⁰	β ¹	C ^φ	(m _{max} /m°) ^a
MgBr ₂	0.43268	1.75275	0.0031236	5
MgI ₂	0.49020	1.80413	0.0079337	5
CaBr ₂	0.38160	1.61325	−0.002572	2
CaI ₂	0.43793	1.8068	−0.000838	2
SrBr ₂	0.33113	1.7115	0.0012251	2
SrI ₂	0.40125	1.8600	0.0026570	2
BaBr ₂	0.31455	1.5698	−0.01596	2
BaI ₂	0.42188	1.6868	−0.01743	1.8

^aThe maximum molality to which the equations apply (m° = 1 mol·kg^{−1}).

Table 3. Results from the Parameter Estimation for the Hückel Equations (eqs 1 and 2) of Alkaline Earth Metal Bromides and Iodides at 25 °C by the Least-Squares Fitting Using Equation 13

	B/(mol·kg ^{−1}) ^{−1/2}	b ₁	s(b ₁) ^a	N ^b	(m _{max} /m°) ^c	(s ₀ /Pa) ^d	ref
MgBr ₂	1.59	0.726	0.005	13	0.8688	0.3	3
MgI ₂	1.69	0.847	0.008	11	0.7496	0.4	3
CaBr ₂	1.56	0.563	0.005	9	0.7250	0.2	4
CaI ₂	1.68	0.698	0.007	10	0.7628	0.3	4
SrBr ₂	1.54	0.470	0.006	12	0.9517	0.5	4
SrI ₂	1.63	0.646	0.005	10	0.9367	0.4	4
BaBr ₂	1.50	0.369	0.003	11 ^e	1.047	0.3	6
BaI ₂	1.64	0.630	0.004	9	0.9686	0.3	4

^aThe standard deviation of parameter b₁. ^bNumber of points included in the estimation. ^cMaximum molality of alkaline earth metal bromide or iodide solution included in the estimation (m° = 1 mol·kg^{−1}). ^dStandard error between the vapor pressures of water over the tested and reference solutions (see eq 14). ^eThe point (m_x/m° = 0.7140, m_y/m° = 0.4900) was omitted from the estimation as a probably erroneous point, see footnote a and the caption of Figure 1.

value as that for dilute solutions was used for parameter B. New values of b₁ and b₂ for less dilute solutions were obtained from the same isopiestic set as that used for dilute solutions but all experimental points were included in the estimation. The resulting parameter values were tested with the data used in the estimation and, additionally, the parameters for MgBr₂ and MgI₂ with the few points from the data of Stokes,¹ and the parameters for CaBr₂ with those from Robinson and McCoach.⁵ In these data, the reference salt was CaCl₂.

As in the previous studies, where the thermodynamic activity values in solutions of uniunivalent^{14–25} and biunivalent^{9–12} electrolytes were considered, the present tests were carried out with the raw data of real measurements. The method of

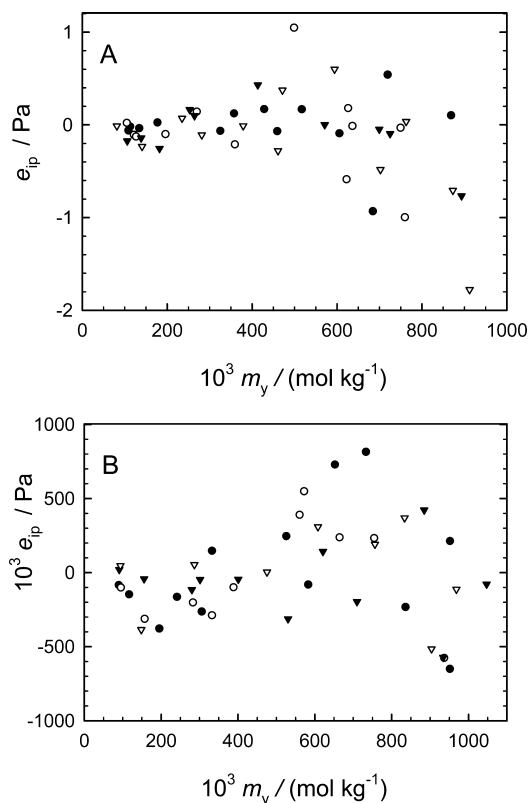


Figure 1. Difference, e_p in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the dilute isotonic KCl (x) and alkaline earth metal bromide or iodide (y) solutions for the data sets shown in Table 3. The vapor pressures have been calculated by eqs 3 and 4 using eq 2 with $B = 1.3$ (mol·kg^{−1})^{−1/2} and $b_1 = 0.011$ for KCl and with the parameter values shown in this table for MgBr₂ (symbol ●, graph A), MgI₂ (○, A), CaBr₂ (▼, A), CaI₂ (▽, A), SrBr₂ (●, B), SrI₂ (○, B), BaBr₂ (▼, B), and BaI₂ (▽, B). The error of the point ($m_x/m° = 0.7140$, $m_y/m° = 0.4900$) in the BaBr₂ set lays outside the scale of graph B; its value is 2.6 Pa.

evaluation has the advantage that the prediction error can be compared to the experimental error. In these comparisons, the Hückel equations proved to be very reliable. The mean activity coefficients and osmotic coefficients in the MBr₂ and MI₂ solutions were calculated using the resulting Hückel equations and tabulated here at rounded molalities. These recommended values were also compared to the literature values, and the resulting activity coefficient deviations between the new and literature values are plotted here as the cell-potential deviations for galvanic cells without a liquid junction (as in refs 9 to 12 and 14 to 25) and the

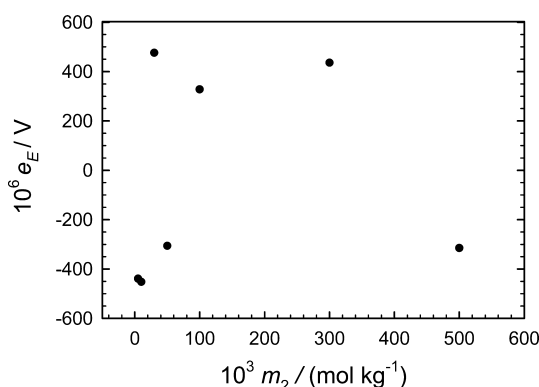


Figure 2. Plot of e_E (eq 18), the deviation between the observed and predicted cell potential difference (cpd) from the concentration cell data on cell 16 reported by Gelbach and Huppke¹³ ($m_1 = 0.003 \text{ mol}\cdot\text{kg}^{-1}$) as a function of molality m_2 . The predicted cpd was calculated by using eq 17 where eq 1 with $B = 1.50 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.369$ for the activity coefficients. The error of the point where $m = 1.000 \text{ mol}\cdot\text{kg}^{-1}$ is outside the scale of the figure, and its value is 3.25 mV.

osmotic coefficient deviations as the vapor pressure deviations (refs 9 to 12 and 15 to 25) as functions of the molality. In the same way as in refs 9 to 12 for MCl_2 solutions, the new thermodynamic activity values for MBr_2 and MI_2 solutions are traceable because all results of the parameter estimations and tests and all sources of data are given in detail here or in the previous studies.

