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Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Rubidium and Cesium Chloride Solutions at 25 °C

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The Hückel equation used in this study to correlate the experimental activities of dilute RbCl and CsCl solutions up to a molality of about 3.5 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 the saturated molality of RbCl (= 7.78 mol·kg^{-1}) and up to a molality of about 8 mol·kg^{-1} for CsCl, an extended Hückel equation was used. 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 RbCl were determined from the isopiestic data measured by Rard for NaCl and RbCl solutions (*J. Chem. Eng. Data* **1984**, *29*, 443−450) and all parameters for CsCl from the isopiestic data measured by Rard and Miller for NaCl and CsCl solutions (*J. Chem. Eng. Data* **1982**, *27*, 169−173). In these estimations, the Hückel parameters determined recently for NaCl 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 RbCl and CsCl solutions. Most of these data can be reproduced within experimental error by means of the extended Hückel equation up to a molality of about 8.0 mol·kg^{-1}. Reliable activity and osmotic coefficients for RbCl and CsCl 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 Rard (RbCl, see citation above), Rard and Miller (CsCl, see citation above), and Robinson and Stokes (*Electrolyte Solutions*, 2nd ed.; Butterworths Scientific Publications: London, 1959). These values were also compared to those calculated by using the Pitzer equations with the parameters of Pitzer and Mayorga (*J. Phys. Chem.* **1973**, *77*, 2300−2308) and Pitzer (*Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, 2000; pp 100−101) and to those calculated by using the extended Hückel equation 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 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 RbCl and CsCl solutions in these tables have been based on the isopiestic data measured by Robinson and Sinclair[3] for RbCl and CsCl solutions against KCl solutions and on the more recent isopiestic data measured by Robinson for RbCl[4] and CsCl[5] solutions. In ref 4 osmotic coefficients for RbCl solutions (without the isopiestic molalities) are reported, and in ref 5 isopiestic molalities for CsCl and NaCl solutions are given. The tables of Robinson and Stokes give activity and osmotic coefficients from a molality of 0.1 mol·kg^{-1} up to 5.0 mol·kg^{-1} for RbCl and up to 6.0 mol·kg^{-1} for CsCl 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[6] for various electrolytes in their famous article[7] on the thermodynamics of single electrolytes. In 1982, Rard and Miller[8] reported new isopiestic data for CsCl and NaCl solutions and in 1984 Rard[9] for RbCl and NaCl solutions, and these data are more reliable than the previous data. In the present study, all parameter estimations were based on the data of Rard[9] and of Rard and Miller.[8] Also, the Pitzer parameters of RbCl and CsCl have been revised[8−10] by using these data.

In the present study, it is shown that reliable thermodynamic activity values for RbCl and CsCl solutions at 25 °C can also be obtained by such a simple equation as the Hückel equation up to a molality of about 3.5 mol·kg^{-1}. The form of the Hückel equation used in this investigation (see below and, e.g., refs 11 and 12) contains two parameters being 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). Additionally, it is shown here that very reliable activity values for RbCl solutions at 25 °C can be obtained up to the molality of the saturated solution (i.e., up to 7.7832 mol·kg^{-1}) and for CsCl solutions up to a molality of about 8.0 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.

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The resulting parameters for the Hückel equation (B and b_1) and for the extended Hückel equation (B, b_1, and b_2) for RbCl and CsCl solutions were tested with the data used in the parameter estimations[8,9] and, additionally, with the following data: with the isopiestic data of Robinson and Sinclair[3] for both RbCl and CsCl solutions, of Robinson[5] for CsCl solutions, of Bahia et al.[13] for CsCl solutions (the reference electrolyte in these four studies is KCl), of Frolov et al.[14] for CsCl solutions (against NaCl solutions), and of Kirgintsev and Luk'yanov for CsCl solutions (against NaCl,[15,16] LiCl,[16] and KCl[16] solutions); with the osmotic coefficients reported by Robinson[4] for RbCl solutions and by Makarov et al.[17] for concentrated RbCl and CsCl solutions; with the cell potential differences (cpd) measured by Longhi et al.[18] or Mussini et al.[19] for RbCl or CsCl solutions on cells containing a rubidium or cesium amalgam electrode, respectively, and a Ag−AgCl electrode; and with the cpd data measured by Harned and Schupp[20] and Caramazza[21] on concentration cells with two Ag−AgCl electrodes and one cesium amalgam electrode.

All tests of this study, such as for example in ref 12, were performed on the raw experimental results of appropriate measurements to test whether these could be predicted with the Hückel equations. New activity coefficients of the electrolyte and new osmotic coefficients and vapor pressures of water were tabulated using the recommended Hückel equations at rounded molalities of RbCl and CsCl. 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) in the same way as in refs 11, 12, 22, and 23.

Theory

In previous studies, it was found that the following Hückel equations apply very well to the thermodynamic properties of NaCl,[12] KCl,[12] and LiCl[23] solutions up to the molalities that are slightly higher than 1 mol·kg^{-1}

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

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

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 1.1744 (mol·kg^{-1})$^{-1/2}$, see Archer and Wang[24]], m^{o} 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 water 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 it 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[25]).

In more concentrated solutions, the following extended Hückel equations were used here as earlier[12,23] for the activity and osmotic coefficients

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

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

Hamer and Wu[26] suggested the following extended Hückel equations for the activity and osmotic coefficients of RbCl or CsCl solutions at 25 °C, and these equations apply near the saturated solution for both electrolytes (i.e., to $m = 7.8$ mol·kg^{-1} for RbCl and to $m = 11$ mol·kg^{-1} for CsCl)

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

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

where the Debye−Hückel parameter A has a value of 0.5108 (mol·kg^{-1})$^{-1/2}$ [= α/ln(10)] and the parameters being dependent on the electrolyte are: B^*(RbCl) = 1.1439 (mol·kg^{-1})$^{-1/2}$, β(RbCl) = 8.1·10^{-4}, C(RbCl) = 3.2460·10^{-3}, D(RbCl) = −2.2672·10^{-4}, E(RbCl) = 0, B^*(CsCl) = 0.975 (mol·kg^{-1})$^{-1/2}$, β(CsCl) = −8.5074·10^{-3}, C(CsCl) = 4.8702·10^{-3}, D(CsCl) = −4.0260·10^{-4}, and E(CsCl) = 1.0233·10^{-5}.

