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Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Alkali Metal Bromide Solutions at 25 °C

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The Hückel equation used in this study to correlate the experimental activities of dilute alkali metal bromide solutions up to a molality of about 1.5 $\mathrm{mol \cdot kg^{-1}}$ contains two parameters that are dependent on the electrolyte: B [that is related closely to the ion-size parameter (a^*) in the Debye−Hückel equation] and b_1 (this parameter is the coefficient of the linear term with respect to the molality, and this coefficient is related to hydration numbers of the ions of the electrolyte). In more concentrated solutions up to a molality of about 5 $\mathrm{mol \cdot kg^{-1}}$, an extended Hückel equation was used, and it contains additionally a quadratic term with respect to the molality, and the coefficient of this term is parameter b_2. All parameter values for the Hückel equations of LiBr, KBr, RbBr, and CsBr were determined from the isopiestic data measured by Robinson for solutions of these salts against KCl solutions (*J. Am. Chem Soc.* **1935**, *57*, 1161−1165), and all parameters for NaBr were determined from the isopiestic data measured by Robinson for KCl and NaBr solutions (*Trans. Faraday Soc.* **1939**, *35*, 1217−1220). In these estimations, the Hückel parameters determined recently for KCl solutions (*J. Chem. Eng. Data* **2009**, *54*, 208−219) were used. The resulting parameter values were tested with the cell potential, vapor pressure, and isopiestic data existing in the literature for alkali metal bromide solutions. Most of these data can be reproduced within experimental error by means of the extended Hückel equations up to a molality of about 5.0 $\mathrm{mol \cdot kg^{-1}}$. Reliable activity and osmotic coefficients for alkali metal bromide solutions can, therefore, be calculated by using the new Hückel equations, and they have been 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), to those calculated by using the Pitzer equations with the parameter values of Pitzer and Mayorga (*J. Phys. Chem.* **1973**, *77*, 2300−2308), and to those calculated by using the extended Hückel equations of Hamer and Wu (*J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1099).

Introduction

In 1949, Robinson and Stokes[1] presented tables for activity and osmotic coefficients of electrolytes in aqueous solution at 25 °C, and later these tables have been widely accepted and used, e.g., in the chemical literature. The suggested activity and osmotic coefficients in Robinson and Stokes' tables[1] are also recommended with some revisions in the well-known book[2] of these authors. The values of the activity quantities of LiBr solutions in these tables have been based on the isopiestic data measured by Robinson[3] for KCl and LiBr solutions and by Robinson and McCoach[4] for $CaCl_2$ and LiBr solutions. The isopiestic data of Robinson[3] were also used in the determination of the activity quantities in these tables for the other alkali metal bromides in addition to those of Robinson[5] for NaBr and KBr solutions against KCl solutions and to the reported osmotic coefficients of Robinson[6] for RbBr and CsBr solutions. The tables of Robinson and Stokes give activity and osmotic coefficients from a molality of 0.1 $\mathrm{mol \cdot kg^{-1}}$ up to 6.0 $\mathrm{mol \cdot kg^{-1}}$ for LiBr, up to 4.0 $\mathrm{mol \cdot kg^{-1}}$ for NaBr, up to 5.5 $\mathrm{mol \cdot kg^{-1}}$ for KBr, and up to 5.0 $\mathrm{mol \cdot kg^{-1}}$ for RbBr and CsBr solutions. The importance of the activities of ref 2 is also reflected by the fact that Pitzer and Mayorga mainly used these values when they determined the parameters of the Pitzer equation[7] for various electrolytes in their famous article[8] on thermodynamics of single electrolytes.

In the present study, it is shown that reliable thermodynamic activity values for alkali metal bromide solutions can also be obtained by such a simple equation as the Hückel equation up to a molality of about 1.5 $\mathrm{mol \cdot kg^{-1}}$. The form of the Hückel equation used in this investigation (see below and, e.g., ref 9) contains two parameters dependent on the electrolyte: B [that is closely related to the ion-size parameter (a^*) in the Debye−Hückel equation] and b_1 (this parameter is the coefficient of the linear term with respect to the molality, and this coefficient is related to the hydration numbers of the ions of the electrolyte). The values of B and b_1 for LiBr, KBr, RbBr, and CsBr in dilute solutions were determined here from the isopiestic data measured by Robinson,[3] and for NaBr these parameters were determined from the more recent data of Robinson.[5] Usually, the points where the alkali metal bromide molality is less than 1.5 $\mathrm{mol \cdot kg^{-1}}$ could be included in the determination. The Hückel parameters needed in this estimation for KCl were taken from the results of a previous study[10] where NaCl and KCl solutions were considered. The resulting parameter values were tested with the data used in the parameter estimation, with the isopiestic data of Robinson for NaBr[3] and KBr[5] solutions, with the cell potential differences (= cpd) measured

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by Harned[11] (for LiBr, NaBr, and KBr solutions), by Harned and Douglas[12] (for NaBr and KBr solutions), and by Harned and Crawford[13] (for NaBr solutions) on concentration cells containing an alkali metal amalgam electrode and two Ag−AgBr electrodes, and with the cpd's measured by Mac William and Gordon[14] for KBr solutions on concentration cells with transference containing two Ag−AgBr electrodes.

Additionally, it is shown here that very reliable activity values for alkali metal bromide solutions can be obtained up to the molality of about 5 mol·kg^{-1} (for LiBr only up to 3.0 mol·kg^{-1}) by extending the Hückel equation with a quadratic term with respect to the molality. The coefficient multiplying the quantity m^2 in this term is b_2. The same value for parameter B was used in this extended Hückel equation for each bromide salt as that for dilute solutions. New values of parameters b_1 and b_2 in this extended Hückel equation were then determined from the same isopiestic set as that used above in the parameter estimation for dilute solutions, but all points in this set were now included in the determination for each salt. The resulting parameter values were tested with all isopiestic points mentioned above and, additionally, with the isopiestic data of Rard and Archer,[15] Covington et al.,[16] and Kirgintsev and Luk'yanov[17] for concentrated NaBr solutions against NaCl solutions. Covington et al.[16] also measured KBr and KCl solutions isopiestically. The osmotic coefficients reported by Penciner and Yizhak,[18] Jakli and van Hook,[19] and Makarov et al.[20] for NaBr solutions and those reported by Robinson[6] for RbBr and CsBr solutions were also used in the tests as well as the vapor pressure data of Pearce et al.[21] for concentrated NaBr solutions. In addition to the data considered here, Holmes and Mesmer[22] have measured isopiestic molalities against NaCl solutions for many solutions of LiBr, NaBr, KBr, and CsBr at elevated temperatures from (110 to 225) °C and Christov[23] for several solutions of NaBr and KBr at 50 °C.

All tests of this study were performed on the raw experimental results of appropriate measurements to test whether these could be predicted with the Hückel equations. This method has the advantage that the prediction error can be compared to the experimental error. The present parameter estimation methods and tests are slightly different from those used by Hamer and Wu[24] or Staples and Nuttall (see, for example, the $CaCl_2$ paper[25]) in their evaluation of the thermodynamic data for pure electrolyte solutions. In the Stables and Nuttall approach, in principle (see the flow diagram in Figure 3 of ref 25), values of the osmotic coefficients ϕ and activity coefficients γ (or $\gamma/\gamma_{\text{reference}}$) are first obtained from the various experimental methods. These values are then weighted, and the best values of the parameters in a correlating equation are obtained by the method of nonlinear least-squares. The choice of the correlating equation used (Pitzer equation, extended Debye−Hückel equation, or some other equation) is arbitrary. Finally, after the parameters in the appropriate correlating equation(s) have been calculated, one can examine the errors between the observed and measured values: e_γ and e_ϕ. It is shown below that the Hückel equations and the equations of Hamer and Wu[24] give for NaBr, KBr, and CsBr solutions almost the same activity and osmotic coefficients at least up to a molality of 3 mol·kg^{-1}, and the results from the two approaches do not, therefore, differ much from each other in these cases. This study shows below that the activity quantities for LiBr and RbBr solutions are more difficult, and the agreement for these salts is not as good. The choice of the weights for the literature data sets, however, seems to be problematic in the approach of Stables and Nuttall, and we also have probably a better knowledge of the experimental error of different techniques than of the activity or osmotic coefficient error.

It is shown below that the Hückel equations are very reliable. In most cases, the measured results can be reproduced within experimental error. The activity coefficients of the electrolyte and the osmotic coefficients and the vapor pressures of water were calculated using the new Hückel equations at rounded molalities of these bromide salts, and these values are tabulated as recommended values. These activity and osmotic coefficients were compared to those of the previous investigations (some of which, in addition to Robinson and Stokes' values,[2] have achieved wide acceptance). Activity coefficient deviations in this comparison are presented as the cell-potential deviations for galvanic cells without a liquid junction (in the same way as in refs 9, 10 and 26), and the osmotic coefficient deviations are presented as vapor pressure deviations (as in refs 10, 27, and 28).