THEORY

In the previous studies,^{15–25} it was observed that the following Hückel equations apply very well to the thermodynamic properties of aqueous solutions of many uniunivalent salts at least up to the molalities of $1 \text{ mol}\cdot\text{kg}^{-1}$

$$\ln \gamma = -\frac{\alpha |z_+ z_-| \sqrt{I_m}}{1 + B \sqrt{I_m}} + b_1(m/m^\circ) \quad (1)$$

$$\varphi = 1 - \frac{\alpha |z_+ z_-|}{B^3 I_m} \left[(1 + B \sqrt{I_m}) - 2 \ln(1 + B \sqrt{I_m}) - \frac{1}{1 + B \sqrt{I_m}} \right] + \frac{1}{2} b_1(m/m^\circ) \quad (2)$$

In refs 9 to 12, it was found that these equations apply also to alkaline earth chloride solutions at least up to I_m of $1.5 \text{ mol}\cdot\text{kg}^{-1}$.

Rowland and May have also in a recent paper²⁶ thoroughly tested the Hückel equations for solutions of single salts of the various charge types with thermodynamic, calorimetric, and density data at 25°C . In the present Hückel equations, m is the molality, I_m is the ionic strength, γ is the mean activity coefficient on the molality scale, ϕ is the osmotic coefficient of the solvent (label 1 refers to the solvent, water in this case), z_+ is the charge number of the cation and z_- that of the anion, α is Debye–Hückel parameter (its value at $t = 25^\circ\text{C}$ and at $p = 101.325 \text{ kPa}$ is $1.1744 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ (see Archer and Wang²⁷), m° is $1 \text{ mol}\cdot\text{kg}^{-1}$, and the parameters dependent on the electrolyte are B and b_1 . For a biunivalent electrolyte, $|z_+ z_-|$ is 2 and I_m is $3m$. The osmotic coefficient is defined now in the following way by using the activity of water (a_1)

$$\ln a_1 = -3mM_1\varphi \quad (3)$$

where M_1 is the molar mass of water ($= 0.018015 \text{ kg}\cdot\text{mol}^{-1}$). The water activity is associated with the vapor pressure of water over the solution (p_1) and that of pure water (p_1^*) by

$$\ln a_1 = \ln \left(\frac{p_1}{p_1^*} \right) + \frac{(B_1 - V_{m,1}^*(\text{liq}))(p_1 - p_1^*)}{RT} \quad (4)$$

where B_1 is the second virial coefficient of water vapor and $V_{m,1}^*(\text{liq})$ is the molar volume of liquid water at 25°C . According to Kell,²⁸ $p_1^* = 3168.6 \text{ Pa}$ and $V_{m,1}^*(\text{liq}) = 18.068 \text{ cm}^3\cdot\text{mol}^{-1}$. According to the eq 3 given in the paper of McCullough et al.,²⁹ the value of B_1 is $-1194 \text{ cm}^3\cdot\text{mol}^{-1}$. This value is also close to modern value calculated from the complicated equations of Harvey and Lemmon.³⁰ In the previous paper,^{9–12,15–25} the non-ideality correction of water vapor was omitted, and eq 4 was used without the latter term on the right-hand side in the calculation of vapor pressures. It is well-known that the influence of this correction in aqueous solutions at 25°C is usually very small and its highest value is obtained for the most concentrated solution. In all vapor pressure values tabulated below in the present study, the absolute nonideality correction is smaller than 1 Pa.

In more concentrated solutions, the following extended Hückel equations were used here as earlier^{9–12,15–25} for the activity and osmotic coefficients

$$\ln \gamma = -\frac{2\alpha \sqrt{I_m}}{1 + B \sqrt{I_m}} + b_1(m/m^\circ) + b_2(m/m^\circ)^2 \quad (5)$$

Table 4. Results from the Parameter Estimation for the Extended Hückel Equations (eqs 5 and 6) of Alkaline Earth Metal Bromides and Iodides at 25°C by the Least-Squares Fitting Using Equation 19

	$[B/(m^\circ)^{-1/2}]^a$	b_2	b_1	$s(b_1)^b$	N^c	$(m_{\text{max}}/m^\circ)^d$	$(s_0/\text{Pa})^e$	ref
MgBr_2	1.59	0.066	0.6844	0.0016	21 ^f	1.894	0.7	3
MgI_2	1.69	0.093	0.7977	0.0015	24	1.787	0.6	3
CaBr_2	1.56	0.0502	0.5375	0.0012	19	2.056	0.5	4
CaI_2	1.68	0.069	0.657	0.002	23	1.915	1.0	4
SrBr_2	1.54	0.065	0.4164	0.0013	24 ^g	2.123	0.6	4
SrI_2	1.63	0.0675	0.5959	0.0012	19	1.969	0.5	4
BaBr_2	1.50	0.021	0.3640	0.0007	19 ^h	2.321	0.4	6
BaI_2	1.64	0.035	0.598	0.004	17	1.998	1.4	4

^aTaken from Table 3 and $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^bThe standard deviation of parameter b_1 . ^cNumber of points included in the estimation. ^dThe maximum molality of alkaline earth metal bromide or iodide included in the estimation, see also footnote a. ^eStandard error between the vapor pressures of water over the tested and reference solutions (see eq 14). ^fThe point ($m_x/m^\circ = 2.307$, $m_y/m^\circ = 1.086$) was omitted from the estimation as a probably erroneous point, see footnote a and the caption of Figure 3. ^gThe point ($m_x/m^\circ = 3.431$, $m_y/m^\circ = 1.610$) was omitted from the estimation as a probably erroneous point, see footnote a and the caption of Figure 3. ^hThe point ($m_x/m^\circ = 0.7140$, $m_y/m^\circ = 0.4900$) was omitted from the estimation as a probably erroneous point, see footnote a.

