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

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The Hückel equation used in this study to correlate the experimental activities of dilute alkali metal iodide solutions up to a molality of about 1.5 mol·kg^{-1} contains two parameters being 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 9 mol·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 NaI, KI, and RbI 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 LiI were determined from the isopiestic data measured by Robinson and Sinclair for KCl and LiI solutions (J. *Am. Chem. Soc.* **1934**, *56*, 1830–1835). In these estimations, the Hückel parameters determined recently for KCl solutions (*J. Chem. Eng. Data* **2009**, *54*, 208–219) were used. The Hückel parameters for CsI were determined from the reported osmotic coefficients of Robinson (*J. Am. Chem. Soc.* **1937**, *59*, 84–90). The resulting parameter values were tested with the cell potential, vapor pressure, and isopiestic data existing in the literature for alkali metal iodide solutions. Most of these data can be reproduced within experimental error by means of the extended Hückel equation at least up to a molality of about 5.0 mol·kg^{-1}. Reliable activity and osmotic coefficients for alkali metal iodide 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 equation of Hamer and Wu (*J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099). The activity quantities of alkali metal iodide solutions obtained in the present study were compared in a new way to those of alkali metal chloride and bromide solutions determined previously.

Introduction

In 1949, Robinson and Stokes[1,2] presented tables for activity and osmotic coefficients of electrolytes in aqueous solution at 25 °C, and these tables have been widely accepted and used, e.g., in the chemical literature. The values of the activity quantities of LiI solutions in these tables have been based on the isopiestic data measured by Robinson and Sinclair[3] for KCl and LiI solutions. The isopiestic data of Robinson[4] were used in the determination of the activity quantities in these tables for the other alkali metal iodides in addition to the isopiestic data of Robinson and Wilson[5] for KI solutions and to the reported osmotic coefficients of Robinson[6] for RbI and CsI solutions. The tables of Robinson and Stokes give activity and osmotic coefficients from a molality of 0.1 mol·kg^{-1} up to 3.0 mol·kg^{-1} for LiI, up to 3.5 mol·kg^{-1} for NaI, up to 4.5 mol·kg^{-1} for KI, up to 5.0 mol·kg^{-1} for RbI, and up to 3.0 mol·kg^{-1} for CsI solutions.

In the present study, it is shown that reliable thermodynamic activity values for alkali metal iodide solutions can also be obtained by such a simple equation as the Hückel equation up to a molality of about 1.5 mol·kg^{-1}. The form of the Hückel equation used in this investigation (see below and, e.g., ref 7) 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). Theoretically, this model is connected to the ionic hydration theory of Stokes and Robinson[8] in ref 9. The values of B and b_1 for NaI, KI, and RbI in dilute solutions were determined here from the isopiestic data of Robinson.[4] For LiI, these parameter values were obtained from the isopiestic data of Robinson and Sinclair[3] and for CsI from the reported osmotic coefficients of Robinson.[6] Usually, the points where the alkali metal iodide molality is less than 1.5 mol·kg^{-1} could be included in the determination. For CsI, however, all points of Robinson[6] could be taken into account (the maximum molality in this set is 3.0 mol·kg^{-1}). The Hückel parameters needed in this estimation for KCl were taken from the results of a previous study[10] where NaCl and KCl solutions are considered. The resulting parameter values were tested with the data used in the parameter estimations, with the isopiestic data of Robinson

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and Wilson[5] for KI solutions and of Robinson[4] for CsI solution, and with the cell potential differences (= cpd) measured by Harned and Douglas[11] (for NaI and KI solutions) on concentration cells containing an alkali metal amalgam electrode and two Ag−AgI electrodes.

Additionally, it is shown here that very reliable activity values for NaI and RbI solutions up to a molality of 5 mol·kg^{-1}, for KI solutions up to the molality of the saturated solution (i.e., up to 8.98 mol·kg^{-1}), and for LiI solutions up to 3.0 mol·kg^{-1} were obtained 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 iodide 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 as many points as possible in this set were now included in the determination for each salt. The resulting parameter values were tested with all isopiestic data mentioned above and, additionally, with the experimental osmotic coefficients reported by Miller and Sheridan,[12] by Jakli and Van Hook,[13] and by Makarov et al.[14] for NaI solutions and by Makarov et al.[15] for KI solutions and by Robinson[6] for RbI solutions as well as with the vapor pressure data of Pearce et al.[16] for KI solutions.

As in ref 10, 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. It was observed in these tests that the Hückel equations are very reliable. 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 iodide salts, and these values are tabulated as recommended values. These activity and osmotic coefficients were compared to those of the previous investigations. 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 7, 10, and 17), and the osmotic coefficient deviations are presented as vapor pressure deviations (as in refs 10, 18, 19, and 20). Cell-potential and vapor pressure deviations are also used in the present study to compare the activity and osmotic coefficients of alkali metal iodide solutions to those of alkali metal chloride and bromide solutions determined previously.[10,18−20]

Theory

In the previous studies, it was found that the following Hückel equations apply very well to the thermodynamic properties of NaCl,[10] KCl,[10] LiCl,[18] RbCl,[19] CsCl,[19] and alkali metal bromide[20] solutions at least up to the molalities of about 1 mol·kg^{-1}

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

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

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[21]]; m^o = 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

$$\ln a_1 = -2mM_1\phi \qquad (3)$$

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

$$a_1 = p_1/p_1^* \qquad (4)$$

This equation is not an exact relation, but it is an excellent approximation because, under the studied conditions, the difference between the fugacity and vapor pressure is very small. For water at 25 °C, p_1^* = 3.1686 kPa (i.e., 23.766 mmHg, see Kell[22]).

In more concentrated solutions, the following extended Hückel equations were used here as earlier[10,18−20] for the activity and osmotic coefficients

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

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

Hamer and Wu[23] suggested the following extended Hückel equations for the activity and osmotic coefficients of alkali metal iodide solutions

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

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

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

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[24,25] has the form

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

where

Table 1. Parameter Values of the Equations of Hamer and Wu[23] (See Equations 7 and 8) for Alkali Metal Iodides at 25 °C

	B^*					$m_{\max}$[a]
	$(\mathrm{mol \cdot kg^{-1}})^{-1/2}$	$10^3\beta$	10^3C	10^3D	10^3E	$(\mathrm{mol \cdot kg^{-1}})$
LiI	1.695	178.10	−44.794	18.282	−2.0254	3
NaI	1.486	68.170	3.05	0	−0.010	12
KI	1.381	25.012	−0.117			4.5
RbI	1.109	−1.2600	2.800	−0.1774		5
CsI	0.9365	−8.3798				3

[a] The maximum molality to which the equations apply.

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

				$m_{\max}$[a]
	β^0	β^1	C^ϕ	$(\mathrm{mol \cdot kg^{-1}})$
LiI	0.2104	0.373	0	1.4
NaI	0.1195	0.3439	0.0018	3.5
KI	0.0746	0.2517	−0.00414	4.5
RbI	0.0397	0.1330	−0.00108	5
CsI	0.0244	0.0262	−0.00365	3

[a] The maximum molality to which the equations apply.