Theory

In previous studies, it was found that the following Hückel equations apply very well to the thermodynamic properties of NaCl,[10] KCl,[10] LiCl,[27] RbCl,[28] and CsCl[28] solutions at least up to the molalities of about 1.0 mol·kg^{-1}

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

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m^\circ) \tag{2}$$

In these equations, m is the molality; γ is the mean activity coefficient on the molality scale; ϕ is the osmotic coefficient of the solvent (symbol 1, water in this case); α is the Debye−Hückel parameter [its value at 25 °C is 1.17444 (mol·kg^{-1})$^{-1/2}$, see Archer and Wang[29]]; m° is 1 mol·kg^{-1}; and the parameters being dependent on the electrolyte are B and b_1. The osmotic coefficient is related to the activity of the water (a_1) in pure solutions of a uniunivalent electrolyte by the following thermodynamic identity

$$\ln a_1 = -2mM_1\phi \tag{3}$$

where M_1 is the molar mass of water (= 0.018015 kg·mol^{-1}) and where the activity of water is related to the vapor pressure of water over the solution (p_1) and to the vapor pressure of pure solvent at the temperature under consideration (p_1^*) by the equation

$$a_1 = \frac{p_1}{p_1^*} \tag{4}$$

This equation is not an exact relation but is an excellent approximation because, under studied conditions, differences between the fugacity and vapor pressure are very small. For water at 25 °C, $p_1^* = 3.1686$ kPa (i.e., 23.766 mmHg; see Kell[30]).

In more concentrated solutions, the following extended Hückel equations were used here as earlier[10,27,28] for the activity and osmotic coefficients

Table 1. Parameter Values of the Equations of Hamer and Wu[24] (see Equations 7 and 8) for Alkali Metal Bromides at 25 °C

	$(B^*)^a$	$10^3\beta$	10^3C	10^6D	10^6E	10^6F	10^9G	$(m_{\max}/m°)^b$
LiBr	1.60	85.164	18.335	−2574.2	241.4	−11.612	204.02	20
NaBr	1.49	35.230	7.1023	−323.48	−36.943	2.6380		9
KBr	1.35	3.9749	3.945	−299.51				5.5
RbBr	1.1343	−0.89	2.211	−132.1				5
CsBr	1.05	−26.208	8.75	−715.11				5

[a] The unit is $(\mathrm{mol\cdot kg^{-1}})^{-1/2}$. [b] The maximum molality to which the equations apply ($m° = 1\ \mathrm{mol\cdot kg^{-1}}$).

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

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1+B\sqrt{m}) - 2\ln(1+B\sqrt{m}) - \frac{1}{1+B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m°) + \frac{2}{3}b_2(m/m°)^2 \qquad (6)$$

Hamer and Wu[24] suggested the following extended Hückel equations for the activity and osmotic coefficients of alkali metal bromide solutions, and these equations apply near the saturated solution of these electrolytes

$$\log(\gamma) = -\frac{A\sqrt{m}}{1+B^*\sqrt{m}} + \beta(m/m°) + C(m/m°)^2 + D(m/m°)^3 + E(m/m°)^4 + F(m/m°)^5 + G(m/m°)^6 \qquad (7)$$

$$\phi = 1 - \ln(10)\left\{\frac{A}{(B^*)^3 m}\left[(1+B^*\sqrt{m}) - 2\ln(1+B^*\sqrt{m}) - \frac{1}{1+B^*\sqrt{m}}\right] - \frac{1}{2}\beta(m/m°) - \frac{2}{3}C(m/m°)^2 - \frac{3}{4}D(m/m°)^3 - \frac{4}{5}E(m/m°)^4 - \frac{5}{6}F(m/m°)^5 - \frac{6}{7}G(m/m°)^6\right\} \qquad (8)$$

where the Debye−Hückel parameter A has a value of 0.5108 $(\mathrm{mol\cdot kg^{-1}})^{-1/2}$ [$= \alpha/\ln(10)$]. The parameter values of these equations for alkali metal bromides are shown in Table 1.

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[7,8] has the form

$$\ln\gamma = f^{\gamma} + B^{\gamma}(m/m°) + (3/2)C^{\phi}(m/m°)^2 \qquad (9)$$

where

$$f^{\gamma} = -\frac{\alpha}{3}\left[\frac{\sqrt{m}}{1+1.2\sqrt{m/m°}} + \frac{2\sqrt{m°}}{1.2}\ln(1+1.2\sqrt{m/m°})\right] \qquad (10)$$

$$B^{\gamma} = 2\beta^0 + \frac{\beta^1 m°}{2m}\left[1 - \mathrm{e}^{-2\sqrt{m/m°}}\left(1 + 2\sqrt{m/m°} - 2\frac{m}{m°}\right)\right] \qquad (11)$$

In eqs 9 and 11, β^0, β^1, and C^{ϕ} are the parameters being dependent on the electrolyte. Pitzer and Mayorga[8] have determined the values shown in Table 2 for these parameters for alkali metal bromides. For osmotic coefficients of water in solutions of a uniunivalent electrolyte, the Pitzer equation has the form

$$\phi = 1 - \frac{\alpha}{3}\frac{\sqrt{m}}{1+1.2\sqrt{m/m°}} + (\beta^0 + \beta^1\mathrm{e}^{-2\sqrt{m/m°}})(m/m°) + C^{\phi}(m/m°)^2 \qquad (12)$$

Table 2. Parameter Values Recommended by Pitzer and Mayorga[8] for the Pitzer Equations (See Equations 9 to 12) of Alkali Metal Bromides at 25 °C

	β^0	β^1	C^{ϕ}	$(m_{\max}/m°)^a$
LiBr	0.1748	0.2547	0.0053	2.5
NaBr	0.0973	0.2791	0.00116	4
KBr	0.0569	0.2212	−0.00180	5.5
RbBr	0.0396	0.1530	−0.00144	5
CsBr	0.0279	0.0139	0.00004	5

[a] The maximum molality to which the equations apply ($m° = 1\ \mathrm{mol\cdot kg^{-1}}$).

Results and Discussion

Determination of Parameters B and b_1 for Dilute Alkali Metal Bromide Solutions and Tests of the Resulting Values. The parameter values suggested in ref 10 for the Hückel equation of KCl [i.e., those of $B = 1.3\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.011$] seem to apply well up to a molality of about 1.5 $\mathrm{mol\cdot kg^{-1}}$. These values together with equation

$$f_1 = \ln a_{1,\mathrm{x}} + 2M_1 m_{\mathrm{y}} - \frac{2\alpha M_1}{B_{\mathrm{y}}^3}\left[(1+B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}) - 2\ln(1+B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}) - \frac{1}{1+B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}}\right] = f_0 - b_{1,\mathrm{y}}M_1(m_{\mathrm{y}}^2/m°) = f_0 + k_1 m_{\mathrm{y}}^2 \qquad (13)$$

where $k_1 = -b_{1,\mathrm{y}}M_1/m°$ were used in the present study to estimate the Hückel parameters for dilute alkali metal bromide solutions. In these determinations, KCl is the reference electrolyte (x) because the activities in its solutions are known. The activity of water in the KCl solutions can be calculated from the isopiestic molality of the KCl solution (m_{x}) using eqs 2 and 3. Alkali metal bromide is the tested electrolyte (y), and the molality of its isotonic solution with the KCl solution is thus regarded as the response variable (m_{y}). In isopiestic equilibrium, the condition that $a_{1,\mathrm{x}} = a_{1,\mathrm{y}}$ is valid, and eq 13 results from this condition (see ref 10). When parameter B_{y} has been fixed, eq 13 represents an equation of the straight line f_1 versus m_{y}^2. The slope of the straight line is k_1, and parameter $b_{1,\mathrm{y}}$ can be calculated from this slope. The straight line should go through the origin, and therefore, parameter B_{y} must be determined so that the value of intercept f_0 is zero. The results of these estimations are shown in Table 3. The standard error s_0 in this table is defined by the equation

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

where N is the number of the points and P is the number of the estimated parameters (now 2). For NaBr and KBr solutions, in this table are shown the results from both the isopiestic sets of Robinson (see refs 3 and 5), and the parameter values from these sets agree quite well with each other. The parameter values from ref 5 are recommended here for NaBr solutions; however, for KBr solutions the parameter values from ref 3 seem to be slightly more reliable, and they are now recommended (see below). The new Hückel equations suggested in Table 3 for alkali metal bromide solutions can first be tested by predicting the vapor pressures of water over the isotonic alkali metal bromide and potassium chloride solutions considered in this

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

	B					s_0	
	$(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$	b_1	$s(b_1)$[a]	N[b]	$(m_{\max}/m°)$[c]	(Pa)[d]	ref
LiBr	1.3	0.2909	0.0011	20	1.316	0.15	3
LiBr	1.6[e,f]	0.245[g,f]		17	0.9969	0.22	3
NaBr[h]	1.45	0.1131[f]	0.0011	15	1.282	0.13	5
NaBr	1.45	0.1120	0.0009	14	1.370	0.12	3
KBr	1.35	0.0223	0.0004	8	1.496	0.05	5
KBr	1.35	0.0185[f]	0.0011	11	1.545	0.15	3
RbBr	1.19	−0.0019	0.0013	8	1.419	0.13	3
CsBr	0.94	−0.0117	0.0015	6	1.658	0.18	3

[a] The standard deviation of parameter b_1. [b] Number of points included in the estimation. [c] Maximum molality of alkali metal bromide solution included in the estimation ($m° = 1$ mol·kg^{-1}). [d] Standard error between the vapor pressures of water over the tested and reference solutions (see eq 14). [e] Based on the B value of LiCl[27] and on the analogy between the B values for sodium and potassium chlorides[10] and bromides. [f] Recommended value. [g] Optimized value based on the square error sum of eq 14. [h] In this set, the point ($m_x/m° = 1.337$, $m_y/m° = 1.238$) was used instead of the point ($m_x/m° = 1.1337$, $m_y/m° = 1.238$) given in ref 5.