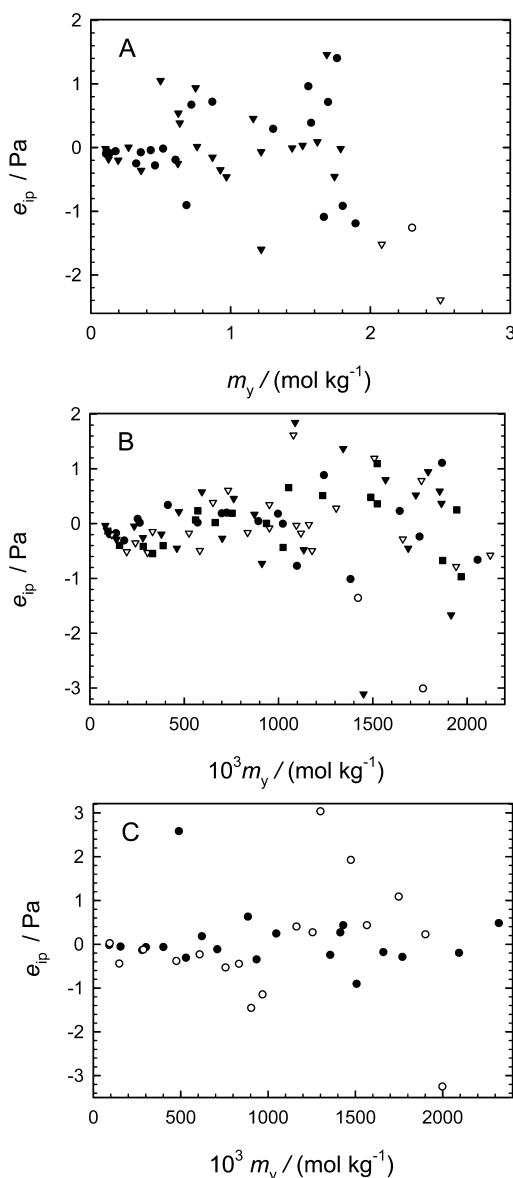


Figure 3. Difference, e_p in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic solutions of KCl or CaCl_2 (x) and alkaline earth metal bromide or iodide (y) for the data sets shown in Table 4 and for the sets of Stokes¹ for MgBr_2 and MgI_2 solutions and for that of Robinson and McCoach⁵ for CaBr_2 solutions. The vapor pressures have been calculated by eqs 3 and 4 using eq 5 with $B = 1.3 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$ for KCl solutions, with $B = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3486$, and $b_2 = 0.0667$ for CaCl_2 solutions, and with the parameter values shown in this table for alkaline earth metal bromide and iodide solutions. Symbols: ●, MgBr_2 (ref 3, graph A), CaBr_2 (4, B), BaBr_2 (6, C); ○, MgBr_2 (1, A), CaBr_2 (5, B), BaI_2 (4, C); ▼, MgI_2 (3, A), CaI_2 (4, B); ▽, MgI_2 (1, A), SrBr_2 (4, B); ■, SrI_2 (4, B). The errors of the point ($m_x/m^\circ = 2.3070$, $m_y/m^\circ = 1.0860$) in the MgBr_2 set³ (graph A), of that (2.7470, 2.2330) in the MgI_2 set¹ (A), and of that (3.4310, 1.6100) in the SrBr_2 set⁴ (B) are -7.7 , 3.7 , and -14.5 Pa, respectively, and are thus outside the scales of the graphs. The errors of the points ($m_x/m^\circ = 2.3090$, $m_y/m^\circ = 2.1400$), (2.3210, 2.1520), (2.764, 2.5540), (2.8010, 2.5840), and (3.0260, 2.7910) in the set of Robinson and McCoach⁵ are also outside the scale of graph B; their values are -9.1 , -8.9 , -19.1 , -21.5 , and -27.3 Pa, respectively.

Table 5. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Magnesium Bromide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.732	0.910	3167.0
0.02	0.670(0.671)	0.891	3165.6
0.05	0.589(0.591)	0.872(0.873)	3161.2
0.1	0.539(0.541)	0.872(0.874)	3153.7
0.2	0.509(0.512)	0.897(0.899)	3138.1
0.3	0.508(0.511)	0.931(0.933)	3121.1
0.4	0.520(0.523)	0.969(0.970)	3103.0(0.1 ^c)
0.5	0.539(0.542)	1.008	3083.6
0.6	0.565	1.049(1.046)	3062.8(−0.4 ^c)
0.7	0.595(0.593)	1.091(1.084)	3040.7(−0.8 ^c)
0.8	0.631(0.625, −0.35 ^b)	1.134(1.122)	3017.2(−1.5 ^c)
0.9	0.671	1.178	2992
1.0	0.717	1.222	2966
1.2	0.824	1.314	2910
1.4	0.958	1.409	2849
1.6	1.123	1.507	2782
1.8	1.327	1.608	2710
2.0	1.580	1.713	2634
2.5	2.515	1.989	2423

^aThe activity values were calculated using the extended Hückel equation with $B = 1.59 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.6844$, and $b_2 = 0.066$ (see text). ^bGalvanic cell deviation in mV calculated using the equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.59 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.726$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

$$\begin{aligned} \phi = 1 - \frac{2\alpha}{B^3 I_m} \left[(1 + B\sqrt{I_m}) - 2 \ln(1 + B\sqrt{I_m}) - \frac{1}{1 + B\sqrt{I_m}} \right] \\ + \frac{1}{2} b_1 (m/m^\circ) + \frac{2}{3} b_2 (m/m^\circ)^2 \end{aligned} \quad (6)$$

Goldberg and Nuttall³¹ suggested the following extended Hückel equations for the activity and osmotic coefficients of MBr_2 and MI_2 solutions at 25 °C

$$\begin{aligned} \ln \gamma = -\frac{2A_m \sqrt{I_m}}{1 + B^* \sqrt{I_m}} + C(m/m^\circ) + D(m/m^\circ)^2 + E(m/m^\circ)^3 \\ + F(m/m^\circ)^4 + G(m/m^\circ)^5 + H(m/m^\circ)^6 \end{aligned} \quad (7)$$

$$\begin{aligned} \phi = 1 - \frac{2A_m}{(B^*)^3 I_m} \left[(1 + B^* \sqrt{I_m}) - 2 \ln(1 + B^* \sqrt{I_m}) - \frac{1}{1 + B^* \sqrt{I_m}} \right] \\ + \frac{1}{2} C(m/m^\circ) + \frac{2}{3} D(m/m^\circ)^2 + \frac{3}{4} E(m/m^\circ)^3 + \frac{4}{5} F(m/m^\circ)^4 \\ + \frac{5}{6} G(m/m^\circ)^5 + \frac{6}{7} H(m/m^\circ)^6 \end{aligned} \quad (8)$$

Table 6. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Magnesium Iodide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.736	0.912	3167.0
0.02	0.676(0.677)	0.895	3165.5
0.05	0.601(0.602)	0.880(0.881)	3161.1
0.1	0.556(0.558)	0.885(0.887)	3153.5
0.2	0.535(0.539, 0.24 ^b)	0.918(0.921)	3137.4(0.1 ^c)
0.3	0.544(0.548, 0.25 ^b)	0.960(0.962)	3119.7(0.1 ^c)
0.4	0.566(0.569)	1.005	3100.6
0.5	0.598	1.052(1.049)	3079.9(−0.3 ^c)
0.6	0.636(0.634)	1.101(1.094)	3057.6(−0.7 ^c)
0.7	0.682(0.674, −0.43 ^b)	1.151(1.138)	3033.8(−1.5 ^c)
0.8	0.735	1.203	3008
0.9	0.796	1.255	2981
1.0	0.865	1.309	2953
1.2	1.032	1.420	2890
1.4	1.247	1.535	2822
1.6	1.522	1.656	2747
1.8	1.877	1.781	2665
2.0	2.335	1.910	2578
2.5	4.190	2.255	2337