Table 3. Results from the Parameter Estimation for the Hückel Equations (Equations 1 and 2) of Alkali Metal Iodides at 25 °C by the Least-Squares Fitting Using Equation 13 with the LiI, NaI, KI, and RbI Data and Using Equation 15 with the CsI Data

	B				$m_{\max}$[c]	s_0	
	$(\mathrm{mol \cdot kg^{-1}})^{-1/2}$	b_1	$s(b_1)$[a]	N[b]	(m°)	(Pa)	ref
LiI	2.1	0.289	0.002	18	1.443	0.4[d]	3
LiI	1.8[g,f]	0.311[e,f]		14	1.098	0.2[d]	3
NaI	1.6	0.1549	0.0012	17	1.289	0.15[d]	4
KI	1.45	0.0490	0.0008	10	1.232	0.08[d]	4
RbI	1.12	−0.0026	0.0013	8	1.429	0.15[d]	4
CsI	0.88	−0.0116	0.0002	10	3.000	0.06[h]	6

[a] The standard deviation of parameter b_1. [b] Number of points included in the estimation. [c] The maximum molality of alkali metal iodide solution included in the estimation ($m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$). [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[18] and on the analogy between B values for sodium and potassium chlorides[10] and iodides. [f] Recommended value. [g] Optimized values based on the square error sum of eq 14, and point ($m_{\mathrm{KCl}} = 0.7964\ m^\circ$, $m_{\mathrm{LiCl}} = 0.6852\ m^\circ$) was omitted from this estimation as a slightly erroneous point. [h] Standard error between the observed and predicted vapor pressures of water (see eq 16).

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

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

In eqs 9 and 11, β^0, β^1, and C^ϕ are the parameters that are dependent on the electrolyte. Pitzer and Mayorga[25] have determined the values shown in Table 2 for these parameters for alkali metal iodides. For alkali metal iodide solutions, Kim and Frederick,[26] Marshall et al.,[27] and Christov[28] (only for KI and RbI) have also presented Pitzer parameters. The values for the two former studies[26,27] are not considered here because they have been determined from the tabulated activity and osmotic coefficients of Hamer and Wu[23] which are included in the present tests. In a very recent study,[29] all of these Pitzer parameter values were tested up to the saturated solutions for several uniunivalent electrolytes including KI and RbI from the iodides. For osmotic coefficients of water in solutions of a uniunivalent electrolyte, the Pitzer equation has the form

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

Results and Discussion

Determination of Parameters B and b_1 for Dilute Alkali Metal Iodide 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

$$\begin{aligned} f_1 &= \ln a_{1,\mathrm{x}} + 2M_1 m_{\mathrm{y}} - \frac{2\alpha M_1}{B_{\mathrm{y}}^3} \times \\ &\quad \left[(1 + B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}) - 2\ln(1 + B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}) - \frac{1}{1 + B_{\mathrm{y}}\sqrt{m_{\mathrm{y}}}}\right] \\ &= f_0 - b_{1,\mathrm{y}}M_1(m_{\mathrm{y}}^2/m^\circ) = f_0 + k_1 m_{\mathrm{y}}^2 \end{aligned} \tag{13}$$

where $k_1 = -b_{1,\mathrm{y}}M_1/m^\circ$ were used in the present study for the estimation of the Hückel parameters for dilute LiI, NaI, KI, and RbI solutions from the isopiestic data mentioned above. 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 iodide 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}). The details of the estimations have been presented in the previous alkali metal bromide paper[20] (see eq 13 and the text associated with this equation in that study). The present results are shown in Table 3. The standard error s_0 in this table is defined by the equation

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

where N is the number of points and P is the number of estimated parameters (now 2).

In Table 3 are also shown the parameter values obtained for CsI solutions from the experimental osmotic coefficients reported by Robinson.[6] The original isopiestic data on which these osmotic coefficients were based are not available in the literature. The parameter values for CsI solutions from these ϕ values were estimated using the following equation

$$f_2 = \ln a_{1,\mathrm{exptl}} + 2M_1 m - \frac{2\alpha M_1}{B^3}\left[(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] = f_0 - b_1 M_1(m^2/m^\circ) \tag{15}$$

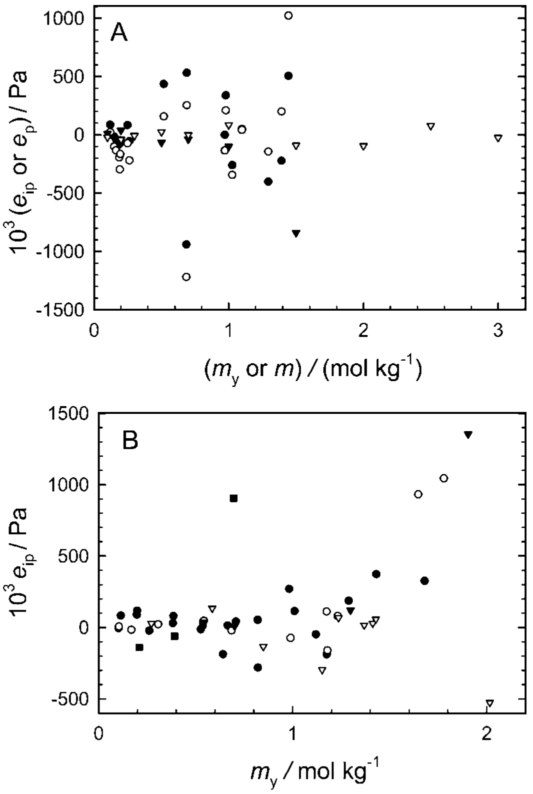

Figure 1. Difference, e_{ip} in eq 17, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and alkali metal iodide (y) solutions of Robinson and Sinclair[3] and of Robinson[4] (graphs A and B) and the difference, e_p in eq 18, between the reported and predicted vapor pressure of water over the RbI (graph A, symbol ▼) and CsI (A, ▽) solution from the data of Robinson[6] as a function of the molality m of the solution. The reported vapor pressures for graph A were obtained from the given osmotic coefficients using eqs 3 and 4. The isopiestic vapor pressures for both graphs were calculated by eqs 3 and 4 using eq 2 with $B = 1.3\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.011$ for KCl and with the parameter values shown in Table 3 for LiI (graph A) and with the recommended parameter values for the other alkali metal iodides (graph B). Symbols: ●, LiI with $B = 2.1\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.289$ (A), NaI (B); ○, LiI with $B = 1.8\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.311$ (A), KI from ref 4 (B); ▼, KI from ref 5 (B); ▽, RbI from ref 4 (B); ■, CsI from ref 4 (B).

where $a_{1,\text{exptl}}$ was calculated from the reported osmotic coefficient using eq 3. The standard error s_0 in this table for CsI solutions was calculated from the equation

$$s_0 = \sqrt{\sum_{i=1}^{N} (p_{i,\text{obsd}} - p_{i,\text{pred}})^2/(N - P)} \qquad (16)$$

where the observed vapor pressure was calculated from the reported osmotic coefficient.

The new Hückel equations suggested in Table 3 can first be tested by predicting the vapor pressures of water over the isotonic alkali metal iodide and potassium chloride solutions considered in this table. The vapor pressures of both solutions in every point were calculated using eqs 2, 3, and 4 with the suggested activity parameters. The results are shown in the two graphs of Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{ip} = p_x - p_y \qquad (17)$$

and presented as a function of the molality m_y. The results for LiI solutions are shown in graph A of this figure, and the results for the other iodide solutions are shown in graph B. The parameters for CsI were tested by predicting the observed vapor pressures (calculated from the reported osmotic coefficients) with the recommended parameter values. The results are shown in graph A of Figure 1 where the vapor pressure error (e_p) is defined by

$$e_p = p(\text{observed}) - p(\text{predicted}) \qquad (18)$$

and presented as a function of the molality m. Almost all absolute e_{ip} errors in these tests at molalities smaller than 1.5 $\text{mol}\cdot\text{kg}^{-1}$ are appreciably less than 1 Pa (= 0.0075 mmHg), and the errors form for all sets a pattern that is not far from random. Thus, the results from these dilute alkali metal iodide solutions support well the suggested parameter values. For CsI solutions, the new Hückel equation applies very well to all data of Robinson[6] (i.e., up to 3 $\text{mol}\cdot\text{kg}^{-1}$) because the largest absolute e_p error is less than 0.1 Pa (= 0.0008 mmHg).