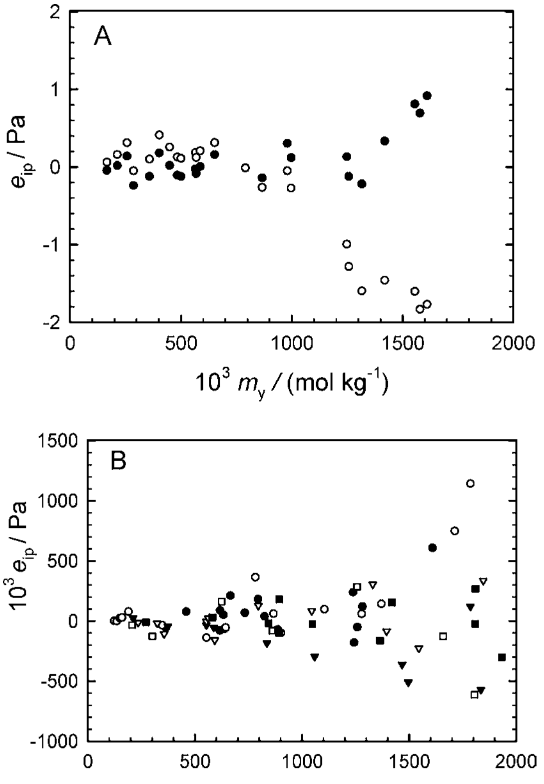

Figure 1. Difference, e_{ip} in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the dilute isotonic KCl (x) and alkali metal bromide (y) solutions for the data sets shown in 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 LiBr (graph A) and with the recommended parameter values for the other alkali metal bromides (graph B). Symbols: ●, LiBr with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2909$ (A), NaBr from ref 5 (B); ○, LiBr with $B = 1.6$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.245$ (A), NaBr from ref 3 (B); ▼, KBr from ref 5 (B); ▽, KBr from ref 3 (B); ■, RbBr (B); □, CsBr (B).

table. The vapor pressures of both solutions in every point were calculated using eqs 2, 3, and 4 with the recommended activity parameters. The results are shown in Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{ip} = p_x - p_y \tag{15}$$

and presented as a function of the molality m_y. The results for LiBr solutions are shown in graph A of this figure, and the results for the other bromide solutions are shown in graph B. The largest absolute error in these tests below the molality of 1.5 mol·kg^{-1} is less than 0.5 Pa (= 0.004 mmHg), and the errors form for all sets an almost random pattern. Thus, the results from these dilute alkali metal bromide solutions support well the suggested parameter values.

When comparing the new value of parameter B (closely related to the ion-size parameter) for LiBr [i.e., that of $B_{\text{LiBr}} = 1.3$ (mol·kg^{-1})$^{-1/2}$] to the value presented in ref 27 for LiCl [1.5 (mol·kg^{-1})$^{-1/2}$] and the new B values for NaBr and KBr [i.e., those of 1.45 and 1.35 (mol·kg^{-1})$^{-1/2}$, respectively] to the corresponding values for NaCl [1.4 (mol·kg^{-1})$^{-1/2}$] and KCl [1.3 (mol·kg^{-1})$^{-1/2}$] in ref 10, it is observed that the LiBr value is not in line with the other values. A more reasonable value would be $B_{\text{LiBr}} = 1.6$ (mol·kg^{-1})$^{-1/2}$. An optimized value of parameter b_1 was also determined for this B by using the square sum presented in eq 14, and the results of this estimation are shown in Table 3. A smaller number of points could be included in this determination than in the fitting with eq 13. The error plots for both B values of LiBr are shown in graph A of Figure 1, and below the results for the extended Hückel equations of LiBr will reveal that the value of $B = 1.6$ (mol·kg^{-1})$^{-1/2}$ is slightly better than that of 1.3 (mol·kg^{-1})$^{-1/2}$. Therefore, also for dilute solutions, this value is now recommended.

Table 4. Data Sets Measured on Alkali Metal Amalgam Cells of Type 16 and Considered in This Study

symbol	M	$(m_1/m°)$[a]	N[b]	$(m_{2,\max}/m°)$[a,c]	ref
Har29Li	Li	0.1	9	4	11
Har29Na	Na	0.1	9	4	11
HaDo26Na	Na	0.1[d]	9	3.021	12
HaCr37Na	Na	0.1	11	4	13
Har29K	K	0.1	11	4	11
HaDo26K	K	0.1[d]	7	2.512	12

[a] $m° = 1$ mol·kg^{-1}. [b] Number of points. [c] The maximum molality m_2 measured. [d] Molality m_1 varied from point to point but was always slightly higher than this value.

The estimated Hückel parameters for alkali metal bromides shown in Table 3 can then be tested with cpd data. Harned,[11] Harned and Douglas,[12] and Harned and Crawford[13] have measured the following concentration cells without transference

$$\text{Ag(s)}|\text{AgBr(s)}|\text{MBr(aq}, m_1)|\text{M(Hg)}|\text{MBr(aq}, m_2)|\text{AgBr(s)}|\text{Ag(s)} \tag{16}$$

where M refers to the alkali metal, and in the sets the molality of solution 1 (= m_1) was constant and molality m_2 was varied. Some details of the sets measured on cell 16 are shown in Table 4. The cpd of this cell is given by

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

These data were predicted by means of the recommended Hückel equations, and the results are shown as error plots in Figure 2. In these plots, the cpd errors were calculated by the equation

$$e_E = E(\text{observed}) - E(\text{predicted}) \tag{18}$$

and are presented as a function of the molality m_2. These data support well the tested Hückel equations up to a molality of

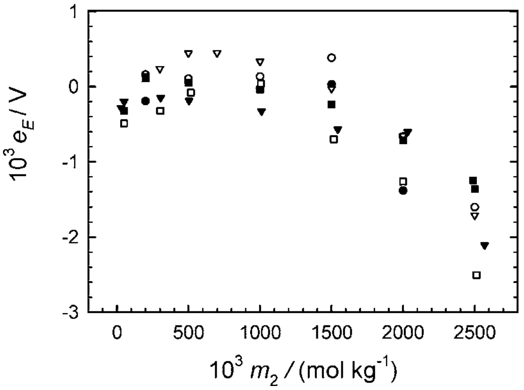

Figure 2. Deviation, e_E in eq 18, between the observed and predicted cell potential difference (cpd) from the amalgam cell data measured in dilute alkali metal bromide solutions on cell 16 (see Table 4) as a function of the molality m_2. The predicted cpd was calculated by using eq 17 where eq 1 with the parameter values recommended in Table 3 was used for the activity coefficients. Symbols (see Table 4): ●, Har29Li; ○, Har29Na; ▼, HaDo26Na; ▽, HaCr37Na; ■, Har29K; □, HaDo26K.

1.5 mol·kg^{-1}. In ref 9, another Hückel equation for NaBr solutions was estimated from the amalgam cell data of Harned and Crawford.[13] In that study, the following parameter values were obtained: $B = 1.1$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1628$. These values were suggested for NaBr solutions up to a molality of 1.0 mol kg^{-1}, and they will be considered below.

