Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Lithium Chloride Solutions at 25 °C up to a Molality of 6.0 mol·kg^{-1}

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The Hückel equation used in this study to correlate the experimental activities of dilute LiCl solutions up to a molality of about 1.0 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 6.0 mol·kg^{-1}, an extended Hückel equation was used. It contains additionally a quadratic term with respect to the molality, and the coefficient of this term is the parameter b_2. The values of parameters B and b_1 for dilute LiCl solutions were determined from the isopiestic data measured by Robinson and Sinclair for KCl and LiCl solutions (*J. Am. Chem. Soc.* **1934**, *56*, 1830−1835) by using the Hückel parameters determined recently by Partanen and Covington for dilute KCl solutions (*J. Chem. Eng. Data* **2009**, *54*, published ASAP July 24, 2008). The resulting parameter values were tested with the sparse cell potential and isopiestic data existing in the literature for dilute LiCl solutions. In more concentrated solutions, new values of parameters b_1 and b_2 were determined for the extended Hückel equation of LiCl but the same value of parameter B was used as for dilute solutions. The values of b_1 and b_2 for LiCl were determined from the isopiestic data measured by Robinson for NaCl and LiCl solutions (*Trans. Faraday Soc.* **1945**, *41*, 756−758) by using the extended Hückel equation determined recently by us for concentrated NaCl solutions (see the citation above). The resulting extended Hückel equation was tested with all reliable experimental data presented in the literature on the basis of electrochemical, isopiestic, and direct vapor pressure measurements. Most of these data can be reproduced within experimental error by means of the extended Hückel equation up to a molality of 6.0 mol·kg^{-1}. Reliable activity and osmotic coefficients for LiCl solutions can, therefore, be calculated by using the new Hückel equations, and they have been tabulated here at rounded molalities. The activity quantities obtained from these equations were compared to the values suggested by Robinson and Stokes (*Trans. Faraday Soc.* **1949**, *45*, 612−624), to those calculated by using the Pitzer equations of Pitzer and Mayorga (*J. Phys. Chem.* **1973**, *77*, 2300−2308), of Kim and Frederick (*J. Chem. Eng. Data* **1988**, *33*, 177−184), and of Marshall et al. (*J. Chem. Eng. Data* **1995**, *40*, 1041−1052), 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 these tables have been later 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 slight revisions in the well-known book[2] of these authors. The values of the activity quantities of LiCl solutions in these tables have been based on the isopiestic data measured by Robinson and Sinclair[3] for KCl and LiCl solutions and by Robinson[4] for NaCl and LiCl solutions, and these tables give the activity and osmotic coefficients from a molality of (0.1 to 6.0) mol·kg^{-1}. 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[5] for various electrolytes in their famous article[6] on the thermodynamics of single electrolytes.

In the present study, it is shown that as reliable activity values as those in Robinson and Stokes' tables[1] for LiCl solutions at 25 °C can be obtained by such a simple equation as the Hückel equation up to a molality of about 1.0 mol·kg^{-1}. In a previous study,[7] it has been shown that reliable activity values for NaCl and KCl solutions at 25 °C can also be obtained with this equation up to this molality. In other previous studies (see, e.g., refs 8−12), the equations of this type have proved to be very useful in the thermodynamic treatment of weak acid solutions (especially those of pH buffer substances[10,12]). LiCl solutions have been thermodynamically investigated in several solution chemistry studies, but the results do not agree well in all cases (see below). The new values for activity and osmotic coefficients are very important in that they have been tested thoroughly with existing experimental data. Additionally, they are fully transparent and traceable because all calculation methods and data sets used in the parameter estimations and tests are presented here in detail. Also, the reliability of the literature data used in the tests is here evaluated, and only the best data are used in the parameter estimation. The form of the Hückel equation used in this investigation (see below and ref 7) 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

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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). The values of B and b_1 for LiCl in dilute solutions were determined here from the isopiestic data measured by Robinson and Sinclair[3] from KCl and LiCl solutions, and the 32 points where the LiCl molality is less than 1.23 $\text{mol}\cdot\text{kg}^{-1}$ were included in the determination. The Hückel parameters B and b_1 for KCl were taken for this estimation from the recent study[7] where NaCl and KCl solutions were considered. The resulting parameter values were tested with the data used in the parameter estimation, with two dilute points from the isopiestic data of Robinson[4] for NaCl and LiCl solutions (the Hückel parameters for NaCl were taken from ref 7), and with the cell potential data measured by Kelley and Lilley[13] and MacInnes and Beattie[14] on concentration cells with transference. Also, amalgam cell data of the latter study[14] were used in the tests.