When comparing the new value of parameter B (closely related to the ion-size parameter) for LiI [i.e., that of $B_{\text{LiI}} = 2.1\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$] to the value presented in ref 18 for LiCl [1.5 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$] and the new B values for NaI and KI [i.e., those of (1.60 and 1.45) $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, respectively] to the corresponding values for NaCl [1.4 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$] and KCl [$B = 1.30\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$] in ref 10, it is observed that the LiI value is not in line with the other values. A more reasonable value would be $B_{\text{LiI}} = 1.8\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$. 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 the both B values of LiI are shown in graph A of Figure 1, and they are very comparable with each other. Below, the results with the extended Hückel equations of LiI will also reveal that there is no significant difference between the B values of (1.8 and 2.1) $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ to predict these more concentrated data. For all LiI solutions, therefore, the value of $B = 1.8\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ is now recommended.

The new Hückel equation with $B = 1.45\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0490$ for KI was then tested with the isopiestic data of Robinson and Wilson[5] containing only four points that are from solutions sufficiently dilute for this test. They were predicted with the parameter values, and the results are shown as e_{ip} errors (see eq 17) in graph B of Figure 1. These points support well the new parameters for KI. The new Hückel parameters of $B = 1.12\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.0026$ for RbI were then tested with the reported osmotic coefficients of Robinson[6] (as for CsI solutions, the original isopiestic data are not available). The results are shown as e_p errors (see eq 18) in graph A of Figure 1, and they support well the suggested parameter values up to $m = 1.5\ \text{mol}\cdot\text{kg}^{-1}$. The parameter values of $B = 0.88\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.0116$ for CsI were finally tested with the isopiestic data of Robinson[4] for KCl and CsI solutions. The results are shown in graph B of Figure 1 as e_{ip} errors (see eq 17), but these errors do not support the parameter values above a molality of 0.6 $\text{mol}\cdot\text{kg}^{-1}$ (only four points of these dilute solutions are shown in the graph). The next point has the CsI molality of 1.096 $\text{mol}\cdot\text{kg}^{-1}$, and the e_{ip} error is close to +3 Pa (= +0.022 mmHg). In the following points, these errors became gradually larger as the molality increases and are thus

Table 4. Cell Potential Differences (*E*) Measured by Harned and Douglas[11] on Concentration Cells of Type 19 for NaI and KI Solutions and the Errors (e_E) Obtained for the Suggested Hückel Equations from These Data

electrolyte	m_1 mol·kg^{-1}	m_2 mol·kg^{-1}	E^a int. mV	$e_E{}^b$ mV
NaI	0.1037	0.0307	57.91	−0.633
	0.1008	0.3020	−53.60	−0.574
	0.1003	0.4970	−78.18	−0.119
	0.0997	1.003	−115.00	0.214
KI	0.1008	0.3017	−52.04	−0.550
	0.1020	0.5103	−75.87	−0.138
	0.1052	1.017	−107.47	−0.034
	0.0988	2.004	−145.32	−0.868

[a] 1 int. V = 1.00034 V. [b] $e_E = E(\text{observed}) - E(\text{predicted})$, and the latter value was calculated from eq 20 with $B = 1.60$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1549$ for NaI solutions and with $B = 1.450$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0490$ for KI solutions.

far outside of the scale of the graph. It seems that this set is erroneous, and it is not considered any more here (see also ref 6).

The recommended Hückel parameters for NaI and KI solutions (see Table 3) were then tested with cell potential difference (= cpd) data. Harned and Douglas[11] have measured the following concentration cells without transference

$$\mathrm{Ag(s)|AgI(s)|MI(aq,}\ m_1\mathrm{)|M(Hg)|MI(aq,}\ m_2\mathrm{)|AgI(s)|Ag(s)} \tag{19}$$

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

$$E = -\frac{2RT}{F}\ln(m_2/m_1) - \frac{2RT}{F}\ln(\gamma_2/\gamma_1) \tag{20}$$

These data were predicted by means of the recommended Hückel equations for NaI and KI solutions, and the errors defined by the equation

$$e_E = E(\text{observed}) - E(\text{predicted}) \tag{21}$$

are also shown in Table 4. They support quite well the tested Hückel equations at all molalities considered.

Determination of Parameters b_1 and b_2 for More Concentrated Alkali Metal Iodide 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

$$\begin{aligned} f_3 &= \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3} \times \\ &\quad \left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \\ &\quad \frac{4M_1 b_{2,y} m_y^3}{3(m^o)^2} \\ &= f_0 - b_{1,y}M_1(m_y^2/m^o) = f_0 + k_3 m_y^2 \end{aligned} \tag{22}$$

where $k_3 = -b_{1,y}M_1/m^o$ were used in the present study for the estimation of the Hückel parameters for more concentrated LiI, NaI, KI, and RbI 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 $b_{2,y}$ has been fixed, eq 22 represents an equation of the straight line f_3 versus m_y^2. The straight line should go through the origin, and therefore, parameter $b_{2,y}$ 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 as many data points as possible were included in these estimations. The results of these calculations are shown in Table 5. For KI solutions, the parameters were also estimated from the set of Robinson and Wilson,[5] but those obtained from the set of Robinson[4] are here recommended. This choice is based below on the vapor pressure data of Makarov et al.[15] The parameter values from both of these KI sets agree, however, quite well with each other. For LiI data, the results with $B = 2.1$ (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 of 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 suggested activity parameters. The results are shown in Figure 2 where the isopiestic vapor pressure error (defined by eq 17) is presented as a function of the molality m_y. Graph A shows the results for both sets of parameters for LiI solutions and graph B for the other iodide 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 LiI solutions (graph A), both sets of parameters apply well to the data, and thus the more reasonable values [i.e., those of $B = 1.8$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.3172$, and $b_2 = 0.0046$] will only be considered below despite less points could be included in their determination.