The most reliable technique to determine activity coefficients of alkali metal halides in very dilute aqueous solutions is to measure appropriate concentration cells with transference. The precision of the data measured by using this technique can be in the best cases as high as 0.001 mV. However, the calculation of activity coefficients from the cpd data obtained on concentration cells of this kind requires that the transference numbers (t_+ or $t_- = 1 - t_+$) of ions in the electrolyte solutions be known. The most reliable transference numbers for these calculations are obtained using the moving boundary method (see, for example, ref 31). In the literature only, one study is available for the present purposes that measured concentration cells with transference in dilute alkali metal bromide solutions, i.e., that of Mac William and Gordon[14] for KBr solutions at 25 °C on cells of the following type

$$\mathrm{Ag(s)|AgBr(s)|KBr(aq,}\ m_1\mathrm{)|KBr(aq,}\ m_2\mathrm{)|AgBr(s)|Ag(s)} \tag{19}$$

These data are shown in Table 5. Theoretically, the cpd of this cell (E) can be expressed by the following equation

$$E = -\frac{2RT}{F}\int_1^2 t_+ \mathrm{d}\ln(\gamma m/m^\circ) \tag{20}$$

where t_+ is the transference number of the cation (K$^+$). In the subsequent calculations, the treatment of Longsworth (see, e.g., ref 9) is followed. The transference number t_+ is first divided into two parts

$$t_+ = t_{+,1} + \Delta t_+ \tag{21}$$

where $t_{+,1}$ is the transference number of K$^+$ at molality m_1. To test the suggested Hückel parameters of $B = 1.35$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0185$, the data in Table 5 were predicted by means of these values. The equation used to predict these cpd values has the following form

Table 5. Cell Potential Differences (*E*) Measured by Mac William and Gordon[14] on Concentration Cells of Type 19 for KBr Solutions and the Errors (e_E, See Equation 18) Obtained for the Suggested Hückel Equation (Equation 1) from These Data

m_1	m_2	E	e_E
mol·kg^{-1}	mol·kg^{-1}	int. mV[a]	mV[b]
0.049983	0.009986	37.552	−0.042
0.050043	0.019877	21.379	−0.021
0.049902	0.029957	11.762	−0.015
0.049942	0.070214	−7.792	0.004
0.049993	0.079835	−10.692	0.007
0.049972	0.089866	−13.388	0.013
0.049925	0.097568	−15.250	0.041

[a] 1 Int. V = 1.00034 V. [b] Calculated from eqs 18, 22, and 24 with the activity coefficients obtained from eq 1 with $B = 1.35$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0185$.

$$E = -\frac{2RTt_{+,1}}{F}\ln(m_2/m_1) - \frac{2RTt_{+,1}}{F}\ln(\gamma_2/\gamma_1) - \frac{2RT}{F}\int_{m_1}^{m_2}\Delta t_+(\mathrm{d}m/m) - \frac{2RT}{F}\int_{\ln\gamma_1}^{\ln\gamma_2}\Delta t_+\mathrm{d}(\ln\gamma) \tag{22}$$

The relationship $t_+ = t_+(m)$ for eq 22 was determined from the moving boundary results of Keenan and Gordon.[32] The transference number data have been reported on the concentration (molarity, c) scale. For the conversion of the data to the molality (m) scale, the following equation (given by Harned and Owen[33]) was used

$$\frac{cm^\circ}{mc^\circ} = 0.9970 - 0.0345\frac{m}{m^\circ} + 0.0005\left(\frac{m}{m^\circ}\right)^2 \tag{23}$$

where c° is 1 mol·dm^{-3}. The following equation has been previously estimated for t_+ for KBr solutions from the moving boundary data of Keenan and Gordon[32] at 25 °C

$$t_+ = 0.48476 - 0.01503\sqrt{m/m^\circ} + 0.0514(m/m^\circ) \tag{24}$$

The functional form of this equation is partially the same one as that used by Longsworth[34] and exactly the same as that used in refs 9 and 31. The integral in the last term on the right-hand side of eq 22 (i.e., in the second activity coefficient term) must be evaluated numerically. The cpd errors defined by eq 18 are shown in Table 5, and they are small. Thus, the data support well the suggested Hückel equation for KBr but probably not within experimental error because the pattern of errors is not completely random. In ref 9, another Hückel equation for KBr solutions was estimated from these concentration cell data.[14] In that study, the following parameter values were obtained: $B = 1.3$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.017$. These values were suggested for KBr solutions up to a molality of 1.0 mol·kg^{-1}, and they will be considered below.

Determination of Parameters b_1 and b_2 for More Concentrated Alkali Metal Bromide Solutions and Tests of the Resulting Values. The parameter values suggested in ref 10 for the extended Hückel equation of KCl [i.e., those of $B = 1.3$ (mol·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 mol·kg^{-1}). These values together with equation

$$f_2 = \ln a_{1,\mathrm{x}} + 2M_1 m_\mathrm{y} - \frac{2\alpha M_1}{B_\mathrm{y}^3}\left[(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - 2\ln(1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}) - \frac{1}{1 + B_\mathrm{y}\sqrt{m_\mathrm{y}}}\right] + \frac{4M_1 b_{2,\mathrm{y}} m^3}{3(m^\circ)^2} = f_0 - b_{1,\mathrm{y}} M_1 (m_\mathrm{y}^2/m^\circ) = f_0 + k_2 m_\mathrm{y}^2 \quad (25)$$

where $k_2 = -b_{1,\mathrm{y}}M_1/m^\circ$ were used in the present study for the estimation of the Hückel parameters for more concentrated alkali metal bromide solutions. In these determinations, KCl is again the reference electrolyte (x), and the values of parameter B_y were taken from Table 3. When parameter $b_{2,\mathrm{y}}$ has been fixed, eq 25 represents an equation of the straight line f_2 versus m_y^2. The straight line in eq 25 should go through the origin, and therefore, parameter $b_{2,\mathrm{y}}$ must be determined again so that the value of intercept f_0 is zero. The same isopiestic sets were used in these parameter estimations as those used for eq 13 (see Table 3), but all data were included in these estimations. The results of these calculations are shown in Table 6. For LiBr data, the results with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$ were included in this table (see above). The resulting parameter values were again first tested by predicting the vapor pressures in the data sets used in the estimations. The vapor pressures of both solutions in each isotonic point in these sets can be calculated using eqs 3, 4, and 6 with the recommended activity parameters. The results are shown in Figure 3 where the isopiestic vapor pressure error (defined by eq 15) is presented as a function of the molality m_y. Graph A shows the results for both sets of parameters for LiBr solutions and graph B for the other bromide solutions. Almost all absolute errors in these tests are less than about 1 Pa (= 0.008 mmHg), and the experimental data in these sets support very well the suggested parameter values. For LiBr solutions (graph A), both sets of parameters apply well to the data, and thus the more reasonable values [i.e., those of $B = 1.6$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2450$, and $b_2 = 0.0131$] will only be considered below. The NaBr and KBr parameters in Table 6 can additionally be tested with the experimental isopiestic data reported by Robinson for NaBr[3] and KBr[5] solutions against KCl solutions and with the isopiestic data of Rard and Archer[15] and of Kirgintsev and Luk'yanov[17] for concentrated NaBr solutions against NaCl solutions. The former NaBr/NaCl data[15] are very precise and useful for the present test, but the NaBr data from these researchers[15] against H_2SO_4 and $CaCl_2$ solutions are only for very concentrated NaBr solutions and thus not considered here. The results from these four included sets are shown in Figure 4 as isopiestic vapor pressure errors (see eq 15), and the parameter values of $B = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$ were used in these calculations for the NaCl solutions. All NaBr data sets in this graph support well the recommended parameter values, but the set of Robinson[5] for

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

	$[B/(m^\circ)^{-1/2}]$[a]	b_2	b_1	$s(b_1)$[b]	N[c]	(m_max/m°)[d]	(s_0/Pa)[e]	ref
LiBr	1.3	0.0052	0.2915	0.0007	36	3.325	0.6	3
LiBr	1.6[f]	0.0131[f]	0.2450[f]	0.0005	36	3.325	0.5	3
NaBr[g]	1.45	0.0061	0.1087	0.0003	41	3.984	0.4	5
KBr	1.35	0.0028	0.0217	0.0002	19	4.755	0.3	3
RbBr	1.19	0.0021	0.0039	0.0002	20	4.861	0.4	3
CsBr	0.94	0.0058	−0.0137	0.0003	18	5.104	0.5	3

[a] Taken from Table 3 and $m^\circ = 1$ mol·kg^{-1}. [b] The standard deviation of parameter b_1. [c] Number of points included in the estimation. [d] The maximum molality of alkali metal bromide included in the estimation, see also footnote *a*. [e] Standard error between the vapor pressures of water over the tested and reference solutions (see eq 14). [f] Recommended value. [g] See footnote *h* to Table 3.

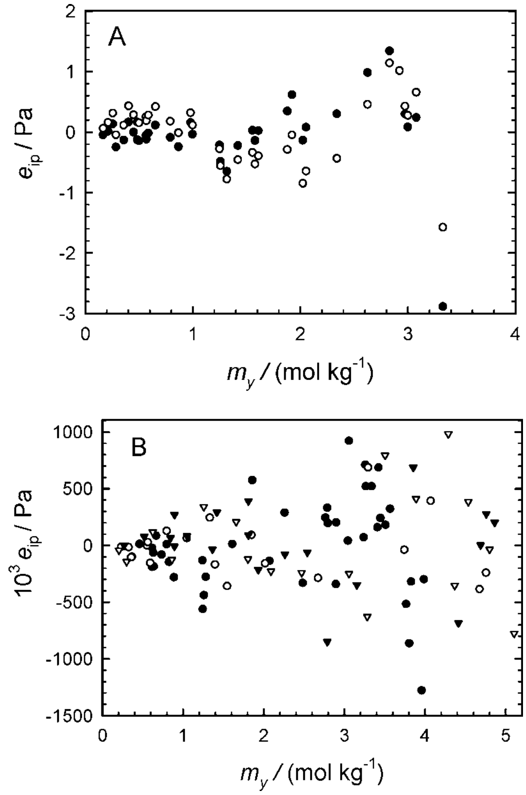

Figure 3. Difference, e_ip in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and alkali metal bromide (y) solutions for the data sets used in the parameter estimation for the extended Hückel equations (see Table 6). The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$ for KCl and with the parameter values shown in this table for alkali metal bromides. Symbols: ●, LiBr with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2915$, and $b_2 = 0.0052$ (graph A); NaBr (graph B); ○, LiBr with $B = 1.6$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2450$, and $b_2 = 0.0131$ (A); KBr (B); ▼, RbBr (B); ▽, CsBr (B).