^aThe activity values were calculated using the extended Hückel equation with $B = 1.69 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.7977$, and $b_2 = 0.093$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.69 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.847$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

where $A_m = 1.17625 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ (i.e., an older value for parameter α) and the parameter values of these equations for MBr_2 and MI_2 solutions are shown in Table 1. For activity and osmotic coefficients of a 2:1 electrolyte, the Pitzer equations^{7,8} have the forms

$$\ln \gamma = 2f^\gamma + \frac{4}{3}B^\gamma(m/m^\circ) + 2^{3/2}C^\varphi(m/m^\circ)^2 \quad (9)$$

$$\begin{aligned} \varphi = 1 - \frac{2\alpha}{3} \frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{4}{3}(\beta^0 + \beta^1 e^{-\alpha_p \sqrt{I_m}})(m/m^\circ) \\ + \frac{2^{5/2}}{3} C^\varphi(m/m^\circ)^2 \end{aligned} \quad (10)$$

where

$$f^\gamma = -\frac{\alpha}{3} \left[\frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b} \ln(1 + b\sqrt{I_m}) \right] \quad (11)$$

Table 7. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Calcium Bromide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.730	0.908	3167.0
0.02	0.667	0.888	3165.6
0.05	0.583	0.867	3161.2
0.1	0.528(0.529)	0.862(0.863)	3153.9
0.2	0.490(0.491)	0.879(0.880)	3138.7
0.3	0.481(0.482)	0.905(0.906)	3122.5
0.4	0.483(0.485)	0.934	3105.4
0.5	0.493	0.965(0.963)	3087.1(−0.2 ^c)
0.6	0.507(0.506)	0.998(0.993)	3067.9(−0.4 ^c)
0.7	0.526(0.522, −0.26 ^b)	1.031(1.023)	3047.6(−0.9 ^c)
0.8	0.547(0.541, −0.45 ^b)	1.065(1.053)	3026.3(−1.5 ^c)
0.9	0.572	1.099	3004
1.0	0.600	1.134	2980
1.2	0.665	1.207	2930
1.4	0.744	1.281	2876
1.6	0.838	1.358	2818
1.8	0.951	1.438	2756
2.0	1.086	1.520	2689

^aThe activity values were calculated using the extended Hückel equation with $B = 1.56 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.5375$, and $b_2 = 0.0502$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.56 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.563$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

$$B^\gamma = 2\beta^0 + \frac{2\beta^1}{\alpha_p^2 I_m} \left[1 - e^{-\alpha_p(I_m)^{1/2}} \left(1 + \alpha_p \sqrt{I_m} - \frac{1}{2} \alpha_p^2 I_m \right) \right] \quad (12)$$

The most often used general parameter values in these equations are $b = 1.2 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $\alpha_p = 2.0 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$. In eqs 9, 10, and 12, β^0 , β^1 , and C^φ are the parameters that are dependent on the electrolyte. Pitzer and Mayorga⁸ have determined the values shown in Table 2 for MBr_2 and MI_2 solutions at 25 °C.

RESULTS AND DISCUSSION

Determination of Hückel Parameters for Dilute Solutions.

The parameter values suggested in ref 15 for the Hückel equation of KCl solutions (i.e., those of $B = 1.3 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.011$) apply well up to a molality of 1.5 $\text{mol}\cdot\text{kg}^{-1}$. They were now used in the determination of the Hückel parameters for dilute MBr_2 and MI_2 solutions from the isopiestic sets mentioned above and based on the equation

Table 8. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Calcium Iodide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.735	0.911	3167.0
0.02	0.674(0.675)	0.893(0.894)	3165.5
0.05	0.596(0.597)	0.876(0.877)	3161.1
0.1	0.547(0.549)	0.877(0.879)	3153.6
0.2	0.519(0.522, 0.21 ^b)	0.903(0.905)	3137.9(0.1 ^c)
0.3	0.519(0.522, 0.23 ^b)	0.936(0.938)	3120.9(0.1 ^c)
0.4	0.532(0.534)	0.973(0.974)	3102.7
0.5	0.552(0.553)	1.012(1.011)	3083.2(−0.1 ^c)
0.6	0.577	1.052(1.048)	3062.5(−0.4 ^c)
0.7	0.608(0.605, −0.20 ^b)	1.093(1.085)	3040.4(−0.9 ^c)
0.8	0.644(0.637, −0.44 ^b)	1.135(1.122)	3017.1(−1.7 ^c)
0.9	0.684	1.178	2992
1.0	0.730	1.221	2966
1.2	0.838	1.311	2911
1.4	0.972	1.404	2850
1.6	1.137	1.501	2783
1.8	1.341	1.601	2712
2.0	1.592	1.704	2636

^aThe activity values were calculated using the extended Hückel equation with $B = 1.68 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.657$, and $b_2 = 0.069$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.68 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.698$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

$$\begin{aligned} f_1 &= \ln a_{1,x} + 3M_1m_y \\ &\quad - \frac{2\alpha M_1}{B_y^3} \left[(1 + B_y\sqrt{I_{m,y}}) - 2 \ln(1 + B_y\sqrt{I_{m,y}}) - \frac{1}{1 + B_y\sqrt{I_{m,y}}} \right] \\ &= f_0 - 3b_{1,y}M_1(m_y^2/2m^0) \\ &= f_0 + k_1m_y^2 \end{aligned} \quad (13)$$

where $k_1 = -3b_{1,y}M_1/(2m^0)$. In this estimation, KCl was the reference electrolyte (x) because the activities in solutions of this salt are known. Salt MBr₂ or MI₂ was the tested electrolyte (y). Some details of the estimations are described, for example, in ref 20 (see eq 13 and the text associated with this equation in that study). The results of these estimations are shown in Table 3. The standard error s_0 in this table is defined by the equation

$$s_0 = \sqrt{\sum_{i=1}^N (p_{x,i} - p_{y,i})^2 / (N - P)} \quad (14)$$

where N is the number of the points and P the number of the estimated parameters (now 2). The new Hückel equations suggested in Table 3 for MBr₂ and MI₂ solutions were tested

Table 9. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Strontium Bromide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.728(0.729)	0.907(0.908)	3167.0
0.02	0.664(0.665)	0.886(0.887)	3165.6
0.05	0.578(0.579)	0.863(0.864)	3161.2
0.1	0.519(0.522)	0.855(0.857)	3154.0
0.2	0.475(0.479, 0.31 ^b)	0.865(0.869)	3139.2(0.1 ^c)
0.3	0.461(0.466, 0.39 ^b)	0.885(0.889)	3123.5(0.2 ^c)
0.4	0.458(0.463, 0.43 ^b)	0.909(0.913)	3107.0(0.2 ^c)
0.5	0.462(0.467, 0.41 ^b)	0.935(0.938)	3089.7(0.2 ^c)
0.6	0.470(0.474, 0.34 ^b)	0.962(0.963)	3071.4
0.7	0.482(0.485, 0.22 ^b)	0.991(0.988)	3052.2(−0.3 ^c)
0.8	0.497	1.020(1.013)	3032.1(−0.8 ^c)
0.9	0.514(0.512)	1.050(1.039)	3011.1(−1.6 ^c)
1.0	0.534	1.081	2989
1.2	0.581	1.145	2942
1.4	0.639	1.213	2891
1.6	0.709	1.284	2836
1.8	0.793	1.358	2777
2.0	0.893	1.436	2714