The recommended activity parameters in Table 5 can further be tested with the experimental isopiestic data reported by Robinson and Wilson[5] for KI solutions against KCl solutions and with the osmotic coefficients reported by Robinson[6] for RbI solutions, by Makarov et al.[14] for NaI solutions (based on isopiestic data against $CaCl_2$ solutions), by Miller and Sheridan[12] for NaI solutions (based on isopiestic data against H_2SO_4 solutions), by Jakli and Van Hook[13] for NaI solutions [based on vapor pressure measurements at various temperatures from (−0.2 to 89) °C at molalities (4, 8, and 10) mol·kg^{-1}], and by Makarov et al.[15] for KI solutions (based on isopiestic measurements against NaCl or $CaCl_2$ solutions). For the KI data set of Robinson and Wilson,[5] the results are shown in Figure 2B as isopiestic vapor pressure errors (see eq 17). For the other sets, the vapor pressure errors were calculated from the osmotic coefficients and are shown in graph A of Figure 3 for the NaI

Table 5. Results from the Parameter Estimation for the Extended Hückel Equations (Equations 5 and 6) of Alkali Metal Iodides at 25 °C by the Least-Squares Fitting with Equation 22

	$[B/(m^o)^{-1/2}]^a$	b_2	b_1	$s(b_1)^b$	N^c	$(m_{max}/m^o)^d$	s_0^e/Pa	ref
LiI	2.1	0.0218	0.2602	0.0012	32	3.152	1.0	3
LiI	$1.8^{f,g}$	0.0046^f	0.3172^f	0.0011	27	2.529	0.6	3
NaI	1.6	0.0074	0.1478	0.0006	33	3.740	0.8	4
KI	1.45	0.0004^f	0.0499^f	0.0005	24	4.581	0.8	4
KI	1.45	−0.0010	0.0581	0.0002	16	4.601	0.2	5
RbI	1.12	0.0024	0.0029	0.0003	20	5.102	0.6	4
CsI	0.88^h	0	-0.0116^h	0.0002	10	3		6

[a] Taken from Table 3 and $m^o = 1$ 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 iodide 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 18). [f] Recommended value. [g] See footnote *e* to Table 3. [h] Parameters were estimated by using eq 15 (see Table 3).

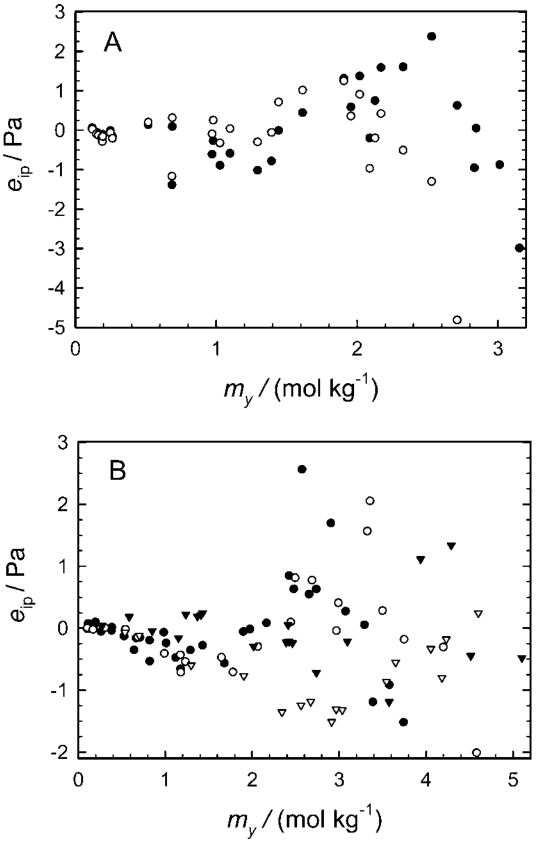

Figure 2. Difference, e_{ip} in eq 17, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and alkali metal iodide (y) solutions for the isopiestic data sets considered in Table 5. 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 LiI and with the recommended parameter values for the other alkali metal iodides. Symbols: ●, LiI with $B = 2.1$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2602$, and $b_2 = 0.0218$ (graph A); NaI (graph B); ○, LiI with $B = 1.8$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.3172$, and $b_2 = 0.0046$ (A); KI from ref 4 (B); ▼, RbI (B); ▽, KI from ref 5 (B). The errors of the four strongest points where m_y = (2.832, 2.845, 3.012, and 3.152) mol·kg^{-1} from ref 3 for the recommended Hückel equation of LiI are outside of the scale of graph A of the figure. These errors are (−7.8, −6.9, −10.1, and −14.3) Pa, respectively.

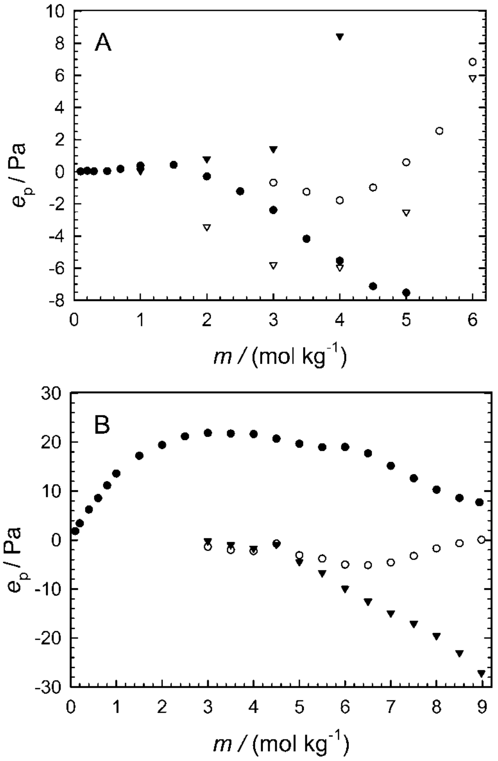

Figure 3. Difference, e_p in eq 18, between the reported and predicted vapor pressure of water over alkali metal iodide solutions as a function of the molality m of the solution. The reported vapor pressures were obtained from the reported osmotic coefficients[6,12−15] using eqs 3 and 4. The vapor pressures were predicted using eqs 3 and 4 with eq 6 with the suggested parameter values shown in Table 5. Symbols: ●, RbI from the data of Robinson[6] (graph A); KI from the data of Pearce et al.[16] (graph B); ○, NaI from the data of Makarov et al.[14] (A); KI with $B = 1.45$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.0499$, and $b_2 = 0.0004$ from the data of Makarov et al.[15] (B); ▼, NaI from the data of Miller and Sheridan[12] (A); KI with $B = 1.45$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.0581$, and $b_2 = -0.0010$ from the data of Makarov et al.[15] (B); ▽, NaI from the data of Jakli and Van Hook[13] (A).

and RbI sets and in graph B for the KI set in the same way as in Figure 1A for the RbI or CsI set of Robinson[6] (see eq 18). According to Figure 2B, the recommended KI parameters are also supported very satisfactorily with all isopiestic data of Robinson and Wilson[5] and, according to Figure 3B, with the osmotic coefficient data of Makarov et al.[15] up to the molality of the saturated solution (i.e., up to 8.98 mol·kg^{-1}). It is important to observe that the parameter values presented in Table 5 for KI on the basis of the data of Robinson and Wilson[5] do not explain the osmotic coefficients from Makarov et al.[15] as well as those recommended in this table. This is shown in Figure 3B.