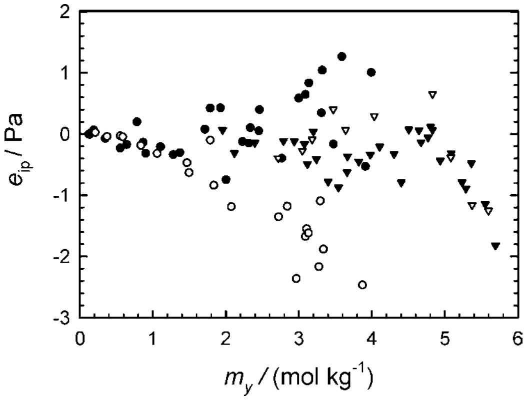

Figure 4. Difference, e_ip in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl or NaCl (x) and alkali metal bromide (y) solutions for the following data sets: ●, NaBr against KCl, Robinson;[3] ○, KBr against KCl, Robinson;[5] ▼, NaBr against NaCl, Rard and Archer;[15] and ▽, NaBr against NaCl, Kirgintsev and Luk'yanov.[17] The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B_\mathrm{KCl} = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_{1,\mathrm{KCl}} = 0.01324$ and $b_{2,\mathrm{KCl}} = 0.0036$, $B_\mathrm{NaCl} = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_{1,\mathrm{NaCl}} = 0.0699$ and $b_{2,\mathrm{NaCl}} = 0.0062$ for NaCl and KCl solutions and with the recommended parameter shown in Table 6 for alkali metal bromide solutions.

Table 7. Isopiestic Vapor Pressure Errors (e_{ip}, see Equation 15) Obtained from the Data Measured by Covington et al.[16] for NaCl, KCl, NaBr, and KBr Solutions at 25 °C by Using the Extended Hückel Equations Recommended in the Present Study ($m° = 1\ \mathrm{mol \cdot kg^{-1}}$)

m(NaCl)/$m°$	m(KCl)/$m°$	m(NaBr)/$m°$	m(KBr)/$m°$	[e_{ip}(recd)/Pa][a]	[e_{ip}(ref 5)/Pa][b]
	2.0649		2.0328	−0.96	−0.10
	3.0525		3.0089	−0.70	0.93
	4.3548		4.3134	0.99	3.70
2.9661			3.2388	−0.26	1.56
4.0829			4.6142	1.90	4.83
2.9623		2.8287		0.20	
4.3931		4.1602		1.04	
	2.0841	1.8697		−0.42	
	3.3713	2.9043		0.50	
	4.2494	3.5690		0.07	
		1.0878	1.1598	0.54[c]	0.85[c]
		1.8872	2.0795	0.18[c]	1.07[c]
		3.7627	4.4657	0.83[c]	3.66[c]

[a] Calculated by using eq 15 with the recommended parameter values. [b] The parameter values of $B = 1.35\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = 0.0264$, and $b_2 = 0.0025$ (determined from data of ref 5) were used for KBr. [c] NaBr is regarded as the reference electrolyte.

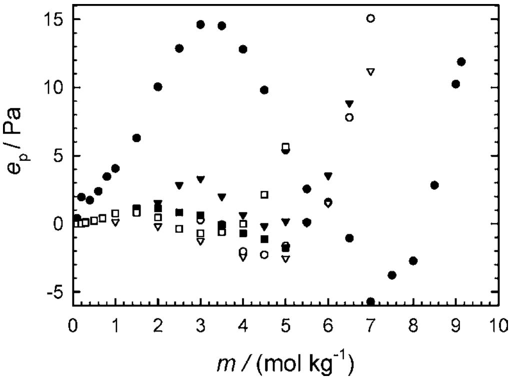

Figure 5. Difference, e_p in eq 26, between the reported and predicted vapor pressure of water over the NaBr, KBr, RbBr, and CsBr solutions as a function of the molality m of the solution. These differences are shown for the reported vapor pressures of Pearce et al.[21] (●, NaBr) and for the vapor pressures obtained from the osmotic coefficients reported by Makarov et al.[20] (○, NaBr), Penciner and Marcus[18] (▼, NaBr), Jakli and Van Hook[19] (▽, NaBr), and Robinson[6] (■, RbBr; □, CsBr) by using eqs 3 and 4. The vapor pressures have been predicted by using eqs 3 and 4 with eq 6 with the recommended parameter values for alkali metal bromides (see Table 6). Point ($m = 6.0\ \mathrm{mol \cdot kg^{-1}}$, $\phi = 1.334$) was omitted from the set of Makarov et al.[20]

KBr supports those only satisfactorily. Covington et al.[16] have determined the isopiestic molalities shown in Table 7 for NaCl, KCl, NaBr, and KBr solutions. The isopiestic vapor pressure errors (eq 15) have been calculated for these points by using the extended Hückel equations suggested in Table 6 for NaBr and KBr solutions, and they are shown in Table 7. These errors support well the recommended parameter values.

The NaBr parameters were also tested with the osmotic coefficients reported by Makarov et al.[20] (based on isopiestic data against $CaCl_2$ solutions), by Penciner and Marcus[18] (based also on isopiestic data against $CaCl_2$ solutions), and by Jakli and van Hook[19] [based on vapor pressure measurements at various temperatures from (−0.5 to 89) °C at molalities (2, 5, and 7) mol·kg^{-1}]. The RbBr and CsBr parameters can be tested with the osmotic coefficients reported by Robinson.[6] Also, these values were based on isopiestic, data but no details of the experiments are given in the original paper.[6] The reason for the remeasurements of RbBr and CsBr solutions by Robinson was that experimental problems existed in the determination of the most concentrated points of iodides (and possibly also bromides) of these metal ions in the previous study.[3] Vapor pressures were first calculated from these osmotic coefficient data, and then these values were predicted using eqs 3, 4, and 6 with the suggested parameters. The results are shown in Figure 5 where the vapor pressure error (e_p) is defined by

$$e_p = p(\text{reported}) - p(\text{predicted}) \tag{26}$$

and presented as a function of the molality m for each set. The isopiestic data for NaBr and RbBr solutions support quite well the suggested Hückel equations up to molalities of about (6 and 5) mol·kg^{-1}, respectively, but the CsBr data only up to 4.5 mol·kg^{-1}.

The new NaBr parameters were attempted to test, in addition, with the vapor pressure data of Pearce et al.[21] The vapor pressures of this set were predicted using eqs 3, 4, and 6. For this data set, the older value of 3.1667 kPa (= 23.752 mmHg) was used for the vapor pressure of pure water (i.e., in the same way as in the original paper[21]). The results are shown in Figure 5 where the vapor pressure error (e_p in eq 26) is presented as a function of the molality. As can be seen, these data are not sufficiently accurate for use in a critical evaluation of the validity of the suggested Hückel parameters.

Finally, the suggested Hückel parameters for more concentrated LiBr, NaBr, and KBr solutions can also be tested with all cpd data measured by amalgam cells of type 16 and are shown in Table 4. These data were predicted with the new extended Hückel equations by using eq 17, and the results are shown in Figure 6 (which corresponds exactly to Figure 2). The cpd errors in this figure support quite well

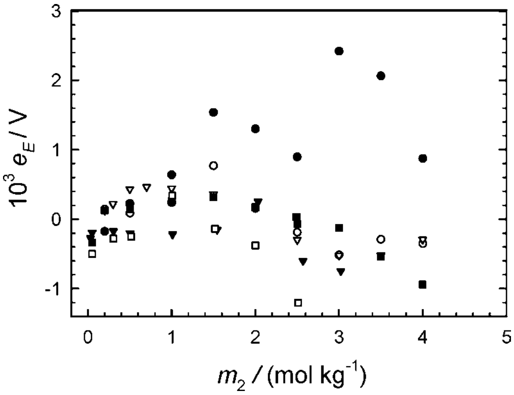

Figure 6. Deviation, e_E in eq 18, between the observed and predicted cell potential difference (cpd) from the amalgam cell data measured in LiBr, NaBr, and KBr solutions on cell 16 (see Table 4) as a function of the molality m_2. The predicted cpd was calculated by using eq 17 where eq 5 with the parameter values recommended in Table 6 was used for the activity coefficients. Symbols (see Table 4): ●, Har29Li; ○, Har29Na; ▼, HaDo26Na; ▽, HaCr37Na; ■, Har29K; □, HaDo26K.