^aThe activity values were calculated using the extended Hückel equation with $B = 1.54 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.4164$, and $b_2 = 0.065$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.54 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.470$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

by predicting the vapor pressures of water over the isotonic solutions of the alkaline earth halide and potassium chloride. The vapor pressures of both solutions in every point were calculated using eqs 2, 3, and 4 with the given activity parameters. In eq 4, the nonideality correction can be omitted when small pressure differences are considered because practically the same value is obtained for this quantity for both solutions. Below, this is also true for all other vapor pressure difference quantities. The results are shown in the two graphs of Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{\text{ip}} = p_x - p_y \quad (15)$$

and presented as a function of molality m_y . The largest absolute error in these tests below the molality of $1.5 \text{ mol}\cdot\text{kg}^{-1}$ is less than 0.5 Pa and the errors for all sets form an almost random pattern. Thus, the results from these dilute MBr₂ and MI₂ solutions support well the suggested parameter values.

The estimated Hückel parameters for BaBr₂ solutions in Table 3 can also be tested with cell potential difference (=cpd) data. Gelbach and Huppke¹³ measured several types of barium amalgam and silver–silver bromide cells and their main results

Table 10. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Strontium Iodide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.733	0.910	3167.0
0.02	0.671	0.891(0.892)	3165.6
0.05	0.590(0.591)	0.872(0.873)	3161.1
0.1	0.538(0.541)	0.870(0.873)	3153.8(0.1 ^c)
0.2	0.505(0.509, 0.28 ^b)	0.892(0.895)	3138.2(0.1 ^c)
0.3	0.501(0.506, 0.35 ^b)	0.922(0.926)	3121.7(0.2 ^c)
0.4	0.509(0.514, 0.36 ^b)	0.956(0.959)	3103.9(0.3 ^c)
0.5	0.525(0.529, 0.32 ^b)	0.991(0.992)	3085.0(0.2 ^c)
0.6	0.545(0.548, 0.22 ^b)	1.028(1.027)	3064.9(0.1 ^c)
0.7	0.570(0.571)	1.065(1.061)	3043.6(−0.5 ^c)
0.8	0.599(0.597)	1.104(1.095)	3021.1(−1.1 ^c)
0.9	0.632(0.626, −0.37 ^b)	1.144(1.130)	2997.4(−2.0 ^c)
1.0	0.670	1.184	2972
1.2	0.758	1.267	2919
1.4	0.867	1.354	2861
1.6	1.000	1.444	2797
1.8	1.163	1.537	2729
2.0	1.363	1.633	2656

^aThe activity values were calculated using the extended Hückel equation with $B = 1.63 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.5959$, and $b_2 = 0.0675$ (see text). ^bGalvanic cell deviation in mV calculated using equation

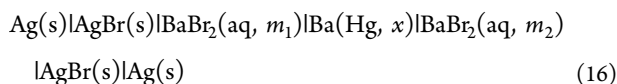
$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.63 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.646$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

were collected by Goldberg and Nuttall³¹ to the results of the following concentration cell without transference



where $\text{Ba(Hg, } x)$ refers to the barium metal in the amalgam with a mole fraction of x . The value of 0.000424 was used for x . In the resulting set, the molality of reference solution 1 ($=m_1$) was at a constant value of $0.003 \text{ mol}\cdot\text{kg}^{-1}$ and several molalities (m_2) of the tested solutions were measured against this molality. The cpd of this cell is given by

$$E = -\frac{3RT}{2F} \ln(m_2/m_1) - \frac{3RT}{2F} \ln(\gamma_2/\gamma_1) \quad (17)$$

From the data given in the original paper,¹³ eight cpd values from (0.005 to 1.000) $\text{mol}\cdot\text{kg}^{-1}$ can be obtained for cell 16, and these values are given by Goldberg and Nuttall (on page 281 in ref 31). These data were predicted by means of the suggested Hückel equation for BaBr_2 , and the results are shown as an error plot in Figure 2. In this plot, the cpd errors were calculated by the equation

$$e_{\text{E}} = E(\text{observed}) - E(\text{predicted}) \quad (18)$$

Table 11. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Barium Bromide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.727	0.906	3167.1
0.02	0.661	0.885	3165.6
0.05	0.573	0.859	3161.3
0.1	0.512	0.849	3154.1
0.2	0.464	0.854	3139.5
0.3	0.446(0.445)	0.870	3124.3
0.4	0.438	0.889(0.888)	3108.4(−0.1 ^c)
0.5	0.437(0.436)	0.909(0.907)	3091.8(−0.2 ^c)
0.6	0.440(0.438)	0.931(0.927)	3074.6(−0.3 ^c)
0.7	0.446(0.443, −0.26 ^b)	0.952(0.947)	3056.7(−0.6 ^c)
0.8	0.454(0.450, −0.36 ^b)	0.975(0.968)	3038.1(−0.9 ^c)
0.9	0.463(0.458, −0.48 ^b)	0.997(0.988)	3018.8(−1.3 ^c)
1.0	0.474	1.020	2999
1.2	0.501	1.066	2957
1.4	0.532	1.113	2913
1.6	0.569	1.161	2866
1.8	0.610	1.210	2817
2.0	0.658	1.260	2766
2.5	0.804	1.389	2627

^aThe activity values were calculated using the extended Hückel equation with $B = 1.50 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3640$, and $b_2 = 0.021$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.5 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.369$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

and are presented as a function of molality m_2 . These data support well the tested activity coefficient equation for BaBr_2 up to I_m of $1.5 \text{ mol}\cdot\text{kg}^{-1}$.

Determination of Parameters for the Extended Hückel Equation for More Concentrated Solutions. The parameter values suggested in ref 15 for the extended Hückel equation of KCl [i.e., those of $B = 1.3 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$] seem to apply well up to the saturated solution (i.e., up to $4.8 \text{ mol}\cdot\text{kg}^{-1}$). These values were used in the equation

$$\begin{aligned} f_2 = \ln a_{1,x} + 3M_1m_y - \frac{2\alpha M_1}{B_y^3} \left[(1 + B_y\sqrt{I_{m,y}}) \right. \\ \left. - 2 \ln(1 + B_y\sqrt{I_{m,y}}) - \frac{1}{1 + B_y\sqrt{I_{m,y}}} \right] + \frac{2M_1b_{2,y}m_y^3}{(m^\circ)^2} \\ = f_0 - 3b_{1,y}M_1(m_y^2/2m^\circ) \\ = f_0 + k_2m_y^2 \end{aligned} \quad (19)$$

where $k_2 = -3b_{1,y}M_1/2m^\circ$ when the new values for parameters b_1 and b_2 for MBr_2 and MI_2 solutions were determined.