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[6,7] has the form

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

where

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

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

In eqs 9 and 11, β^0, β^1, and C^{ϕ} are the parameters that are dependent on the electrolyte. Pitzer and Mayorga[7] have determined the following values of these parameters for RbCl and CsCl at 25 °C: β^0(RbCl) = 0.0441, β^1(RbCl) = 0.1483, C^{ϕ}(RbCl) = −0.00101, β^0(CsCl) = 0.0300, β^1(CsCl) = 0.0558, and C^{ϕ}(CsCl) = 0.00038. Later,[10] the following Pitzer parameters have been recommended on the basis of the studies[8,9] from Rard's group: β^0(RbCl) = 0.0396, β^1(RbCl) = 0.15398, C^{ϕ}(RbCl) = −0.001908, β^0(CsCl) = 0.03478, β^1(CsCl) = 0.03974, and C^{ϕ}(CsCl) = −0.000496. For osmotic coefficients of water in solutions of a uniunivalent electrolyte, the Pitzer equation has the form

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

Results and Discussion

Determination of Parameters B and b_1 for Dilute RbCl Solutions and Tests of the Resulting Values. The parameter values suggested in ref 12 for the Hückel equation of NaCl seem to apply well up to a molality of about 1.5 mol·kg^{-1}, but the preliminary calculations with the isopiestic data of Rard[9] revealed that the Hückel equation for RbCl applies to much stronger solutions. In the parameter estimation for these less concentrated RbCl solutions, therefore, the extended Hückel equation of NaCl of ref 12 was used. In this determination, NaCl is the reference electrolyte (x) because the activities in its solutions are known. The activity of water in the NaCl solutions can be calculated from the isopiestic molality of the NaCl solution (m_x) using eqs 3 and 6 with the suggested values of B = 1.4 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.0699, and b_2 = 0.0062. RbCl is now the tested electrolyte (y), and the molality of the isotonic RbCl solution is thus regarded as the response variable (m_y). In isopiestic equilibrium, the condition $a_{1,x} = a_{1,y}$ is valid, and thus the following equation can be derived with eqs 2 and 3 for the determination of B and b_1 for RbCl (see ref 12)

$$f_1 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] = f_0 - b_{1,y}M_1(m_y^2/m^{\circ}) = f_0 + k_1 m_y^2 \quad (13)$$

where $k_1 = -b_{1,y}M_1/m^{\circ}$. 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 $b_{1,y}$ 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.

In the determination of the Hückel parameters for RbCl, the points where the RbCl molality is less than 3.7 mol·kg^{-1} could be included. This means that 51 points in the set of Rard[9] were taken into account in the least-squares fitting with eq 13. The following results were obtained: B_y = 1.04 (mol·kg^{-1})$^{-1/2}$ and $b_{1,y}$ = 0.03320 ± 0.00013 where the standard deviation is also given. The estimated parameters can first be tested by predicting the vapor pressures of water over these isotonic rubidium and sodium chloride solutions. The vapor pressures of both solutions were calculated by using eqs 2 (or 6), 3, and 4 with the suggested activity parameters. The results are shown in Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{ip} = p_x - p_y \quad (14)$$

and presented as a function of the molality m_y. The largest absolute error in this plot for the points used in the estimation is less than 0.4 Pa (= 0.003 mmHg), and the errors form a pattern that is not far from random. Thus, the results of the less concentrated solutions from Rard's set[9] support well the suggested parameter values.

The errors for the most dilute solutions up to a RbCl molality of 1.0441 mol·kg^{-1} [the number of points (N) is 9] in Figure 1 are all negative of the order of 0.13 Pa (= 0.001 mmHg). Another Hückel equation was determined from these dilute points (up to m = 1.561 mol·kg^{-1}, N = 16) in the same way by using for NaCl the Hückel equation with B = 1.4 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.072.[12] The parameter values of B = 1.16 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.0071 ± 0.0003 were obtained for this equation. It will be shown below, however, that this equation gives in dilute solutions only slightly different activity and osmotic coefficients from those obtained with the equation with B = 1.04 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.0332.

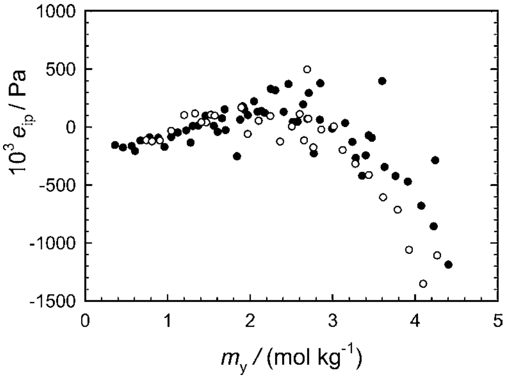

Figure 1. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and that over the tested (y) as a function of the molality of the tested solution (m_y) ●, in the isotonic NaCl (x) and RbCl (y) solutions of Rard;[9] and ○, in the isotonic NaCl (x) and CsCl (y) solutions of Rard and Miller.[8] The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with B = 1.4 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.0699, and b_2 = 0.0062 for NaCl (see ref 12) and eq 2 with B_{RbCl} = 1.04 (mol·kg^{-1})$^{-1/2}$, $b_{1,RbCl}$ = 0.0332, B_{CsCl} = 0.84 (mol·kg^{-1})$^{-1/2}$, and $b_{1,CsCl}$ = 0.0341.

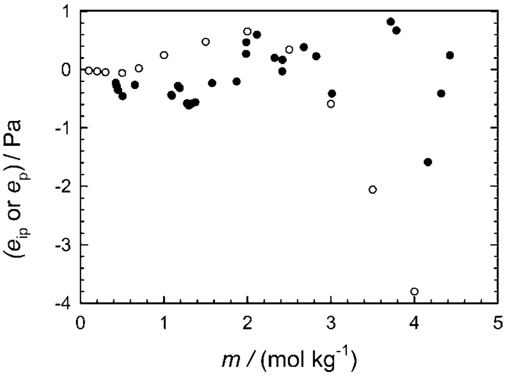

Figure 2. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and that over the tested (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and RbCl (y) solutions of Robinson and Sinclair[3] (symbol ●) and the difference, e_p in eq 15, between the reported and predicted vapor pressure of water over the RbCl solution from the data of Robinson[4] (symbol ○) as a function of the molality m of the solution. The vapor pressures for the KCl solutions[3] were obtained from eqs 3 and 4 with eq 6 with B = 1.3 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.01324, and b_2 = 0.0036 (see ref 12), and the reported vapor pressures were obtained from the osmotic coefficients of Robinson[4] using eqs 3 and 4. The vapor pressures for RbCl solutions were predicted using eqs 3 and 4 with eq 2 with B = 1.04 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.0332. The result from the point for which m_{KCl} = 3.136 mol·kg^{-1} and m_{RbCl} = 3.064 mol·kg^{-1} was omitted as a probable outlier from the set of ref 3.