The reported osmotic coefficients of Robinson[6] support in Figure 3A the recommended RbI parameters well but only up to a molality of 3.0 mol·kg^{-1}. The osmotic coefficients of Makarov et al.[14] support well the recommended NaI parameters up to a molality of 5.5 mol·kg^{-1}, and those of Jakli and Van Hook[13] support these parameters satisfactorily up to 5.0 mol·kg^{-1}. At molalities above 3 mol·kg^{-1}, the osmotic coefficients of Miller and Sheridan[12] are probably erroneous because they do not agree with the recommended values and the other

Table 6. Mean Activity Coefficient Obtained from the Solubility Data for the Saturated Solution of KI, RbI, and CsI at 25 ºC (γ_{obs}) and That Obtained by the Extended Hückel Equation with the Recommended Parameter Values (γ_{pred}) for This Solution

electrolyte	$\Delta_f G^o(cr)$[a] / kJ·mol^{-1}	$\Delta_f G^o(aq)$[b] / kJ·mol^{-1}	(m_s/m^o)	γ_{obs}	γ_{pred}	$e_{E,GC}$[d] / mV
KI	−324.892	−334.850	8.98	0.830	0.837	0.4
RbI	−328.860	−335.560	7.63	0.506	0.532	2.6
CsI	−340.580	−343.590	3.27	0.42	0.56	−14.4

[a] The standard molar Gibbs energy of formation for the crystalline state. [b] The standard molar Gibbs energy of formation for aqueous solutions at infinite dilution. [c] The molality of the saturated solution (m^o = 1 mol·kg^{-1}). [d] Galvanic cell deviation in millivolts that has been calculated from the equation $e_{E,GC} = -(2RT)/(F)\ln(\gamma_{obs})/(\gamma_{pred})$.

literature values. The recommended KI parameters were attempted to test, in addition, with the vapor pressure data of Pearce et al.[16] 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[16]). These results are shown as vapor pressure errors in Figure 3B. As can be seen, these data are not sufficiently accurate for the use in a critical evaluation of the validity of the suggested Hückel parameters.

The new parameter values for the Hückel equations of KI, RbI, and CsI probably apply up to the saturated solutions. Therefore, these values can also be tested with solubility data. The NBS tables of thermodynamic properties[30] give the values shown in Table 6 for the standard molar Gibbs energy of formation for the crystalline state [$\Delta_f G^o(cr)$] and for aqueous solutions at infinite dilution [$\Delta_f G^o(aq)$] at 25 °C for these three salts. These values are related to the solubility product (K_{sp}), to the molality of the saturated solution (m_s), and to the mean activity coefficient of that solution by equation

$$-RT\ln K_{sp} = -2RT\ln(\gamma m_s/m^o) = \Delta_f G^o(aq) - \Delta_f G^o(cr) \tag{23}$$

In this table are shown the observed activity coefficients (obtained using eq 23) and those predicted with the new extended Hückel equations for KI, RbI, and CsI solutions. The molalities of the saturated solution of these salts were taken from refs 15, 28, and 31, respectively. The observed and predicted activity coefficients correspond well to each other for KI solutions, satisfactorily for RbI solutions, but poorly for CsI solutions. In the last case, the predicted value seems to be more reliable because of the experimental evidence obtained with the reported osmotic coefficients of Robinson[6] (see Figure 1A).

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 and Tables 4 and 6), 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 iodides at 25 °C have been calculated on the basis of these equations. For LiI, the new values are given in Table 7, for NaI in Table 8, for KI in Table 9, for RbI in Table 10, and for CsI in Table 11. Also, the vapor pressures of water are included in these tables.

For all other alkali metal iodides than CsI, the values of activity quantities have been calculated in these tables by using the parameter values suggested for the extended Hückel equations. For CsI solutions, only the Hückel equation was estimated above. 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 between these two values is always quite small [less than 0.6 mV for galvanic cell deviation for γ (the definition will be given below) and less than 0.7 Pa (= 0.005 mmHg) for vapor pressure deviation for ϕ]. For KI solutions in Table 9, the values of activity quantities from the Hückel equation agree well with those recommended in this table up to a molality of 2.5 mol·kg^{-1}.

Table 7. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Lithium Iodide Solutions at 25 °C as a Function of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.815(0.814)	0.954	3.1577
0.2	0.797(0.795)	0.962(0.961)	3.1467
0.3	0.796(0.794)	0.974(0.973)	3.1354(3.1355)
0.4	0.803(0.800)	0.988(0.986)	3.1238(3.1239)
0.5	0.814(0.811)	1.003(1.001)	3.1118(3.1120)
0.6	0.829(0.824)	1.019(1.016)	3.0996(3.0998)
0.7	0.846(0.840)	1.035(1.031)	3.0870(3.0872)
0.8	0.864(0.858)	1.051(1.047)	3.0740(3.0744)
0.9	0.885(0.877)	1.068(1.062)	3.0608(3.0613)
1.0	0.907(0.897)	1.084(1.078)	3.0472(3.0479)
1.2	0.955	1.118	3.0191
1.4	1.009	1.152	2.9897
1.6	1.068	1.186	2.9591
1.8	1.133	1.221	2.9274
2.0	1.202	1.256	2.8945
2.5	1.403	1.344	2.8074
3.0	1.647	1.433	2.7138

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.8 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.311, and the other activity values with the extended Hückel equation with B = 1.8 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.3172, and b_2 = 0.0046.

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

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.793(0.794)	0.941(0.942)	3.1579
0.2	0.759	0.939	3.1472
0.3	0.742(0.744)	0.942	3.1365
0.4	0.734(0.735)	0.947	3.1257(3.1256)
0.5	0.731(0.732)	0.953	3.1147(3.1146)
0.6	0.730(0.731)	0.960	3.1035
0.7	0.731(0.732)	0.967	3.0922
0.8	0.734(0.735)	0.975	3.0808
0.9	0.738(0.739)	0.983(0.982)	3.0692
1.0	0.743	0.992(0.990)	3.0574(3.0575)
1.2	0.756(0.755)	1.009(1.006)	3.0334(3.0337)
1.4	0.772(0.768)	1.027(1.022)	3.0087(3.0094)
1.6	0.790	1.045	2.9834
1.8	0.810	1.064	2.9574
2.0	0.832	1.083	2.9308
2.5	0.896	1.133	2.8613
3.0	0.971	1.185	2.7877
3.5	1.059	1.239	2.7102
4.0	1.162	1.296	2.6287
4.5	1.281	1.356	2.5434
5.0	1.420	1.417	2.4546
5.5	1.580	1.481	2.3625
6.0	1.765	1.548	2.2675

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.6 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.1549 and the other activity values with the extended Hückel equation with B = 1.6 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.1478, and b_2 = 0.0074.

Comparison of the Recommended Activity Values to the Literature Values. The values in Tables 7 to 11 were compared to the activity and osmotic coefficients presented by Robinson

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

m / $\mathrm{mol \cdot kg^{-1}}$	γ	ϕ	p / kPa
0.1	0.779	0.933	3.1580
0.2	0.734	0.924	3.1476
0.3	0.709	0.921(0.920)	3.1372
0.4	0.693(0.692)	0.920(0.919)	3.1269
0.5	0.680	0.920	3.1165
0.6	0.671	0.921	3.1061(3.1062)
0.7	0.664	0.923(0.922)	3.0957(3.0958)
0.8	0.659(0.658)	0.925(0.924)	3.0853
0.9	0.655(0.654)	0.927(0.926)	3.0748(3.0749)
1.0	0.651(0.650)	0.929(0.928)	3.0643(3.0644)
1.2	0.646(0.645)	0.934(0.933)	3.0432(3.0433)
1.4	0.643(0.642)	0.939(0.938)	3.0220(3.0221)
1.6	0.642(0.640)	0.945(0.943)	3.0006(3.0009)
1.8	0.642(0.640)	0.950(0.949)	2.9792(2.9795)
2.0	0.642(0.640)	0.956(0.954)	2.9576(3.0580)
2.5	0.646(0.643)	0.971(0.968)	2.9033(2.9040)
3.0	0.653	0.985	2.8484
3.5	0.662	1.000	2.7931
4.0	0.673	1.015	2.7373
4.5	0.685	1.030	2.6811
5.0	0.698	1.045	2.6247
5.5	0.712	1.061	2.5680
6.0	0.727	1.076	2.5111
6.5	0.744	1.091	2.4541
7.0	0.761	1.106	2.3971
7.5	0.779	1.122	2.3400
8.0	0.797	1.137	2.2829
8.5	0.817	1.153	2.2259
8.98	0.837	1.168	2.1714

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.45\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.049$ and the other activity values with the extended Hückel equation with $B = 1.45\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = 0.0499$, and $b_2 = 0.0004$.