Table 8. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Lithium Bromide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.801	0.946	3.1578
0.2	0.774(0.773)	0.949(0.948)	3.1470
0.3	0.765(0.764)	0.957(0.956)	3.1360
0.4	0.764(0.762)	0.967(0.965)	3.1248
0.5	0.768(0.766)	0.978(0.976)	3.1133(3.1134)
0.6	0.775(0.772)	0.990(0.987)	3.1015(3.1017)
0.7	0.785(0.780)	1.003(0.999)	3.0894(3.0898)
0.8	0.796(0.790)	1.016(1.011)	3.0771(3.0776)
0.9	0.809(0.801)	1.030(1.023)	3.0645(3.0652)
1.0	0.824(0.813)	1.044(1.035)	3.0516(3.0526)
1.2	0.857	1.073	3.0250
1.4	0.894	1.102	2.9973
1.6	0.936	1.132	2.9684
1.8	0.983	1.163	2.9383
2.0	1.034	1.195	2.9071
2.5	1.183	1.278	2.8241
3.0	1.368	1.365	2.7340
3.5	1.596	1.456	2.6371

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.6\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.245$, and the other activity values with the extended Hückel equation with $B = 1.6\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.245$, and $b_2 = 0.0131$.

Table 9. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Bromide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.784	0.936	3.1579
0.2	0.743(0.744)	0.930	3.1474
0.3	0.722(0.723)	0.930	3.1369
0.4	0.710	0.932	3.1263
0.5	0.702	0.936	3.1156
0.6	0.697	0.940	3.1049
0.7	0.694	0.945	3.0940
0.8	0.693	0.951(0.950)	3.0830
0.9	0.693	0.956(0.955)	3.0718(3.0720)
1.0	0.694(0.693)	0.962(0.960)	3.0606(3.0608)
1.2	0.699(0.697)	0.975(0.972)	3.0378(3.0383)
1.4	0.706(0.702)	0.988(0.983)	3.0146(3.0153)
1.6	0.716	1.002	2.9908
1.8	0.726	1.016	2.9666
2.0	0.739	1.030	2.9419
2.5	0.776	1.068	2.8780
3.0	0.820	1.108	2.8110
3.5	0.872	1.150	2.7409
4.0	0.933	1.194	2.6678
4.5	1.001	1.240	2.5917
5.0	1.080	1.287	2.5127
5.5	1.169	1.337	2.4310
6.0	1.271	1.389	2.2467

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.45\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.1131$, and the other activity values with the extended Hückel equation with $B = 1.45\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.1087$, and $b_2 = 0.0061$.

the suggested models for NaBr and KBr but only satisfactorily the model for LiBr.

Table 10. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Bromide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.773(0.772)	0.929	3.1580
0.2	0.724(0.723)	0.917	3.1477
0.3	0.696(0.695)	0.912(0.911)	3.1375
0.4	0.676(0.675)	0.909(0.908)	3.1273(3.1274)
0.5	0.661(0.660)	0.908(0.907)	3.1172(3.1173)
0.6	0.650(0.648)	0.907(0.906)	3.1070(3.1072)
0.7	0.641(0.639)	0.907(0.905)	3.0969(3.0971)
0.8	0.633(0.631)	0.908(0.906)	3.0867(3.0870)
0.9	0.627(0.624)	0.909(0.906)	3.0766(3.0769)
1.0	0.622(0.618)	0.910(0.906)	3.0664(3.0668)
1.2	0.613(0.608)	0.912(0.908)	3.0460(3.0467)
1.4	0.607(0.601)	0.915(0.910)	3.0256(3.0265)
1.6	0.602	0.919	3.0051
1.8	0.599	0.923	2.9846
2.0	0.597	0.927	2.9639
2.5	0.594	0.937	2.9120
3.0	0.595	0.949	2.8595
3.5	0.599	0.962	2.8065
4.0	0.605	0.976	2.7527
4.5	0.612	0.991	2.6983
5.0	0.622	1.007	2.6431

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.35\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0185$, and the other activity values with the extended Hückel equation with $B = 1.35\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0217$, and $b_2 = 0.0028$.

Table 11. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Rubidium Bromide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.764(0.763)	0.924	3.1581
0.2	0.710	0.909	3.1479
0.3	0.678(0.677)	0.902(0.901)	3.1379
0.4	0.656(0.654)	0.897(0.895)	3.1279
0.5	0.639(0.636)	0.894(0.892)	3.1180(3.1181)
0.6	0.625(0.622)	0.891(0.889)	3.1081(3.1083)
0.7	0.613(0.610)	0.890(0.887)	3.0983(3.0985)
0.8	0.604(0.600)	0.889(0.886)	3.0884(3.0887)
0.9	0.596(0.592)	0.888(0.885)	3.0786(3.0790)
1.0	0.588(0.584)	0.888(0.884)	3.0688(3.0693)
1.2	0.576(0.571)	0.888(0.882)	3.0493(3.0500)
1.4	0.567	0.888	3.0297
1.6	0.559	0.889	3.0102
1.8	0.553	0.891	2.9907
2.0	0.547	0.892	2.9713
2.5	0.537	0.897	2.9226
3.0	0.531	0.903	2.8739
3.5	0.526	0.910	2.8252
4.0	0.524	0.917	2.7762
4.5	0.524	0.925	2.7271
5.0	0.524	0.934	2.6777

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.19\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.0019$, and the other activity values with the extended Hückel equation with $B = 1.19\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0039$, and $b_2 = 0.0021$.

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 6 and Tables 5 and 7), 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 alkali metal bromide solutions at 25 °C have been calculated on the basis of these equations. For LiBr, the new values are given in Table 8, for NaBr in Table 9, for KBr in Table 10, for RbBr in Table 11, and for CsBr in Table 12. Also, the vapor pressures of water are included in these tables.

The values of all activity quantities have been calculated in these tables by using parameter values suggested for the extended Hückel equations. In dilute solutions (i.e., when m is less than about 1.5 mol·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

Table 12. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Cesium Bromide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.750	0.916	3.1582
0.2	0.689	0.896	3.1482
0.3	0.652	0.885	3.1384
0.4	0.625	0.877	3.1288
0.5	0.604	0.871	3.1193
0.6	0.587	0.867(0.866)	3.1098
0.7	0.573(0.572)	0.863(0.862)	3.1004
0.8	0.561(0.560)	0.861(0.859)	3.0910(3.0911)
0.9	0.551(0.549)	0.858(0.856)	3.0816(3.0818)
1.0	0.542(0.540)	0.857(0.854)	3.0723(3.0726)
1.2	0.526(0.523)	0.854(0.850)	3.0537(3.0543)
1.4	0.514(0.510)	0.853(0.847)	3.0351(3.0361)
1.6	0.504(0.498)	0.853(0.845)	3.0166(3.0180)
1.8	0.495	0.853	2.9980
2.0	0.488	0.854	2.9795
2.5	0.475	0.859	2.9328
3.0	0.466	0.866	2.8855
3.5	0.461	0.875	2.8375
4.0	0.460	0.887	2.7884
4.5	0.460	0.901	2.7380
5.0	0.463	0.917	2.6863

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 0.94$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = -0.0117$, and the other activity values with the extended Hückel equation with $B = 0.94$ (mol·kg^{-1})$^{-1/2}$, $b_1 = -0.0137$, and $b_2 = 0.0058$.

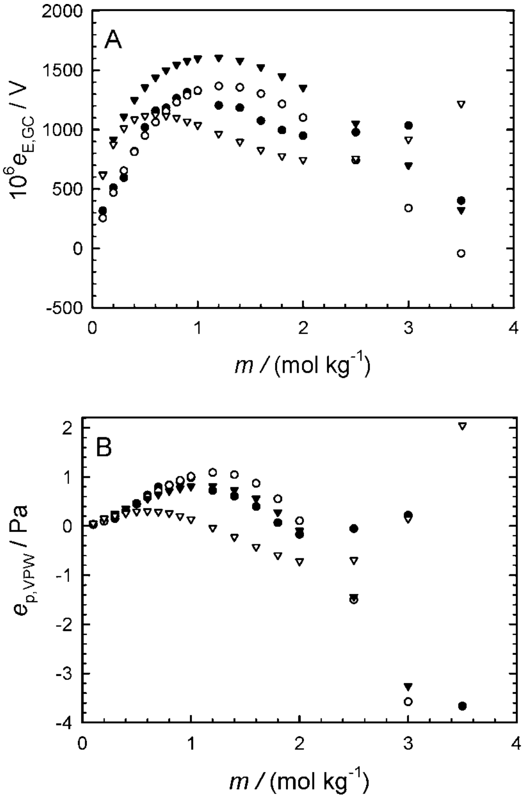

Figure 7. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 27, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 28, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for LiBr solutions as a function of the molality m (see Table 8). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[24] ▼, Pitzer and Mayorga;[8] ▽, the extended Hückel equation with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2915$, and $b_2 = 0.0052$ (see text and Table 6).