The Hückel equation with B = 1.04 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.0332 was then tested with the isopiestic data of Robinson and Sinclair[3] and with the reported osmotic coefficients of Robinson[4] (the original isopiestic data on which these osmotic coefficients were based are not available in the literature). The results are shown in Figure 2. In the calculation of the isopiestic errors (see eq 14) from the set of Robinson and Sinclair,[3] the values of B = 1.3 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.01324, and b_2 = 0.0036 were used for KCl (see ref 12). The osmotic coefficients reported by Robinson[4] were first converted into the vapor pressures of water

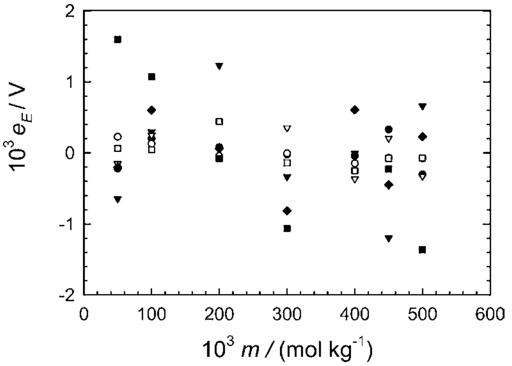

Figure 3. Deviation, e_E in eq 18, between the observed and predicted cell potential difference (cpd) from the data measured by Longhi et al.[18] in RbCl solutions on cell 16 as a function of molality *m*. The predicted cpd was calculated using eq 17 where eq 1 with $B = 1.04$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0332$ was used for the activity coefficients and the following values were used for the standard cpds: ●, $x = 0.000820$, $E^o = 2.01107$ V; ○, 0.001778, 2.03316; ▼, 0.002690, 2.04633; ▽, 0.007070, 2.08010; ■, 0.01187, 2.10200; □, 0.01344, 2.11097; ◆, 0.02121, 2.13994.

by using eqs 3 and 4, and the vapor pressure errors were calculated by the equation

$$e_p = p(\text{reported}) - p(\text{predicted}) \qquad (15)$$

and presented as a function of the molality. All vapor pressures from the data of Robinson and Sinclair[3] and from those of Robinson[4] support quite well the suggested Hückel equation for RbCl up to a molality of 4.5 and up to 3.5 mol·kg^{-1}, respectively.

The estimated Hückel parameters for RbCl [i.e., those of *B* = 1.04 (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0332$] can also be tested with cpd data. Longhi et al.[18] have measured directly RbCl solutions on amalgam cells of the following type

$$\text{M(Hg}, x)|\text{MCl(aq}, m)|\text{AgCl(s)}|\text{Ag(s)} \qquad (16)$$

where in this case M is Rb$^+$ (or Rb) and M(Hg, *x*) refers to the alkali metal amalgam electrode. The data consist of seven series of measurements, and the mole fraction (*x*) of rubidium in the amalgam was constant in each series where the molality of RbCl (*m*) varied from (0.05 to 0.5) mol·kg^{-1}. The cpd for this cell can be calculated from the following equation

$$E = E^o - (2RT/F)\ln(\gamma m/m^o) \qquad (17)$$

where E^o is the standard cpd and depends on *x*. These data were predicted with the new Hückel equation for RbCl, and the resulting error plots are shown in Figure 3. In these plots, the cpd errors were calculated from the equation

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

and are presented as a function of the molality. The best value of E^o was used in the calculation of the predicted cpd values (see eq 17) for each series, and these E^o values are also given in the caption of Figure 3. These data support well the suggested Hückel equation.

Determination of Parameters b_1 and b_2 for Concentrated RbCl Solutions and Tests of the Resulting Values. The most reliable values of parameters b_1 and b_2 for more concentrated RbCl solutions can then be determined from all isopiestic results of Rard[9] for NaCl and RbCl solutions. In this determination, the following equation was used

$$f_2 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \frac{4M_1 b_{2,y} m^3}{3(m^o)^2} = f_0 - b_{1,y}M_1(m_y^2/m^o) = f_0 + k_2 m_y^2 \qquad (19)$$

where $k_2 = -b_{1,y}M_1/m^o$. NaCl is again the reference electrolyte (x), and the value of parameter *B* is known to be 1.04 (mol·kg^{-1})$^{-1/2}$ for RbCl (= y) (see above). When parameter $b_{2,y}$ has been fixed, eq 19 represents an equation of the straight line f_2 versus m_y^2. The slope of the straight line is k_2, and parameter $b_{1,y}$ can be calculated from this slope. The straight line should again go through the origin, and therefore, parameter $b_{2,y}$ must be determined so that the value of intercept f_0 is zero. For the extended Hückel equation of RbCl, the following results were obtained from Rard's data[9] by using regression analysis with this equation: $b_{2,y} = 0.00063$ and $b_{1,y} = 0.03083 \pm 0.00003$. The uncertainty of the value of $b_{2,y}$ can be described in the following way: It is possible to calculate from eq 19 the value of this parameter for each experimental point by assuming the determined value of 0.03083 for parameter $b_{1,y}$. The resulting values are shown in Figure 4. They are finely constant above the molality of 2.0 mol·kg^{-1} and very close to the suggested value. The standard deviation of this mean value is about 0.00015. The resulting parameters were then tested by predicting the vapor pressures in the data used in the estimation. In these tests, the vapor pressures of the NaCl and RbCl solutions were calculated using eqs 3, 4, and 6 with the suggested activity parameters. The results are shown in Figure 5 where the isopiestic vapor pressure error (defined by eq 14) is presented as a function of the molality m_{RbCl}. The largest absolute error in these tests is about 0.8 Pa (= 0.006 mmHg), and the results of Rard's set,[9] therefore, support very well the suggested parameter values.