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

m / $\mathrm{mol \cdot kg^{-1}}$	γ	ϕ	p / kPa
0.1	0.760	0.922	3.1581
0.2	0.705(0.704)	0.906	3.1480
0.3	0.672(0.671)	0.898(0.897)	3.1380
0.4	0.648(0.647)	0.892(0.891)	3.1281
0.5	0.630(0.628)	0.889(0.887)	3.1183(3.1184)
0.6	0.616(0.613)	0.886(0.884)	3.1085(3.1086)
0.7	0.604(0.601)	0.884(0.881)	3.0987(3.0989)
0.8	0.594(0.590)	0.883(0.880)	3.0890(3.0893)
0.9	0.585(0.581)	0.882(0.878)	3.0793(3.0796)
1.0	0.578(0.573)	0.881(0.877)	3.0696(3.0700)
1.2	0.565(0.559)	0.881(0.875)	3.0502(3.0509)
1.4	0.555	0.881	3.0308
1.6	0.547	0.882	3.0115
1.8	0.540	0.883	2.9922
2.0	0.534	0.885	2.9729
2.5	0.523	0.889	2.9247
3.0	0.516	0.895	2.8763
3.5	0.512	0.902	2.8278
4.0	0.509	0.910	2.7791
4.5	0.508	0.919	2.7300
5.0	0.509	0.928	2.6806

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.12\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = -0.0026$ and the other activity values with the extended Hückel equation with $B = 1.12\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = 0.0029$, and $b_2 = 0.0024$.

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

m / $\mathrm{mol \cdot kg^{-1}}$	γ	ϕ	p / kPa
0.1	0.747	0.914	3.1582
0.2	0.684	0.893	3.1483
0.3	0.646	0.881	3.1386
0.4	0.618	0.872	3.1290
0.5	0.596	0.865	3.1196
0.6	0.578	0.860	3.1102
0.7	0.563	0.856	3.1009
0.8	0.550	0.852	3.0917
0.9	0.539	0.849	3.0825
1.0	0.529	0.847	3.0734
1.2	0.512	0.842	3.0553
1.4	0.498	0.839	3.0373
1.6	0.486	0.836	3.0195
1.8	0.475	0.834	3.0018
2.0	0.466	0.832	2.9843
2.5	0.447	0.827	2.9411
3.0	0.431	0.824	2.8986

[a] The activity values have been calculated with the Hückel equation with $B = 0.88\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = -0.0116$.

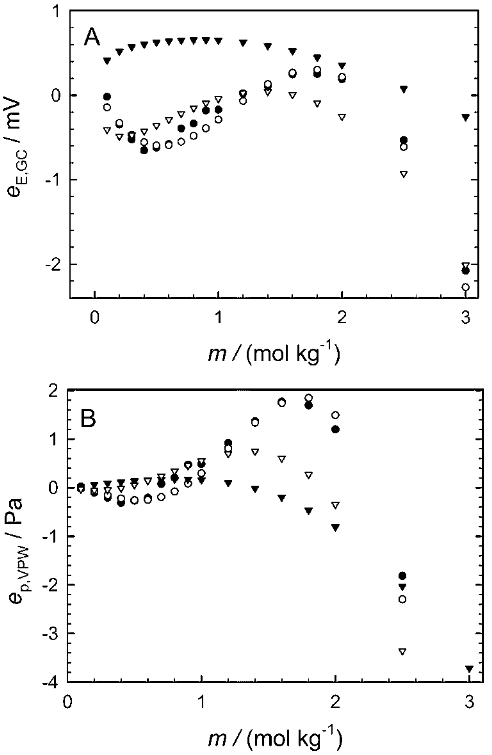

Figure 4. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 24, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 25, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for LiI solutions as a function of the molality m (see Table 7). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[23] ▼, Pitzer and Mayorga;[25] ▽, the extended Hückel equation with $B = 2.1\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = 0.2602$, and $b_2 = 0.0218$ (see text and Table 5). The errors for the points where $m = 3.0\ \mathrm{mol \cdot kg^{-1}}$ from the data of Robinson and Stokes, from the equation of Hamer and Wu, and from the latter extended Hückel equation are outside of the scale of graph B of this figure. The values of these errors are (−9.9, −11.0, and −9.0) Pa, respectively.

and Stokes,[2] Hamer and Wu,[23] and Pitzer and Mayorga.[25] The results of the comparison of the activity coefficients are shown in graphs A of Figures 4, 5, 6, 7, and 8 for LiI, NaI, KI, RbI, and CsI solutions, respectively, and the results for the osmotic coefficients in graphs B of these figures. The quantity presented on the y axis in these graphs is the cell potential deviation (graph A, $e_{E,GC}$) or the vapor pressure deviation (graph B, $e_{p,VPW}$).

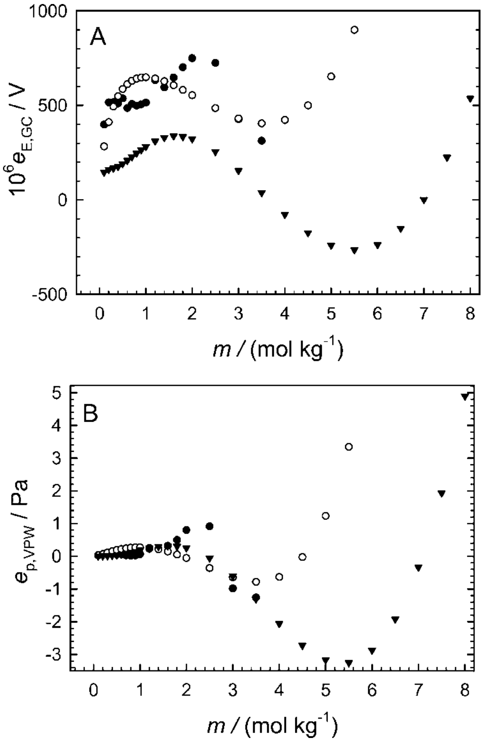

Figure 5. Deviation, expressed as galvanic cell error $e_{\mathrm{E,GC}}$ in eq 24, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{\mathrm{p,VPW}}$ in eq 25, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for NaI solutions as a function of the molality m (see Table 8). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[23] ▼, Pitzer and Mayorga.[25]