Table 12. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Barium Iodide Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/Pa
0.01	0.733	0.910	3167.0
0.02	0.671(0.672)	0.891(0.892)	3165.6
0.05	0.591(0.592)	0.873	3161.1
0.1	0.539(0.541)	0.871(0.872)	3153.7
0.2	0.506(0.509)	0.892(0.894)	3138.2
0.3	0.502(0.505, 0.25 ^b)	0.922(0.924)	3121.7(0.1 ^c)
0.4	0.509(0.513, 0.28 ^b)	0.954(0.956)	3104.0(0.2 ^c)
0.5	0.523(0.527, 0.28 ^b)	0.987(0.989)	3085.3(0.2 ^c)
0.6	0.542(0.545, 0.25 ^b)	1.022(1.023)	3065.5(0.1 ^c)
0.7	0.564(0.567, 0.20 ^b)	1.057	3044.6
0.8	0.590(0.592)	1.092(1.090)	3022.7(−0.3 ^c)
0.9	0.620	1.128(1.124)	2999.7(−0.7 ^c)
1.0	0.653(0.651)	1.165(1.157)	2975.6(−1.2 ^c)
1.2	0.729	1.238	2924
1.4	0.820	1.314	2869
1.6	0.929	1.391	2810
1.8	1.057	1.470	2747
2.0	1.208	1.550	2680

^aThe activity values were calculated using the extended Hückel equation with $B = 1.64 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.598$, and $b_2 = 0.035$ (see text). ^bGalvanic cell deviation in mV calculated using equation

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{eq 5})}{\gamma(\text{eq 1})}$$

where the $\gamma(\text{eq 1})$ values were calculated using the Hückel equation with $B = 1.64 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.63$, and the $\gamma(\text{eq 5})$ values using the recommended parameter values (see footnote a). ^cVapor pressure deviation in Pa calculated using equation

$$e_{\text{p,VPW}} = p(\phi \text{ from eq 6}) - p(\phi \text{ from eq 2})$$

where the $\phi(\text{eq 2})$ values were calculated using the recommended Hückel equation and the $\phi(\text{eq 6})$ values using the extended Hückel equation (see footnotes a and b).

Some details of these estimations are described in ref 20, see eq 25 in that study. The present regression analysis leads to the results that are presented in Table 4. In these determinations, the values of parameter B_γ were taken from Table 3. The goodness of the estimated parameters was first evaluated by predicting the vapor pressures for all points used in the determination and comparing the results. For each isotonic point, the vapor pressures were calculated using eqs 3, 4, and 6 with the suggested parameter values. The three graphs of Figure 3 show the results as such error plots which correspond to those in Figure 1. In these error plots for the points used in the estimation, the absolute errors are less than 1.2 Pa and no clear trends can be seen in the plots. Therefore, the data support well the suggested parameters.

The MgBr_2 and MgI_2 parameters in Table 4 were additionally tested with the experimental isopiestic data of Stokes¹ for solutions of these salts and CaCl_2 . These results up to an ionic strength of about $9 \text{ mol}\cdot\text{kg}^{-1}$ for CaCl_2 (this is the upper applicability limit of the extended Hückel equation for this reference salt⁹) are given in graph A of Figure 3 (see also the caption of this figure). These data support quite well the new three-parameter Hückel equation for these two magnesium salts

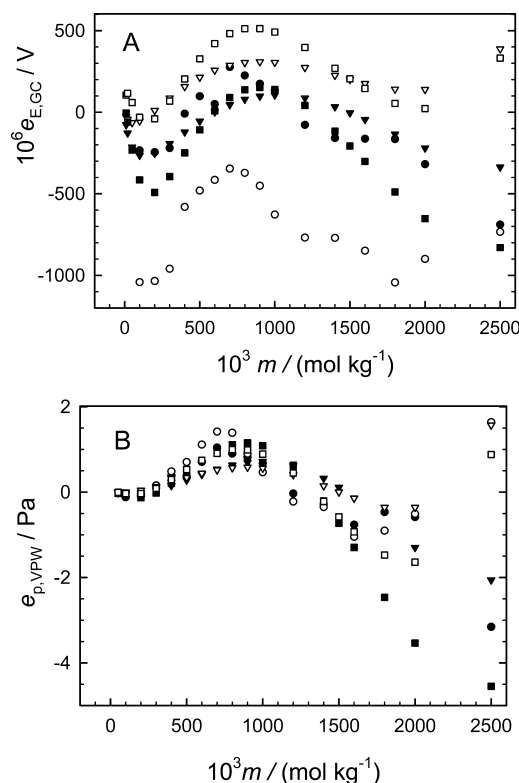


Figure 4. Deviation, expressed as galvanic cell error $e_{\text{E,GC}}$ in eq 20, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{\text{p,VPW}}$ in eq 21, between the literature osmotic coefficients and those recommended in this study (eq 6, B) for MgBr_2 and MgI_2 solutions as functions of molality m (see Tables 5 and 6). Symbols: ●, MgBr_2 , Robinson and Stokes;² ○, MgI_2 , Robinson and Stokes;² ▼, MgBr_2 , Goldberg and Nuttall;³¹ ▽, MgI_2 , Goldberg and Nuttall;³¹ ■, MgBr_2 , Pitzer and Mayorga;⁸ □, MgI_2 , Pitzer and Mayorga.⁸

up to I_m of $7.5 \text{ mol}\cdot\text{kg}^{-1}$. For CaBr_2 solutions, the extended Hückel equation can be tested with the seven isopiestic points of Robinson and McCoach⁵ against CaCl_2 solutions where $I_m(\text{CaCl}_2)$ is less than $9 \text{ mol}\cdot\text{kg}^{-1}$. These results are shown in graph B of Figure 3 (see also the caption of this figure). These results show that the new extended Hückel equation for CaBr_2 solutions applies only up to I_m of $6.0 \text{ mol}\cdot\text{kg}^{-1}$.

Recommended Activity and Osmotic Coefficients at 25 °C. Because of the experimental evidence indicated in the tests of the present study (see Figures 1 to 3), the new Hückel equations for dilute solutions and the new extended Hückel equations for more concentrated solutions are very reliable. New tables for the activity and osmotic coefficients of alkaline earth metal bromides and iodides at 25 °C have been calculated on the basis of these equations. For MgBr_2 the new values are given in Table 5, for MgI_2 in Table 6, for CaBr_2 in Table 7, for CaI_2 in Table 8, for SrBr_2 in Table 9, for SrI_2 in Table 10, for BaBr_2 in Table 11, and for BaI_2 in Table 12. Also the vapor pressures of water are included in these tables, and these values were calculated using the full eq 4.