The RbCl parameters can additionally be tested with the experimental osmotic coefficients reported by Robinson[4] and Makarov et al.[17] for RbCl solutions. Again the vapor pressures were first calculated from these data, and then these values were predicted using eqs 3, 4, and 6 with the suggested parameters. The results are shown in Figure 6 where the vapor pressure error (e_p) defined by eq 15 is presented as a function of the

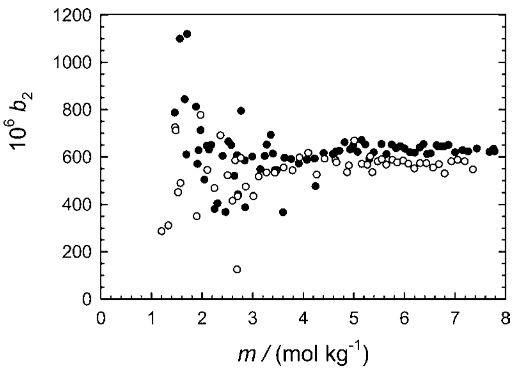

Figure 4. Values of activity parameter b_2 solved from eq 19 for each experimental point ●, in the RbCl set of Rard[9] and ○, in the CsCl set of Rard and Miller[8] as a function of molality *m*. The following parameter values were used in the calculations: $B_{\text{NaCl}} = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_{1,\text{NaCl}} = 0.0699$, $b_{2,\text{NaCl}} = 0.0062$, $B_{\text{RbCl}} = 1.04$ (mol·kg^{-1})$^{-1/2}$, $b_{1,\text{RbCl}} = 0.03083$, $B_{\text{CsCl}} = 0.84$ (mol·kg^{-1})$^{-1/2}$, and $b_{1,\text{CsCl}} = 0.03234$. The points for the most dilute solutions in these sets are not shown in the figure (these points are not relevant in the determination of activity parameters for concentrated solutions).

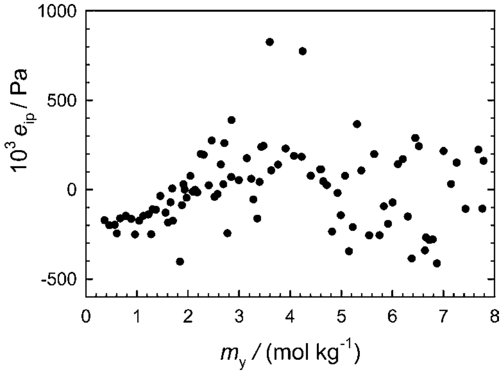

Figure 5. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic NaCl (x) and RbCl (y) solutions of Rard.[9] The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$ for NaCl (see ref 12) and with $B = 1.04\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.03083$, and $b_2 = 0.00063$ for RbCl.

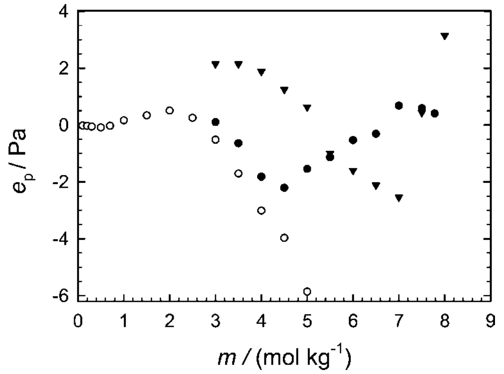

Figure 6. Difference, e_p in eq 15, between the reported and predicted vapor pressure of water over the RbCl and CsCl solutions as a function of molality m. The reported vapor pressures were obtained from the osmotic coefficients given by Robinson[4] (○, RbCl) and Makarov et al.[17] (●, RbCl; ▼, CsCl) using eqs 3 and 4. The vapor pressures were predicted by using eqs 3 and 4 with eq 6 with the suggested parameter values for RbCl and CsCl.

molality m. The data of Robinson[4] support the new parameter values quite well up to a molality of 4 mol·kg^{-1} and the data of Makarov et al.[17] for concentrated RbCl solutions up to the saturated solution.

Determination of Parameters B and b_1 for Dilute CsCl Solutions and Tests of the Resulting Values. In the same way as for RbCl solutions, the preliminary calculations with the isopiestic data of Rard and Miller[8] revealed that the Hückel equation of CsCl applies to much stronger solutions than is the applicability limit of the corresponding equation for NaCl (i.e., about 1.5 mol·kg^{-1}). Therefore, again in the parameter estimation for dilute CsCl solutions, the extended Hückel equation of NaCl was used. Equation 13 was applied to this estimation, and NaCl was the reference electrolyte (= x). The molality of the isotonic CsCl solution is the response variable (m_y). In this determination, the points where the CsCl molality is less than 3.2 mol·kg^{-1} could be included. This means that 24 points in the set of Rard and Miller[8] were taken into account in the least-squares fitting with eq 13. The following results were obtained: $B_y = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_{1,y} = 0.0341 \pm 0.0002$ where the standard deviation is also given. The estimated parameters were again first tested by predicting the vapor pressures of water over these isotonic cesium and sodium chloride solutions. The results are shown as an error plot in Figure 1, and this plot corresponds exactly to that presented for RbCl in this figure.

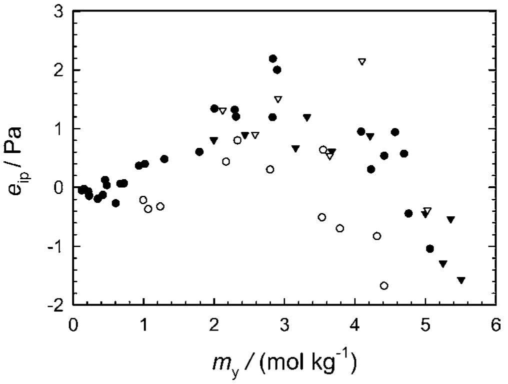

Figure 7. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and CsCl (y) solutions reported ●, by Robinson and Sinclair[3] and ○, by Bahia et al.[13] and in the isotonic NaCl (x) and CsCl (y) solutions reported ▼, by Robinson[5] and ▽, by Frolov et al.[14] The vapor pressures have been calculated using eqs 3 and 4 with eq 6 with the suggested parameter values for NaCl and KCl (see ref 12) and with eq 2 with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0341$ for CsCl.