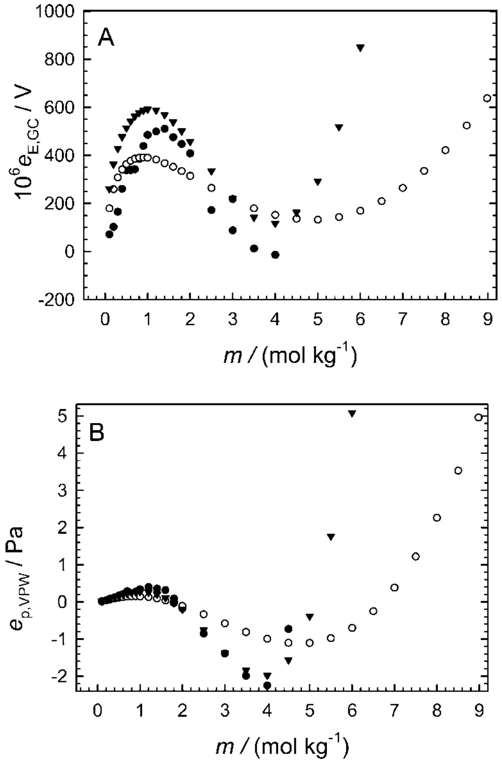

Figure 6. Deviation, expressed as galvanic cell error $e_{\mathrm{E,GC}}$ in eq 24, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{\mathrm{p,VPW}}$ in eq 25, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for KI solutions as a function of the molality m (see Table 9). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[23] ▼, Pitzer and Mayorga.[25]

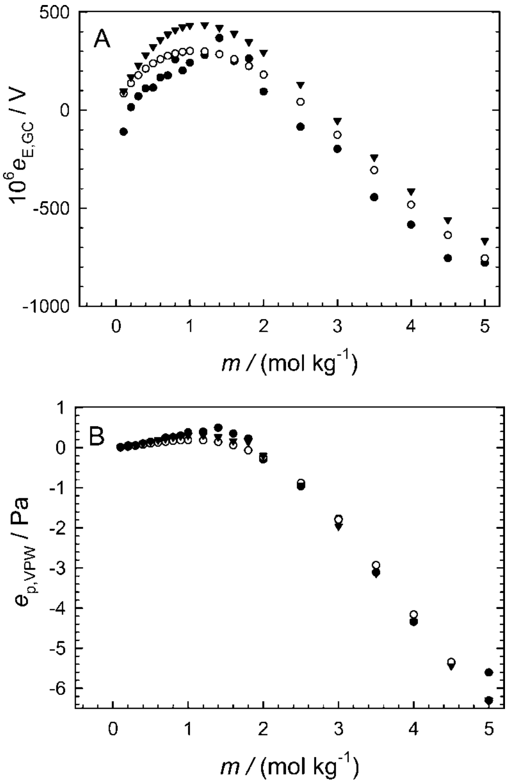

Figure 7. Deviation, expressed as galvanic cell error $e_{\mathrm{E,GC}}$ in eq 24, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{\mathrm{p,VPW}}$ in eq 25, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for RbI solutions as a function of the molality m (see Table 10). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[23] ▼, Pitzer and Mayorga.[25]

Details from these quantities are presented, e.g., in ref 20 (see eqs 27 and 28 in that study). They are defined by equations

$$e_{\mathrm{E,GC}} = -\frac{2RT}{F}\ln\frac{\gamma(\mathrm{literature})}{\gamma(\mathrm{recd})} \tag{24}$$

and

$$e_{\mathrm{p,VPW}} = p(\mathrm{literature}) - p(\mathrm{recd}) \tag{25}$$

For the recommended values, the values obtained from eq 5 or 6 (except for CsI solutions, see above) were used.

For LiI solutions, in Figure 4 are also included the results obtained by using the extended Hückel equation with the unreasonable large value of parameter B [i.e., that of 2.1 (mol·kg^{-1})$^{-1/2}$] (see Table 5). The activity and osmotic coefficients suggested in the literature for LiI solutions agree satisfactorily in this figure with those recommended in Table 7 up to a molality of only 2.5 mol·kg^{-1} which was also the upper limit for the molalities that could be included above in the parameter estimation for the recommended model. The new γ and ϕ values from the recommended model do not agree with the literature values of Robinson and Stokes[2] and Hamer and Wu[23] as well as those obtained with the more unreasonable Hückel model considered in this figure. Nevertheless, the recommended parameters are probably more reliable because of the reasons explained above. All these results for LiI solutions have been based only on a single data set (i.e., on that of Robinson and Sinclair[3]), and new data will be required,

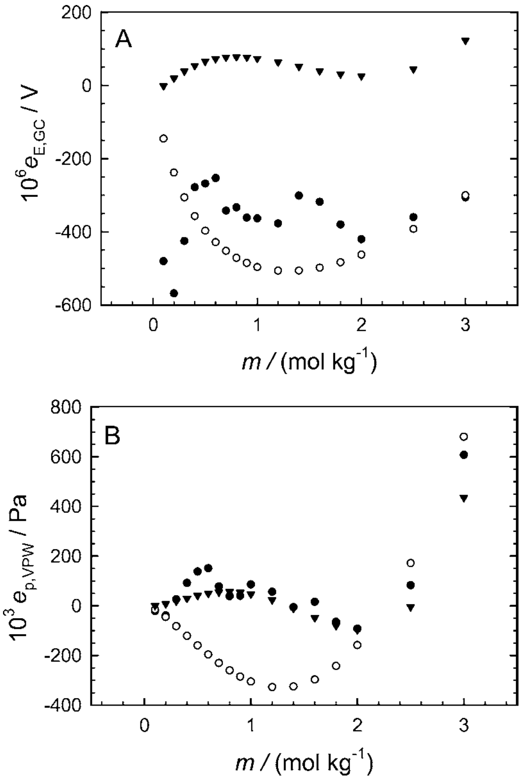

Figure 8. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 24, between the literature activity coefficients and those recommended in this study (eq 1, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 25, between the literature osmotic coefficients and those recommended in this study (eq 2, graph B) for CsI solutions as a function of the molality m (see Table 11). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[23] ▼, Pitzer and Mayorga.[25]

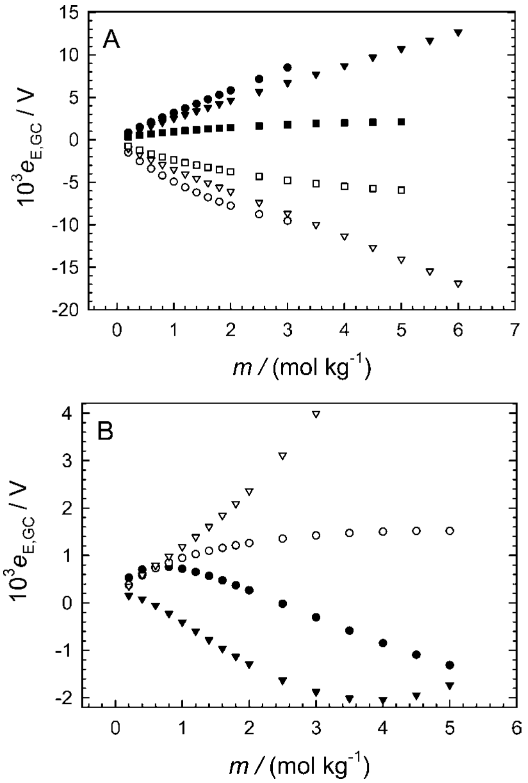

Figure 9. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 26, between the activity coefficients of alkali metal chloride[10,18,19] or iodide and those of alkali metal bromide[20] solutions as a function of the molality m. The activity coefficients have been calculated using the extended Hückel equation (eq 5) with the recommended parameter values. Symbols: ●, LiCl (graph A), RbCl (graph B); ○, LiI (A), RbI (B); ▼, NaCl (A), CsCl (B); ▽, NaI(A), CsI (B); ■, KCl (A); □, KI (A).

therefore, to solve the problems associated with the thermodynamic properties of the dilute LiI solutions.