The values of all activity quantities have been calculated in the tables using the parameters suggested for the extended Hückel equations. In dilute solutions (i.e., when I_m is less than about $2 \text{ mol}\cdot\text{kg}^{-1}$), the values obtained with the suggested Hückel equations are given in parentheses when they differ from those presented in the tables. The absolute difference

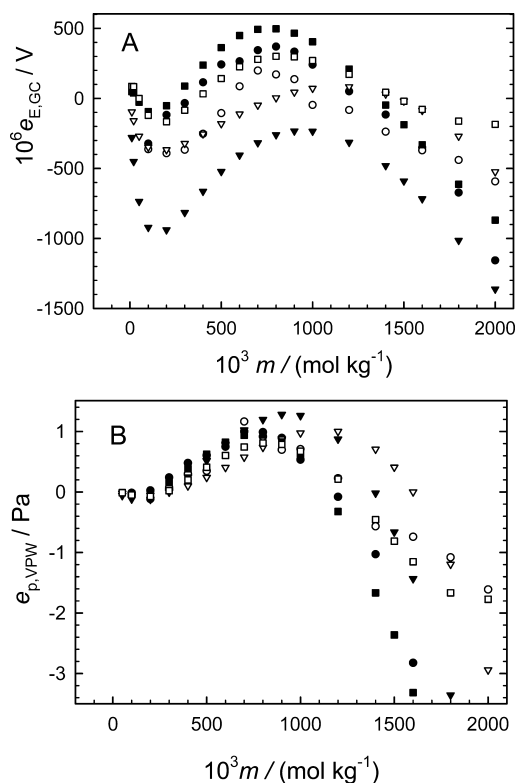


Figure 5. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 20, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 21, between the literature osmotic coefficients and those recommended in this study (eq 6, B) for CaBr_2 and CaI_2 solutions as functions of molality m (see Tables 7 and 8). Symbols: ●, CaBr_2 , Robinson and Stokes;² ○, CaI_2 , Robinson and Stokes;² ▼, CaBr_2 , Goldberg and Nuttall;³¹ ▽, CaI_2 , Goldberg and Nuttall;³¹ ■, CaBr_2 , Pitzer and Mayorga;⁸ □, CaI_2 , Pitzer and Mayorga.⁸ The errors of the CaBr_2 points ($m = 1.800 \text{ mol}\cdot\text{kg}^{-1}$, $\phi = 1.455$) and (2.000 , $\phi = 1.547$) from Robinson and Stokes, that of the CaBr_2 point (2.000 , 1.5340) from Goldberg and Nuttall, and those of the CaBr_2 points (1.800 , 1.457) and (2.000 , 1.543) from Pitzer and Mayorga lay outside the scale of graph B; these errors are -4.6 , -7.8 , -5.8 , -5.1 , and -6.8 Pa, respectively.

between these two values is always quite small [less than 0.7 mV for galvanic cell deviations for γ (the definition is given in the tables) and less than 1.5 Pa for vapor pressure deviations for ϕ].

Comparison of the New Activity and Osmotic Coefficients to the Values Presented in the Literature.

The values of the thermodynamic activity quantities in Tables 5 to 12 for 25°C were compared to the corresponding values given by Robinson and Stokes,² Goldberg and Nuttall,³¹ and Pitzer and Mayorga.⁸ The results from these comparisons are given in Figure 4 (MgBr_2 and MgI_2), Figure 5 (CaBr_2 and CaI_2), Figure 6 (SrBr_2 and SrI_2), and Figure 7 (BaBr_2 and BaI_2). Graph A in these figures gives the results for the activity coefficients, and graph B gives those for the osmotic coefficients. The comparison was carried out as, for example, in ref 9 for CaCl_2 solutions using cell potential deviations ($e_{E,GC}$) and vapor pressure deviations ($e_{p,VPW}$) defined by the following equations, respectively,

$$e_{E,GC} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{literature})}{\gamma(\text{recd})} \quad (20)$$

$$e_{p,VPW} = p(\text{literature}) - p(\text{recd}) \quad (21)$$

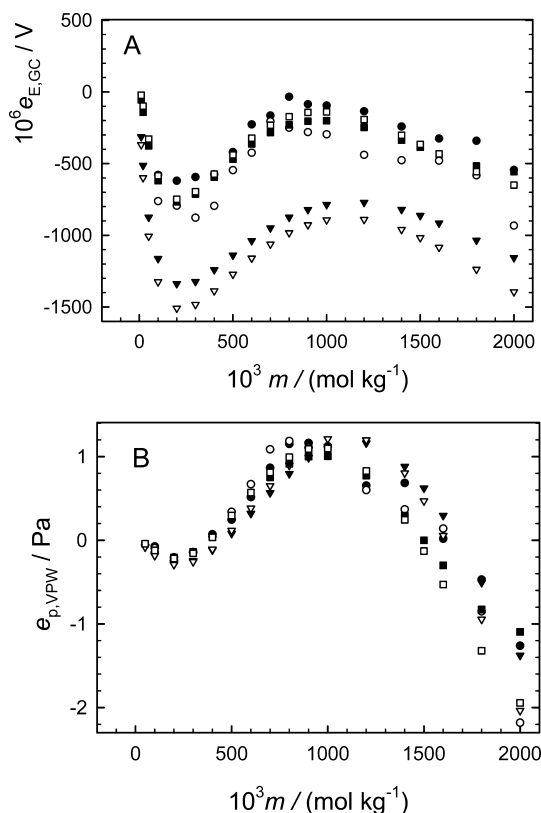


Figure 6. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 20, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 21, between the literature osmotic coefficients and those recommended in this study (eq 6, B) for SrBr_2 and SrI_2 solutions as functions of molality m (see Tables 9 and 10). Symbols: ●, SrBr_2 , Robinson and Stokes;² ○, SrI_2 , Robinson and Stokes;² ▼, SrBr_2 , Goldberg and Nuttall;³¹ ▽, SrI_2 , Goldberg and Nuttall;³¹ ■, SrBr_2 , Pitzer and Mayorga;⁸ □, SrI_2 , Pitzer and Mayorga.⁸

where GC refers to the galvanic cell without a liquid junction and VPW to the vapor pressure of water. Vapor pressures were calculated for eq 21 from the osmotic coefficients using eqs 3 and 4. For the recommended values, the values obtained from eqs 5 and 6 in Tables 5 to 12 were used.

In general, the literature activity and osmotic coefficients considered in Figures 4 to 7 are in a quite good agreement with the values recommended up to I_m of $6.0 \text{ mol}\cdot\text{kg}^{-1}$. Only the osmotic coefficients in graph B for CaBr_2 and BaI_2 solutions at ionic strengths from 5.5 to $6.0 \text{ mol}\cdot\text{kg}^{-1}$ differ significantly from those recommended in Tables 7 and 12, respectively (see also the captions of the Figures 5 and 7). In the CaBr_2 case, the recommended osmotic coefficients seem to be more reliable because the new extended Hückel equation for these salt solutions explains very well the only data available for the parameter estimation (i.e., those from Robinson,⁴ see Table 4 and Figure 3B). In the BaI_2 case, on the other hand, the recommended osmotic coefficients are not as reliable as those for the other salts in Table 4, and new experimental data for BaI_2 solutions are probably required to obtain more reliable activity and osmotic coefficients than those presented in Table 12. Also the activity coefficients from the equations of Goldberg and Nuttall for SrBr_2 and SrI_2 solutions in Figure 6A seem to be quite different from the other values considered in the graph.