The largest absolute error in these tests is less than 0.5 Pa (= 0.004 mmHg), and thus the results of the less concentrated solutions of Rard and Miller's set[8] support well the suggested parameter values.

The new Hückel equation with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0341$ was then tested with the isopiestic data of Robinson and Sinclair[3] (measured against KCl solutions), Bahia et al.[13] (KCl), Robinson[5] (NaCl), and Frolov et al.[14] (NaCl). The tests were carried out in the same way as the above corresponding RbCl tests, and the results are shown in Figure 7. All isopiestic data in this figure support quite well the suggested Hückel equation at least up to a molality of 4.5 mol·kg^{-1}. The new estimated Hückel parameters for CsCl can then be tested with cpd data. Mussini et al.[19] measured at 25 °C CsCl solutions on amalgam cells of the type 16 where M is Cs$^+$ (or Cs). The data consist of six series of measurements where the mole fraction (x) of cesium in the amalgam is constant, and in each series the molality of CsCl (m) varied from (0.05 to 0.6) mol·kg^{-1} or from (0.1 to 0.7) mol·kg^{-1}. The cpd for these data was calculated from eq 17 as for the RbCl data above. The error plots are shown in Figure 8, and these data support well the suggested Hückel equation.

Harned and Schupp[20] and Caramazza[21] measured on the following concentration cell without transference

$$\text{Ag(s)}|\text{AgCl(s)}|\text{CsCl(aq},m_1)|\text{Cs(Hg)}|\text{CsCl(aq},m_2)|\text{AgCl(s)}|\text{Ag(s)} \qquad (20)$$

In both of these sets, the molality of solution 1 was constant at a value of $m_1 = 0.1000$ mol·kg^{-1} and molality m_2 was varied. The cpd of this cell is given by

$$E = -\frac{2RT}{F}\ln(m_2/m_1) - \frac{2RT}{F}\ln(\gamma_2/\gamma_1) \qquad (21)$$

Also, these data were predicted by means of the suggested Hückel equation for CsCl, and the results are shown as error plots (see eq 18) in Figure 9. Measurements on cells with a dilute amalgam electrode are usually not very precise, but the agreement in this case can be regarded as satisfactory only in dilute solution where the molality is less than about 2 mol·kg^{-1}. Therefore, these two amalgam sets are probably not fully reliable in more concentrated solutions despite the fact they are very consistent with each other. In ref 11, another Hückel equation

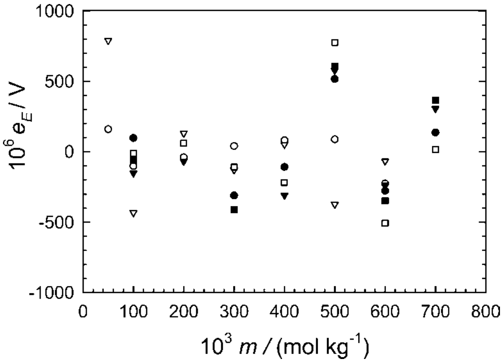

Figure 8. Deviation, e_E in eq 18, between the observed and predicted cell potential difference (cpd) from the data measured by Mussini et al.[19] in CsCl solutions on cell 16 as a function of molality m. The predicted cpd was calculated by using eq 17 where eq 1 with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0341$ was used for the activity coefficients and the following values were used for the standard cpds: ●, $x = 0.0006650$, $E^o = 1.98538$ V; ○, 0.001289, 2.00473; ▼, 0.005521, 2.05169; ▽, 0.006073, 2.05607; ■, 0.009942, 2.07742; □, 0.01337, 2.09347.

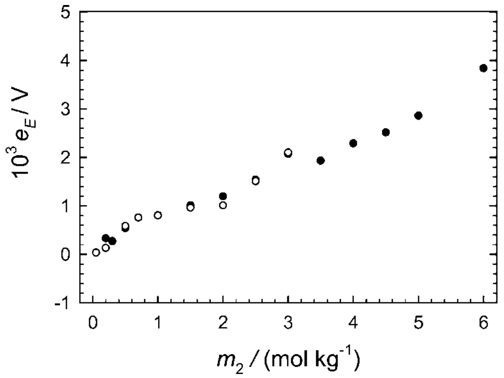

Figure 9. Deviation, e_E in eq 18, between the observed and predicted cell potential difference (cpd) from the data measured by Harned and Schupp[20] (●, $m_1 = 0.1\ \text{mol}\cdot\text{kg}^{-1}$) and Caramazza[21] (○, $m_1 = 0.1\ \text{mol}\cdot\text{kg}^{-1}$) in CsCl solutions on cell 20 as a function of molality m_2. The predicted cpd was calculated by using eq 21 where eq 1 with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0341$ was used for the activity coefficients.

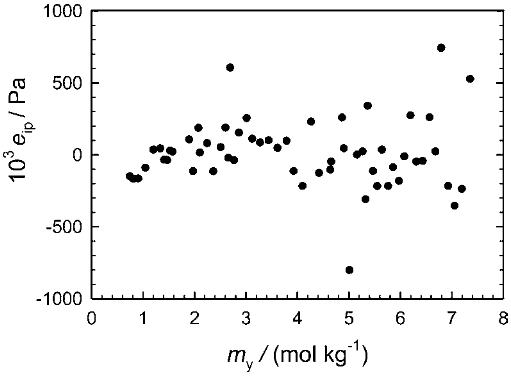

Figure 10. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic NaCl (x) and CsCl (y) solutions of Rard and Miller.[8] The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$ for NaCl (see ref 12) and with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.03234$, and $b_2 = 0.00057$ for CsCl.