The activity quantities suggested in the literature for NaI solutions agree satisfactorily in Figure 5 with those recommended in Table 8 up to a molality of about 5.5 mol·kg^{-1}. This molality is considerably larger than the largest molality used in the parameter estimation (i.e., that of 3.5 mol·kg^{-1}, see Table 5). This appears also with the experimental data in the error plots of Figure 3A. For the Pitzer equation, the agreement extends up to a molality of about 8 mol·kg^{-1}, but the activity values from (5.5 to 8) mol·kg^{-1} are not supported by the experimental data of Makarov et al.[14] The activity values from Hamer and Wu[23] for these concentrated solutions up to a molality of 12 mol·kg^{-1} were based mainly on the data of Makarov et al.[14] and seem more reliable than those from the new Hückel equation or from the Pitzer equation. In Figure 6, the activity and osmotic coefficients suggested in the literature for KI solutions agree quite well with those recommended in Table 9 up to a molality of about 5 mol·kg^{-1}. The three-parameter equation of Hamer and Wu[23] predicts in this case the activity or osmotic coefficients much better than they are reported (i.e., only up to a molality of 4.5 mol·kg^{-1}) because it applies, according to this figure, quite well up to the molality of the saturated solution (i.e., up to 8.98 mol·kg^{-1}). In the recent study,[29] the parameters recommended here for the extended Hückel equations of KI and RbI (and also of several salts other than iodides) have been used in the tests of the many literature activity coefficient equations especially for concentrated solutions up to the saturation.

Figures 3A and 7B show that the activity and osmotic coefficients in the tables of Robinson and Stokes[2] solutions for RbI have been determined in more concentrated solutions from the reported osmotic coefficient of Robinson,[6] and the Hückel parameters recommended here do not predict these osmotic coefficients very well. However, it seemed to me more reasonable to estimate the Hückel parameters for this electrolyte from the real experimental data[4] than from the smoothed osmotic coefficients.[6] It is shown in Figure 2B, in addition, that the Hückel parameters apply very well to the experimental data[4] used in their estimation (also in the most concentrated solutions). The deviations between the present values and literature values for the activity quantities in these concentrated solutions in Figure 7 are not very large, and it is not clear at all whether the more recent values from ref 6 are more reliable than those from ref 4. The activity values from the Hamer and Pitzer equations follow closely the activity and osmotic coefficients of Robinson and Stokes. The agreement in this figure for all values is good up to a molality of 3 mol·kg^{-1}. Figure 8 shows that the activity and osmotic coefficients of Robinson and Stokes[2] and of Hamer and Wu[23] for CsI solutions agree quite well and those of Pitzer and Mayorga[25] very well with the values suggested in Table 11 to all molalities considered in this figure.

Comparison of Activity and Osmotic Coefficients of Alkali Metal Halides. In Figure 9 are compared the activity coefficients of alkali metal chlorides or iodides to those of alkali metal bromides. The differences are also presented in this case as galvanic cell deviations defined by

$$e_{E,GC} = -\frac{2RT}{F} \ln \frac{\gamma_{MX}}{\gamma_{MBr}} \qquad (26)$$

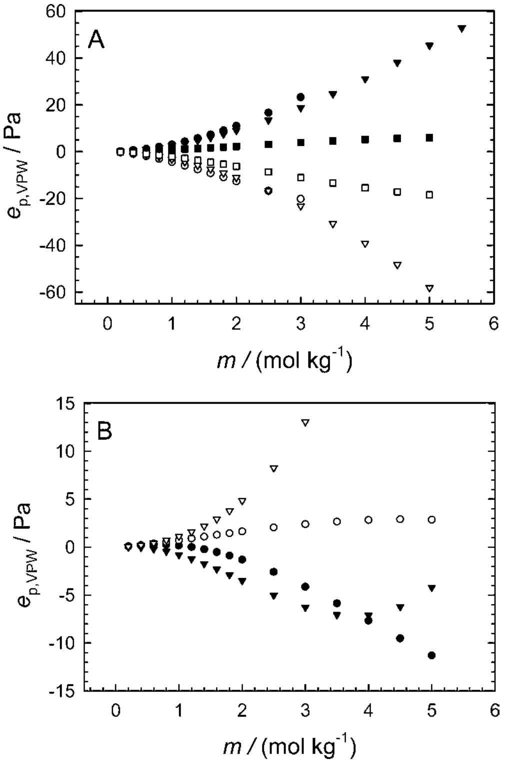

Figure 10. Deviation, expressed as vapor pressure error $e_{\mathrm{p,VPW}}$ in eq 27, between the osmotic coefficients of alkali metal chloride[10,18,19] or iodide and those of alkali metal bromide[20] solutions as a function of the molality *m*. The osmotic coefficients have been calculated using the extended Hückel equation (eq 6) with the recommended parameter values. Symbols: ●, LiCl (graph A), RbCl (graph B); ○, LiI (A), RbI (B); ▼, NaCl (A), CsCl (B); ▽, NaI(A), CsI (B); ■, KCl (A); □, KI (A).

where X is either $\mathrm{Cl^-}$ or $\mathrm{I^-}$ and these deviations are presented as a function of the molality. The recommended activity coefficients for alkali metal bromides were taken from ref 20 and those for LiCl from ref 18, for NaCl and KCl from ref 10, and for RbCl and CsCl from ref 19. The results are shown in two graphs of Figure 9. Graph A shows the results for lithium, sodium, and potassium salts and graph B for rubidium and cesium salts. The deviation plots are interesting: The activity coefficients in graph A for lithium, sodium, and potassium bromides are higher than those of the corresponding chlorides but smaller than those of the corresponding iodides. Also, the absolute galvanic cell deviation for the lithium salts is at any molality higher than that for the sodium salts and much higher than that for the potassium salts. Contrary to the results in graph A, the activity coefficients in graph B for cesium bromide are generally higher than those of the cesium iodide and smaller than those of the cesium chloride. For the rubidium salts, all deviations are small, and the activity coefficients of only rubidium chloride are known very accurately; however, the same trend is observed for the more concentrated solutions of the rubidium salts as that for the cesium salts.

In Figure 10 are similarly compared the osmotic coefficients of alkali metal chlorides or iodides to those of alkali metal bromides. The differences are presented as vapor pressure deviations defined by

$$e_{\mathrm{p,VPW}} = p_{\mathrm{MX}} - p_{\mathrm{MBr}} \tag{27}$$

where X is either $\mathrm{Cl^-}$ or $\mathrm{I^-}$ and vapor pressures were calculated from osmotic coefficients using eqs 3 and 4. The recommended osmotic coefficients for alkali metal chlorides and bromides were taken from the previous studies.[10,18−20] Graph A shows the results for lithium, sodium, and potassium salts and graph B for rubidium and cesium salts. Almost the same observations can be made in this figure as in Figure 9. The osmotic coefficients in graph A for lithium, sodium, and potassium bromides are larger than those of the corresponding chlorides but smaller than those of the corresponding iodides. Also, the absolute vapor pressure deviation for the lithium salts is at almost any molality higher than that for the sodium salts and much higher than that for the potassium salts. Contrary to the results in graph A, the osmotic coefficients in graph B for rubidium and cesium bromide are generally smaller than those of the corresponding chlorides and larger than those of the iodides. The less accurately known osmotic coefficients of cesium bromide (see above) behave probably in this graph, however, in a slightly irregular way above a molality of 3.5 $\mathrm{mol \cdot kg^{-1}}$.

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