According to Tables 5 to 12, the activity and osmotic coefficients of alkaline earth metal chlorides (see also refs 9 to 12)

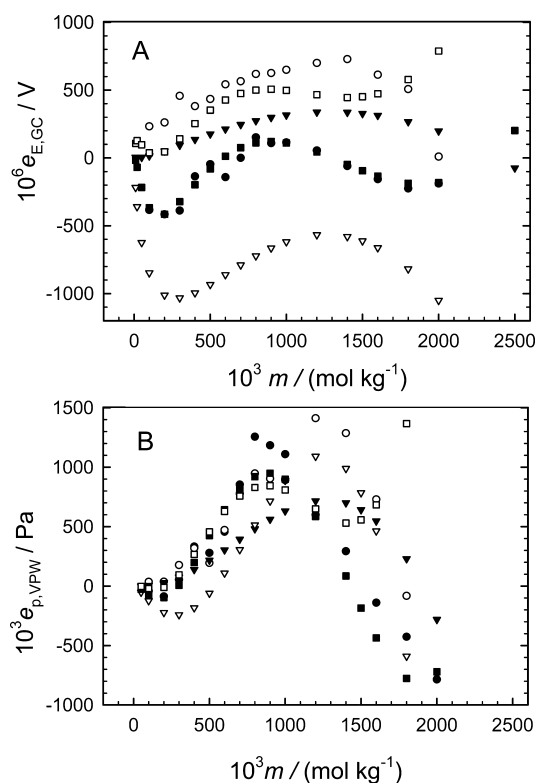


Figure 7. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 20, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 21, between the literature osmotic coefficients and those recommended in this study (eq 6, B) for $BaBr_2$ and BaI_2 solutions as functions of molality m (see Tables 11 and 12). Symbols: ●, $BaBr_2$, Robinson and Stokes;² ○, BaI_2 , Robinson and Stokes;² ▼, $BaBr_2$, Goldberg and Nuttall;³¹ ▽, BaI_2 , Goldberg and Nuttall;³¹ ■, $BaBr_2$, Pitzer and Mayorga;⁸ □, BaI_2 , Pitzer and Mayorga.⁸ The error of the BaI_2 point ($m = 2.000 \text{ mol} \cdot \text{kg}^{-1}$, $\phi = 1.599$) from Robinson and Stokes, those of the $BaBr_2$ point ($2.500, 1.397$) and BaI_2 point ($2.000, 1.558$) from Goldberg and Nuttall, and those of the $BaBr_2$ point ($2.500, 1.382$) and BaI_2 point ($2.000, 1.540$) from Pitzer and Mayorga lay outside the scale of graph B; these errors are -14.2 , -2.6 , -2.3 , 2.6 , and 2.8 Pa, respectively.

are smaller than those of the corresponding bromides and the latter values are moreover smaller than those of the corresponding iodides at the same molality. The vapor pressures in solutions of these alkaline earth halides were also studied in the following way: The difference defined by

$$e_p = p(MX_2) - p(CaX_2) \quad (22)$$

where X is Cl^- , Br^- or I^- and M refers to the alkaline earth metal are calculated using the new extended Hückel equations and presented as a function of the molality. The plots are shown in Figure 8. The vapor pressure of each alkaline earth metal halide solutions is thus compared to that of the calcium halide solution at the same molality. The recommended osmotic coefficients were taken for $CaCl_2$, $MgCl_2$, $SrCl_2$, and $BaCl_2$ solutions from refs 9 10 11, and 12, respectively. The deviations for $BaCl_2$ solutions are given only up to about $1.8 \text{ mol} \cdot \text{kg}^{-1}$ because of the low solubility of this salt, see ref 12. The difference plots are very interesting: The vapor pressures of magnesium halides are always lower than those of the calcium halides and the vapor pressures of strontium and barium halides are higher than those of calcium halides at the same molality. The solutions of barium halides have

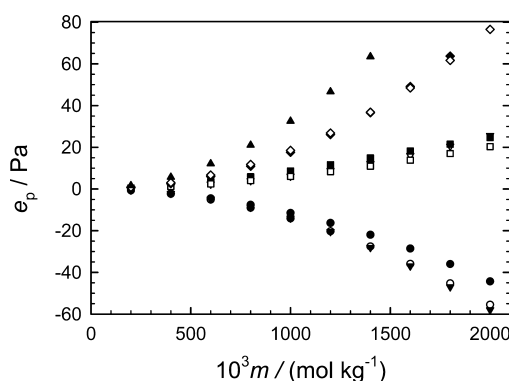


Figure 8. Difference, expressed as the vapor pressure deviation e_p in eq 22, between the osmotic coefficient in the magnesium, strontium, and barium halide solution and that of the calcium halide solution as a function of molality m . The osmotic coefficients have been calculated using the extended Hückel equation (eq 6) with the recommended parameter values. The $CaCl_2$, $MgCl_2$, $SrCl_2$, and $BaCl_2$ results were taken from refs 9 10 11, and 12, respectively. Symbols: ●, $MgCl_2$; ○, $MgBr_2$; ▼, MgI_2 ; ▽, $SrCl_2$; ■, $SrBr_2$; □, SrI_2 ; ◆, $BaCl_2$; ◇, $BaBr_2$; ▲, BaI_2 . The differences for BaI_2 solutions at molalities of 1.6, 1.8, and $2.0 \text{ mol} \cdot \text{kg}^{-1}$ lay outside the scale of figure. Their values are 83, 105, and 130 Pa, respectively.

the highest vapor pressures of these salts. Water molecules in aqueous barium halide solutions are, therefore, less thermodynamically stabilized than those in aqueous strontium, calcium, or magnesium halide solutions. Up to a molality of $2.0 \text{ mol} \cdot \text{kg}^{-1}$ used in the figure, the vapor pressure differences for the magnesium and strontium halides are quite close to each other and this is also true for barium chloride and bromide solutions. For BaI_2 solutions, the e_p values differ more from those of $BaCl_2$ and $BaBr_2$ solutions. It is possible, however, that the latter result is not scientifically important and occurs because the osmotic coefficients in Table 12 are not as reliable as the values for the other salts. At a molality of $1.8 \text{ mol} \cdot \text{kg}^{-1}$, the smallest difference between the e_p values is obtained for pair $SrCl_2$ and $SrBr_2$ and it is absolutely as small as 0.9 Pa. The points for these salts are not discernible in this figure as also are not the points for pair $BaCl_2$ and $BaBr_2$. The largest difference between these quantities at this molality is obtained for pair $MgCl_2$ and MgI_2 (omitting the uncertain BaI_2 results) and it is absolutely 11 Pa. Therefore, the calculation of the difference e_p in eq 22 quite efficiently eliminates the influence of the anion on the vapor pressure and gives almost only the influence of Mg^{2+} , Sr^{2+} , or Ba^{2+} ions when compared to that of Ca^{2+} ions.

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