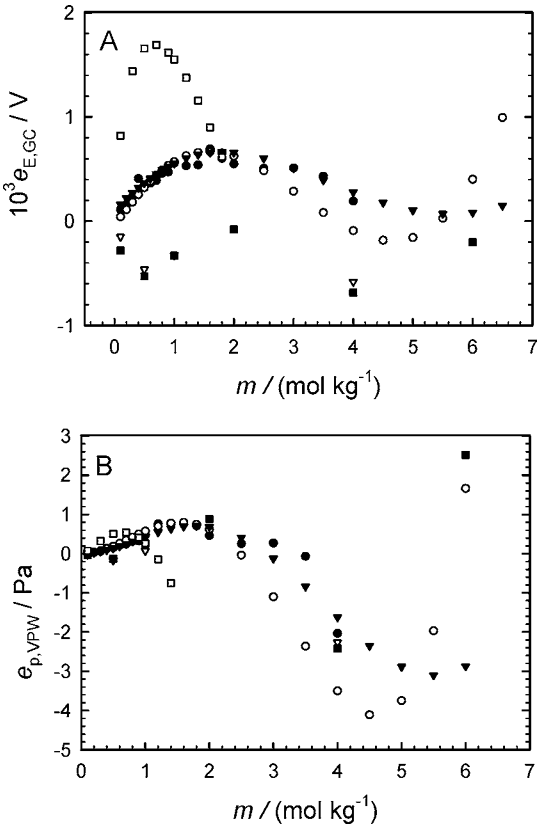

Figure 8. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 27, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 28, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for NaBr solutions as a function of the molality m (see Table 9). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[24] ▼, Pitzer and Mayorga;[8] ▽, Rard and Archer;[15] ■, Archer;[35] □, Partanen[9] [deviations $e_{E,GC}$ and $e_{p,VPW}$ were calculated for these values[9] using eqs 29 (graph A) and 30 (graph B), respectively].

between these two values is always quite small [less than 0.7 mV for galvanic cell deviations for γ (the definition will be given below) and less than 1.4 Pa (= 0.01 mmHg) for vapor pressure deviations for ϕ].

Comparison of the Recommended Activity Values to the Literature Values. The values in Tables 8 to 12 were compared to the activity and osmotic coefficients presented by Robinson and Stokes,[2] Hamer and Wu,[24] and Pitzer and Mayorga.[8] The comparison of the activity coefficients are shown in graphs A of Figures 7, 8, 9, 10, and 11 for LiBr, NaBr, KBr, RbBr, and CsBr, respectively. The quantity presented on the y-axis in these graphs is the cell potential deviation [$e_{E,GC}$, where GC refers to the appropriate galvanic cell without a liquid junction containing electrodes reversible to the cation (alkali metal cation in this case) and anion (Br^-) of the electrolyte (see, for example, ref 9 or 26)] that resulted from the use of the literature activity coefficients of various sources [i.e., γ(literature)] when compared to the recommended values [i.e., γ(recd)] shown in Tables 8 to 12. Thus, $e_{E,GC}$ is defined by

$$e_{E,GC} = -\frac{2RT}{F}\ln\frac{\gamma(\text{literature})}{\gamma(\text{recd})} \qquad (27)$$

For the recommended values, the values obtained from eq 5 were used.

The comparison of the osmotic coefficients in Tables 8 to 12 with the literature values is shown in the same way in graphs B of Figures 7 to 11 for these electrolytes. The quantity presented on the y-axis in these graphs is the vapor pressure deviation ($e_{p,VPW}$ where VPW refers to the vapor

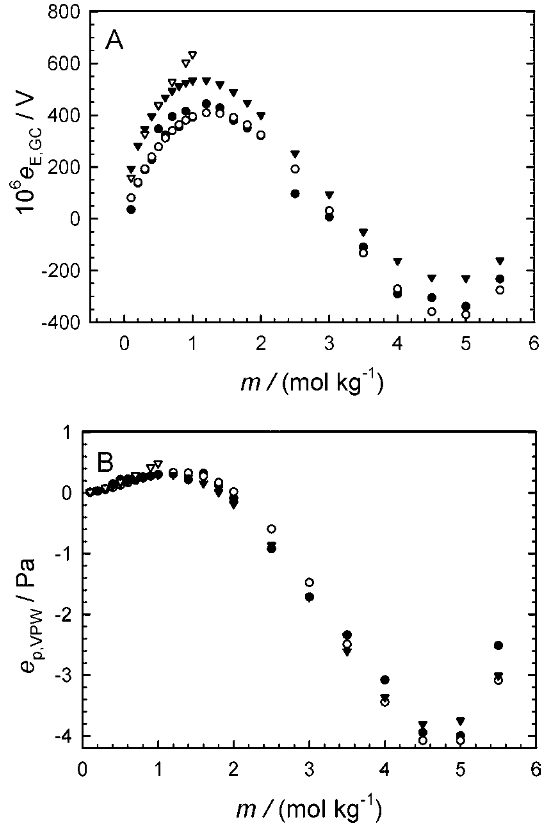

Figure 9. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 27, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 28, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for KBr solutions as a function of the molality m (see Table 10). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[24] ▼, Pitzer and Mayorga;[8] ▽, Partanen[9] [deviations $e_{E,GC}$ and $e_{p,VPW}$ were calculated for these values[9] using eqs 29 (graph A) and 30 (graph B), respectively].

pressure of water) that resulted from the use of the literature osmotic coefficients [i.e., ϕ(literature)] when compared to the recommended values [i.e., to ϕ(recd)] shown in Tables 8 to 12 (see, for example, ref 10). Literature vapor pressure p(literature) and recommended vapor pressure p(recd) have been calculated from the osmotic coefficients by using eqs 3 and 4 and the deviations in these graphs by using the following equation

$$e_{p,VPW} = p(\text{literature}) - p(\text{recd}) \qquad (28)$$

For the recommended values, the values obtained from eq 6 were used.

In Figure 7 are also included the results obtained by using the extended Hückel equation with the unreasonable small value of parameter B [i.e., that of 1.3 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$] (see Table 6). The activity and osmotic coefficients suggested in the literature for LiBr solutions agree only satisfactorily in this figure with those recommended in Table 8, and the other new Hückel parameters considered in these graphs for LiBr predict the literature activity coefficients slightly better (graph A). Nevertheless, the recommended parameters are probably more reliable because of the reasons explained above. All these results for LiBr solutions have been based only on a single data set (i.e., on that of Robinson[3]). In the other isopiestic set for this electrolyte (Robinson and McCoach[4]), data are only for more concentrated solutions, and they cannot be used in this connection. New data will be required, therefore, to solve the problems associated with the thermodynamic properties of dilute LiBr solutions.

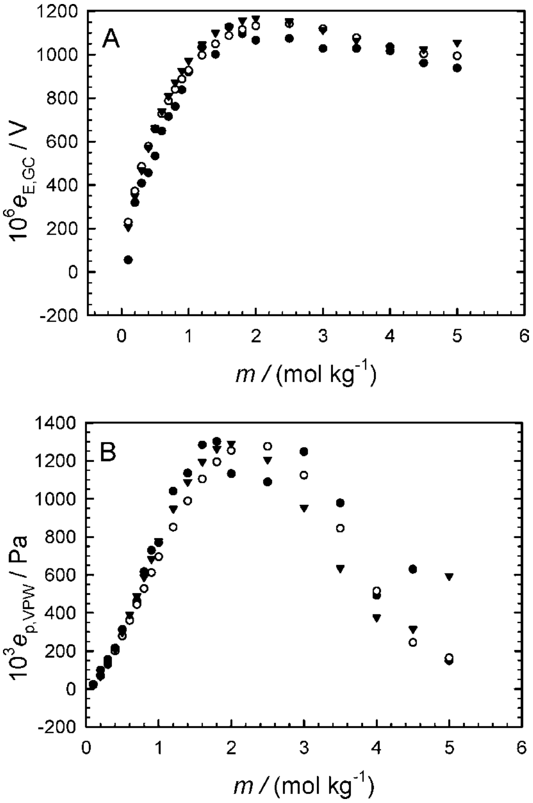

Figure 10. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 27, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 28, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for RbBr solutions as a function of the molality m (see Table 11). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[24] ▼, Pitzer and Mayorga.[8]

The activity quantities in the literature for NaBr solutions agree at least very satisfactorily in Figure 8 with those recommended in Table 9 up to a molality of 6.0 mol·kg^{-1}. This molality is considerable larger than the largest molality used in the parameter estimation (i.e., that of 4.0 mol·kg^{-1}, see Table 6). This appears also in the error plots of Figures 4 and 5. For NaBr solutions, Archer[35] and Rard and Archer[15] have presented the equations of activity quantities that apply up to the saturated solution over wide ranges of temperatures and pressures. In Figure 8 are also included the activity and osmotic coefficients suggested by Archer[35] at the rounded molalities of (0.1, 0.5, 1, 2, 4, and 6) mol·kg^{-1} and by Rard and Archer[15] at (0.1, 0.5, 1, and 4) mol·kg^{-1} on the basis of such equations at 25 °C and at 0.1 MPa. These values support well the recommended Hückel parameters.