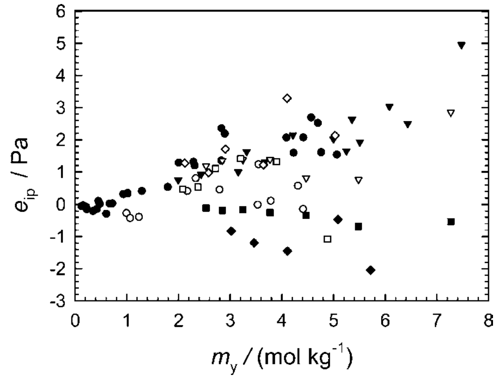

Figure 11. Difference, e_{ip} in eq 14, between the vapor pressure of water over the reference solution (x) and over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic KCl (x) and CsCl (y) solutions reported ●, by Robinson and Sinclair;[3] ○, by Bahia et al.;[13] and □, by Kirgintsev and Luk'yanov;[16] in the isotonic NaCl (x) and CsCl (y) solutions reported ▼, by Robinson;[5] ◇, by Frolov et al.;[14] and ◆,■ by Kirgintsev and Luk'yanov (◆, ref 15 and ■, ref 16); and in the isotonic LiCl (x) and CsCl (y) solutions reported ▽, by Kirgintsev and Luk'yanov.[16] The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with the suggested parameter values for NaCl,[12] KCl,[12] and LiCl[23] and with $B = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.03234$, and $b_2 = 0.00057$ for CsCl.

for CsCl solutions was estimated from the amalgam cell data of Caramazza.[21] In that study, the following new parameter values were obtained: $B = 0.85\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0219$. These values were suggested for CsCl solutions up to a molality of $1.0\ \text{mol}\cdot\text{kg}^{-1}$, and they will be considered below in the present study. Kelley and Lilley[27] have measured very dilute CsCl solutions (i.e., only up to a molality of $0.1\ \text{mol}\cdot\text{kg}^{-1}$) by using concentration cells with transference. These data were considered in the previous paper[11] by using the Hückel equation with $B = 0.85\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0219$, and they support quite well the equation as well as the new Hückel equation determined in the present study.

Determination of Parameters b_1 and b_2 for Concentrated CsCl Solutions and Tests of the Resulting Values. The most reliable values of parameters b_1 and b_2 for more concentrated CsCl solutions can be determined from all isopiestic results of Rard and Miller[8] by using eq 19. In this determination, the value of $B_y = 0.84\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ was accepted for CsCl. The following results were obtained from these data in the same way as for RbCl above: $b_{2,y} = 0.00057$ and $b_{1,y} = 0.03234 \pm 0.00004$. The uncertainty of the value of $b_{2,y}$ can be described as above for this parameter of RbCl. The experimental values of this parameter for each point are shown in Figure 4. They are finely constant above the molality $2.0\ \text{mol}\cdot\text{kg}^{-1}$ and very close to the suggested value. The standard deviation of this mean value is about 0.00010. The estimated parameters were then tested by predicting the vapor pressures of this data set. The vapor pressures of both isotonic solutions can be calculated using eqs 3, 4, and 6 with the suggested activity parameters. The results are shown in Figure 10 where the isopiestic vapor pressure error (defined by eq 14) is presented as a function of the molality m_{CsCl}. The largest absolute error in these tests is about 0.7 Pa (= 0.005 mmHg), and the data of Rard and Miller's set,[8] thus, support well the suggested parameters.

The new extended Hückel equation for CsCl was then tested with the isopiestic data of Robinson and Sinclair,[3] Robinson,[5] Bahia et al.,[13] and Frolov et al.[14] (see above). Also the isopiestic CsCl data reported by Kirgintsev and Luk'yanov against LiCl,[16] NaCl,[15,16] and KCl[16] solutions were included in the tests. For LiCl solutions, the following Hückel parameters were determined in ref 23: $B = 1.5\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.2028$, and $b_2 = 0.0117$. The results of these tests are shown in Figure 11. All isopiestic data of Bahia et al.[13] and Kirgintsev and Luk'yanov[15,16] support well the suggested Hückel parameter values, but the isopiestic data of Robinson and Sinclair,[3]

Table 1. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Rubidium Chloride Solutions at 25 °C as a Function of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.759	0.921	3.1581
0.2	0.703	0.905(0.906)	3.1480
0.3	0.670	0.897(0.898)	3.1380
0.4	0.647	0.892(0.893)	3.1281
0.5	0.629(0.630)	0.889(0.890)	3.1182
0.6	0.616	0.888	3.1084(3.1083)
0.7	0.604(0.605)	0.887	3.0985
0.8	0.595(0.596)	0.886(0.887)	3.0887(3.0886)
0.9	0.587(0.588)	0.886(0.887)	3.0788
1.0	0.580(0.581)	0.886(0.887)	3.0690(3.0689)
1.2	0.569(0.570)	0.888(0.889)	3.0493(3.0492)
1.4	0.561(0.562)	0.890(0.891)	3.0295(3.0294)
1.6	0.554(0.555)	0.892(0.893)	3.0097(3.0096)
1.8	0.549(0.550)	0.895(0.896)	2.9899(2.9897)
2.0	0.544(0.546)	0.898(0.899)	2.9700(2.9698)
2.5	0.537(0.538)	0.907	2.9200(2.9199)
3.0	0.534	0.916	2.8698(2.8699)
3.5	0.532(0.533)	0.926(0.925)	2.8193(2.8197)
4.0	0.533	0.936(0.934)	2.7686(2.7694)
4.5	0.535(0.534)	0.947(0.944)	2.7176
5.0	0.538	0.958	2.6664
5.5	0.542	0.969	2.6151
6.0	0.547	0.980	2.5636
6.5	0.553	0.991	2.5120
7.0	0.559	1.003	2.4603
7.5	0.566	1.015	2.4086
7.7832[b]	0.570	1.022	2.3792

[a] Values of all activity quantities have been calculated by using the parameter values suggested here for the extended Hückel equation. In less concentrated solutions, the values obtained with the suggested Hückel equation are given in parentheses when they differ from those presented in the table. [b] The molality of the saturated solution.