In graph A of Figure 9, the activity coefficients suggested in the literature for KBr solutions agree quite well with those recommended in Table 10 up to a molality of 5.5 mol·kg^{-1}, but in graph B of this figure the literature osmotic coefficients agree well with the recommended values only up to 3 mol·kg^{-1}. The negative vapor pressure errors smaller than −2.7 Pa (= −0.02 mmHg) for all literature values above 3.5 mol·kg^{-1} are due to the fact that the older isopiestic data[3] of Robinson were used here in the parameter estimation, and the activity and osmotic coefficients in the tables of Robinson and Stokes[2] were based mainly on the more recent data of Robinson[5] (see Table 6 and also the error plots in Figures 3B and 4). The reason for the present choice to give the priority to the older data[3] was

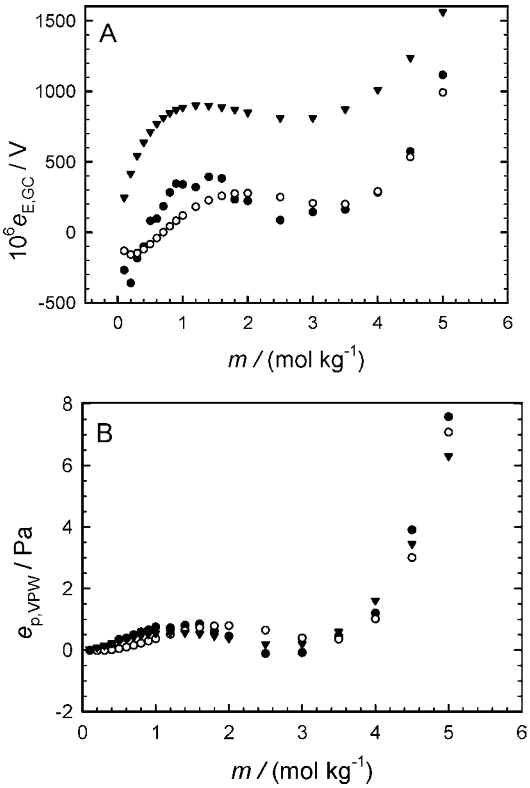

Figure 11. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 27, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 28, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for CsBr solutions as a function of the molality m (see Table 12). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[24] ▼, Pitzer and Mayorga.[8]

the fact that the strongest isopiestic points of Covington et al.[16] for KBr solutions can be explained better with the parameter values estimated from the older data (the details for this fact are presented in Table 7).

According to graph A of Figure 10, it seems possible to me that the activity coefficients in the tables of Robinson and Stokes[2] for RbBr solutions have probably not been estimated in a fully correct way from the isopiestic data reported in refs 3 and 6, and therefore they do not agree well with the recommended values in Table 11. The values from the Pitzer and Hamer equations follow exactly these tabulated literature values,[2] and thus they are probably not entirely reliable. Graph B of this figure shows that the literature osmotic coefficients agree, however, better with the recommended values.

Figure 11 shows that the activity and osmotic coefficients of Robinson and Stokes[2] and Hamer and Wu[24] for CsBr solutions agree well with those suggested in Table 12 up to a molality of 4 mol·kg^{-1}. The recommended values in Table 12 were based on the older isopiestic data[3] of Robinson which (according to Robinson[6]) may suffer some experimental problems (see above). In these data are five points where the molality of CsBr is larger than 4 mol·kg^{-1}, but all of these points support well the new model (see Figure 3B). Therefore, it seems to me that the older data[3] of Robinson are more reliable than the more recent data,[6] and the recommended activity and osmotic coefficients in Table 12 are probably more reliable than the previous literature values for these most concentrated solutions. Pitzer parameters in Figure 11 apply quite well to the osmotic coefficients (graph B) but not as well to the activity coefficients (graph A).

The errors that resulted from the use of the Hückel equations (eqs 1 and 2) presented in ref 9 for dilute NaBr [i.e., those with $B = 1.1$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1628$] and for dilute KBr solutions (i.e., those with $B = 1.3$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.017$) at molalities less than or about 1 mol·kg^{-1} are also shown in the graphs of Figures 8 and 9. These errors have been calculated from the equations

$$e_{E,GC} = -\frac{2RT}{F} \ln \frac{\gamma(\text{ref }9)}{\gamma(\text{eq 1 from this study})} \tag{29}$$

$$e_{p,VPW} = p(\text{ref }9) - p(\text{eq 2 from this study}) \tag{30}$$

According to the error plots of Figure 8A, the parameter values determined from the amalgam cell data of Harned and Crawford[13] for NaBr (see ref 9) do not predict well the activity coefficients calculated with the parameter values recommended in the present study on the basis of isopiestic data[5] (see Table 3). The reason for this disagreement is surely due to the fact that all points from the set of Harned and Crawford[13] up to a molality of 4 mol·kg^{-1} were taken into account in the parameter estimation of ref 9. If only the five points in this set (where all molalities are less than 1.5 mol·kg^{-1}) are used in the corresponding fitting as that in ref 9, very good results are obtained with the parameter values of $B = 1.4$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.113$. These values are almost the same as those recommended here in Table 3 for the Hückel equation of NaBr [i.e., those of $B = 1.45$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1131$]. The recommended osmotic coefficients for NaBr solutions in Figure 8B can, however, be predicted very satisfactorily with the former amalgam parameter values of $B = 1.1$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1628$ up to a molality of 1.5 mol·kg^{-1}. According to the error plots in Figure 9, the activity and osmotic coefficients calculated with the Hückel parameters from the concentration cell data of Mac William and Gordon[14] for KBr solutions (see ref 9) agree quite well with those recommended in the present study on the basis of isopiestic data[3] (see Table 3).

Glossary

A	Debye–Hückel parameter [$= \alpha/\ln(10)$, (mol·kg^{-1})$^{-1/2}$] in the equations of Hamer and Wu (eqs 7 and 8)
a_1	activity of water
B	parameter in Hückel equation [(mol·kg^{-1})$^{-1/2}$]
B^*	parameter in the equations of Hamer and Wu [eqs 7 and 8, (mol·kg^{-1})$^{-1/2}$]
B^γ	the term resulted from the binary interactions in the Pitzer equation (eqs 9 and 11)
b_1	parameter in Hückel equation
b_2	parameter in the extended Hückel equation
C^ϕ	parameter in Pitzer equations (eqs 9 and 12)
C, D, E, F, G	parameters in the equations of Hamer and Wu (eqs 7 and 8)
c	concentration (molarity) in eq 23 (mol·dm^{-3})
$c°$	1 mol·dm^{-3}
cpd	cell potential difference (V)
E	cell potential difference (V)
e_E	cell potential difference error (V) defined by eq 18
$e_{E,GC}$	cell potential deviation (V) defined by eq 27 (GC means galvanic cell)
e_{ip}	isopiestic error (Pa) defined by eq 15 (ip means isopiestic)
e_p	vapor pressure error (Pa) defined by eq 26
$e_{p,VPW}$	vapor pressure deviation (Pa) defined by eq 28 (VPW means vapor pressure of water)
F	Faraday constant (A·s·mol^{-1})
f_0	the intercept term in the linear representations of eqs 13 and 25

f_1	linear function with respect to m^2, defined in eq 13
f_2	linear function with respect to m^2, defined in eq 25
f^{γ}	Debye−Hückel term in Pitzer equation (eqs 9 and 10)
k_1, k_2	defined by equation $k_i = -b_{1,y}M_1/m°$ where $i = 1$ or 2 [$(\text{mol}\cdot\text{kg}^{-1})^{-2}$] (see eqs 13 and 25)
M	alkali metal
M_1	molar mass of water ($\text{kg}\cdot\text{mol}^{-1}$)
m	molality ($\text{mol}\cdot\text{kg}^{-1}$)
$m°$	1 $\text{mol}\cdot\text{kg}^{-1}$
N	number of points
P	number of parameters in a thermodynamic activity model
p_1	vapor pressure of water over the solution (Pa)
p_1^*	vapor pressure of pure water (Pa)
R	the gas constant ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
s_0	standard error (Pa) for isopiestic sets defined by eq 14
T	absolute temperature (K)
t_+	transference number of cation in eqs 20, 21, and 22
$t_{+,1}$	transference number of cation in reference solution ($m = m_1$) of cell 19 in eqs 21 and 22
t_-	transference number of anion
x	reference electrolyte
y	tested electrolyte

Greek Letters

α	Debye−Hückel parameter [$(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$]
β	parameter in the equations of Hamer and Wu (eqs 7 and 8)
β^0, β^1	parameters in Pitzer equations (eqs 9 and 12)
γ	mean activity coefficient
Δ	difference
ϕ	osmotic coefficient

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