Table 2. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Cesium Chloride Solutions at 25 °C as a Function of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.748	0.915	3.1582
0.2	0.687	0.896	3.1482
0.3	0.650	0.885	3.1384
0.4	0.624	0.878	3.1288
0.5	0.604	0.873	3.1192(3.1191)
0.6	0.588	0.870	3.1096
0.7	0.575	0.867(0.868)	3.1001
0.8	0.564	0.866	3.0905
0.9	0.554(0.555)	0.865	3.0810
1.0	0.546(0.547)	0.864	3.0715(3.0714)
1.2	0.532(0.533)	0.864	3.0524
1.4	0.522	0.865	3.0334(3.0333)
1.6	0.513(0.514)	0.866(0.867)	3.0143(3.0142)
1.8	0.506(0.507)	0.868	2.9951
2.0	0.501	0.870(0.871)	2.9760(2.9759)
2.5	0.490(0.491)	0.878(0.877)	2.9278
3.0	0.484	0.886(0.885)	2.8793(2.8795)
3.5	0.480(0.479)	0.895(0.893)	2.8304(2.8310)
4.0	0.478(0.477)	0.905(0.902)	2.7813
4.5	0.478(0.476)	0.915(0.911)	2.7318
5.0	0.479	0.925	2.6821
5.5	0.481	0.936	2.6321
6.0	0.484	0.947	2.5819
6.5	0.487	0.958	2.5315
7.0	0.492	0.970	2.4810
7.5	0.497	0.982	2.4303
8.0	0.502	0.994	2.3795

[a] Values of all activity quantities have been calculated by using the parameter values suggested here for the extended Hückel equation. In less concentrated solutions, the values obtained with the suggested Hückel equation are given in parentheses when they differ from those presented in the table.

Robinson,[5] and Frolov et al.[14] give slightly higher vapor pressures than those obtained by these parameters above a molality of 3.0 mol·kg^{-1}. However, also these three data sets support the new parameter values satisfactorily up to a molality of 6.5 mol·kg^{-1}.

The CsCl parameters can additionally be tested with the experimental osmotic coefficients reported by Makarov et al.[17] for CsCl solutions. Again the vapor pressures were first calculated from these data, and then these values were predicted using eqs 3, 4, and 6 with the suggested parameters. The results are shown in Figure 6 where the vapor pressure errors (e_p) defined by eq 15 are presented as a function of the molality m. These data for concentrated CsCl solutions support the model quite well up to a molality of 8 mol·kg^{-1}.

Recommended Activity and Osmotic Coefficients at 25 °C. Because of the experimental evidence indicated in the tests of the present study (see Figures 1 to 11), 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 RbCl and CsCl solutions at 25 °C have been calculated on the basis of these equations. For RbCl the new values are given in Table 1 and for CsCl in Table 2. Also the vapor pressures of water are included in these tables. The values of all activity quantities have been calculated for these tables by using the parameter values suggested for the extended Hückel equations. In less concentrated solutions, the values obtained with the suggested Hückel equations are given in parentheses when they differ from those presented in the tables. The difference between these two values is always small (less than about 0.002 for both γ and ϕ, when $m < 4$ mol·kg^{-1}) and thus below only the activity and osmotic coefficients from the extended Hückel equations will be considered.

Comparison of the Recommended Activity Values to the Literature Values. The values in Tables 1 and 2 were compared to the activity and osmotic coefficients presented by Rard (RbCl),[9] Rard and Miller (CsCl),[8] Robinson and Stokes,[2] Hamer and Wu,[26] Pitzer and Mayorga,[7] Pitzer,[10] and Partanen.[11] The comparison of the activity coefficients is shown in the two graphs of Figure 12. Graph A shows the results from RbCl solutions and graph B from CsCl solutions. The quantity presented on the y axis in these graphs is the cell potential deviation [$e_{\mathrm{E,GC}}$ where GC refers to the appropriate galvanic cell without a liquid junction containing electrodes reversible to the cation and anion of the electrolyte (i.e., in this case to the cell of type 16, see also ref 12 where these deviations are called errors)] 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 1 and 2. Thus, $e_{\mathrm{E,GC}}$ is defined by

$$e_{\mathrm{E,GC}} = -\frac{2RT}{F}\ln\frac{\gamma(\mathrm{literature})}{\gamma(\mathrm{recd})} \tag{22}$$

The comparison of the osmotic coefficients in Tables 1 and 2 with the literature values is shown in the same way in the two graphs of Figure 13. The quantity presented on the y axis in these graphs is the vapor pressure deviation ($e_{\mathrm{p,VPW}}$ where VPW refers to the vapor 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., ϕ(recd)] shown in Tables 1 and 2 (see also ref 12). 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 Figure 13 by using the following equation

$$e_{\mathrm{p,VPW}} = p(\text{literature}) - p(\text{recd}) \tag{23}$$

The activity coefficients suggested by Rard for rounded molalities of RbCl in Table 6 of ref 9 are discrepant from the other values because their absolute cell potential deviations (see eq 22) are almost always larger than 1 mV. These activity coefficients were based on a six-parameter equation determined from the isopiestic data of Rard[9] and of Robinson and Sinclair,[3] from the osmotic coefficients reported by Makarov et al.,[17] and in dilute solutions from the amalgam cell data measured on cells type 16 by Longhi et al.[18] and by Lebed' and Aleksandrov[28] (5 points), and from the freezing-point depression data (corrected to 25 °C) of Momicchioli et al.[29] (15 points). The data for these dilute solutions are not in good agreement with each other, and so the list of the activity coefficients in Table 6 of ref 9 is a compromise between these data. This probably explains the rather large deviations of these activity coefficients, and they are not shown in Figure 12A. The best agreement between the activity coefficients presented in Tables 1 and 2 and those considered in graphs A (RbCl) and B (CsCl) in Figure 12 is obtained with the Pitzer equations with the parameters presented by Rard[9] and Rard and Miller,[8] respectively. These parameter values have also been most recently recommended by Pitzer.[10] In this case, all absolute galvanic cell deviations are smaller than 0.3 mV for RbCl and 0.25 mV for CsCl. Also, the tabulated activity coefficients in Tables 1 and 2 agree very satisfactorily with the other values considered in this figure.

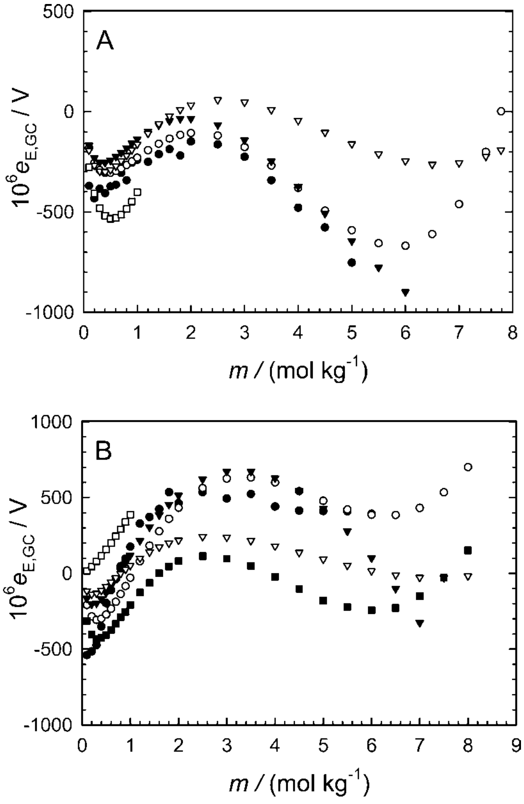

Figure 12. Deviation, expressed as galvanic cell error $e_{\mathrm{E,GC}}$ in eq 22, between the literature activity coefficients ●, of Robinson and Stokes;[2] ○, of Hamer and Wu[25] (eq 7); ▼, of Pitzer and Mayorga[7] (eq 9); ▽, of Pitzer[10] (eq 9, see also Rard[9] and Rard and Miller[8]); ■, and of Rard and Miller[8] (graph B) and those obtained in this study using eq 5 (see Tables 1 and 2) and deviation, expressed in the same way, between the activity coefficients from eq 1 with $B = 1.16\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0071$ for RbCl (see text, □) and with $B = 0.85\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0219$ for CsCl (see ref 11, □) and those obtained using eq 5 (see Tables 1 and 2 and eq 24) as a function of molality m in RbCl (graph A) and CsCl (graph B) solutions.

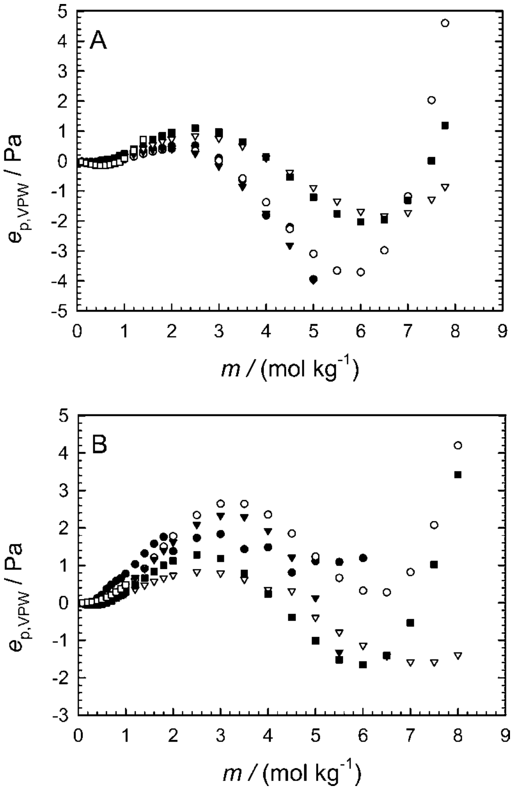

Figure 13. Deviation, expressed as vapor pressure error $e_{\mathrm{p,VPW}}$ in eq 23, between the literature osmotic coefficients ●, of Robinson and Stokes;[2] ○, of Hamer and Wu[25] (eq 8); ▼, of Pitzer and Mayorga[7] (eq 12); ▽, of Pitzer[10] (eq 12, see also Rard[9] and Rard and Miller[8]); ■, of Rard[9] (graph A), and ■, of Rard and Miller[8] (graph B) and those obtained in this study using eq 6 (see Tables 1 and 2) and deviation, expressed in the same way, between the osmotic coefficients from eq 2 with $B = 1.16\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0071$ for RbCl (graph A, see text, □) and with $B = 0.85\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0219$ for CsCl (graph B, see ref 11, □) and those obtained using eq 6 (see Tables 1 and 2 and eq 25) as a function of molality m in RbCl (graph A) and CsCl (graph B) solutions.

The best agreement between the osmotic coefficients presented in Tables 1 and 2 and those considered in graphs A (RbCl) and B (CsCl) in Figure 13 is also obtained with the Pitzer parameters presented by Rard[9] and by Rard and Miller,[8] respectively. Also the osmotic coefficients reported by Rard[9] for RbCl at rounded molalities agree well in graph A with the values in Table 1. For these reported values of RbCl[9] and CsCl[8] (graph B), all absolute vapor pressure deviations are smaller than 1.9 Pa (= 0.014 mmHg) and 1.7 Pa (= 0.012 mmHg), respectively. In general, the tabulated osmotic coefficients in Tables 1 and 2 agree also very satisfactorily with the other values considered in this figure (except the values of Robinson and Stokes[2] and of Pitzer and Mayorga[7] at 5 mol·kg^{-1} and the values of Hamer and Wu[26] above 5 mol·kg^{-1} for RbCl solutions (graph A) and the values of Rard and Miller[8] and Hamer and Wu[26] for CsCl solutions (graph B) at 8.0 mol·kg^{-1}).

The deviations that resulted from the use of the Hückel equations (eqs 1 and 2) presented above for dilute RbCl solutions [i.e., those with $B = 1.16\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0071$] and for dilute CsCl solutions (i.e., those[11] with $B = 0.85\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0219$) at molalities less than or about 1 mol·kg^{-1} are also shown in the graphs of Figures 12 and 13. These deviations have been calculated by the equations

$$e_{\mathrm{E,GC}} = -\frac{2RT}{F}\ln\frac{\gamma(\mathrm{eq}\ 1)}{\gamma(\mathrm{eq}\ 5)} \qquad (24)$$

$$e_{\mathrm{p,VPW}} = p(\mathrm{eq}\ 2) - p(\mathrm{eq}\ 6) \qquad (25)$$

For osmotic coefficients, the deviation is small [the absolute value is always smaller than 0.5 Pa (= 4.0 mmHg)], but for activity coefficients, it is more significant (the largest value is about 0.5 mV). In these dilute solutions, however, it is not possible at the moment to say whether the activity coefficients from eq 1 with the parameter values considered are more reliable than those from eq 5 (see above).

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