Additionally, in the present study it is shown that very reliable activity values for LiCl solutions at 25 °C can be obtained up to a molality of 6.0 $\text{mol}\cdot\text{kg}^{-1}$ 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. Although the Hückel parameters are probably associated with the interactions between species in dilute electrolyte solutions (see the weak acid results in refs 8−12), the use of the extended Hückel equation is more empirical. However, it seems wise to base the equation for more concentrated solutions on the model that explains well the thermodynamic results in these dilute solutions by extending the simple model. The values of the parameters in this extended Hückel equation for LiCl were obtained and tested here in the following way:

1. The same new value was used for parameter B as that determined for dilute solutions.

2. New values of b_1 and b_2 for concentrated LiCl solutions were determined from the isopiestic set of Robinson[4] for NaCl and LiCl solutions. All experimental points of this set (i.e., 17 points) were included in this determination, and the extended Hückel equation for NaCl for these calculations was taken from ref 7.

3. The resulting parameter values were tested with the data used in the parameter estimation and with the following additional data: isopiestic data of Robinson and Sinclair,[3] of Kirgintsev and Luk'yanov[15] (measured against NaCl solutions), and of Frolov et al.[16] (measured against NaCl solutions); vapor pressure data of Gibbard and Scatchard,[17] of Pearce and Nelson,[18] and of Kangro and Groeneveld;[19] and amalgam cell data of Harned[20] and of Caramazza.[21]

All tests of this study were performed on the raw experimental results of appropriate measurements to test whether these could be predicted with the Hückel equations. This method has the advantage that the prediction error can be compared to the experimental error. The present parameter estimation methods and tests are slightly different from those used by Hamer and Wu[22] or Staples and Nuttall (see, for example, the $CaCl_2$ paper[23]) in their evaluation of the thermodynamic data for pure electrolyte solutions. In the Stables and Nuttall approach, in principle (see the flow diagram in Figure 3 of ref 23), values of the osmotic coefficients ϕ and activity coefficients γ (or $\gamma/\gamma_{\text{reference}}$) are first obtained from the various experimental methods. These values are then weighted, and the best values of the parameters in a correlating equation are obtained by the method of nonlinear least-squares. The choice of the correlating equation used (Pitzer equation, extended Debye−Hückel equation, or some other equation) is arbitrary. Finally, after the parameters in the appropriate correlating equation(s) have been calculated, one can examine the errors between the observed and measured values: e_γ and e_ϕ. It is shown below that the Hückel equations and the equations of Hamer and Wu[22] give for LiCl solutions almost the same activity and osmotic coefficients up to a molality of 3.5 $\text{mol}\cdot\text{kg}^{-1}$, and the results from the two approaches do not, therefore, differ much from each other in this case. The choice of the weights for the literature data sets, however, seems to be problematic in the approach of Stables and Nuttall, and we also have probably a better knowledge of the experimental error of different techniques than of the activity or osmotic coefficient error.

It is shown below that the Hückel equations are very reliable. In most cases, the measured results can be reproduced within experimental error. The activity coefficients of the electrolyte and the osmotic coefficients and the vapor pressures of water were calculated using the new Hückel equations at rounded molalities of LiCl, and these values are tabulated as recommended values. These activity and osmotic coefficients were compared to those of the previous investigations (some of which, in addition to Robinson and Stokes' values,[1] have achieved wide acceptance). Activity coefficient errors in this comparison are presented as the cell-potential difference errors for galvanic cells without a liquid junction (in the same way as in refs 7, 24, and 25), and the osmotic coefficient errors are presented as vapor pressure errors (as in ref 7).

Theory

In previous studies,[26,27] it was found that the following Hückel equation applies well to the thermodynamic properties of LiCl solutions at 25 °C up to a molality of 0.1 $\text{mol}\cdot\text{kg}^{-1}$

$$\ln \gamma = -\frac{\alpha\sqrt{m}}{1 + \beta_{\text{DH}} a^{*}\sqrt{m}} + 2M_1(h-1)m \qquad (1)$$

The form has been presented by Pan,[28] and in this equation m is the molality and γ is the mean activity coefficient on the molality scale. M_1 is the molar mass of water (= 0.018015 $\text{kg}\cdot\text{mol}^{-1}$), and α and β_{DH} are the Debye−Hückel parameters at 25 °C with the values of 1.1744 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and 3.2849 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}\cdot\text{nm}^{-1}$ (see Archer and Wang[29]). The parameters that are dependent on the electrolyte are the ion-size parameter a^* and hydration number h. In the previous study,[27] the following values were determined for these parameters for LiCl: $a^* = 0.48$ nm and $h = 3.80$. From eq 1, the following equation can be derived for the osmotic coefficient of water in LiCl solutions (or solutions of any other pure uniunivalent electrolyte) using the Gibbs−Duhem equation

$$\phi = 1 - \frac{\alpha}{(\beta_{\text{DH}} a^{*})^3 m}\left[(1 + \beta_{\text{DH}} a^{*}\sqrt{m}) - 2\ln(1 + \beta_{\text{DH}} a^{*}\sqrt{m}) - \frac{1}{1 + \beta_{\text{DH}} a^{*}\sqrt{m}}\right] + M_1(h-1)m \qquad (2)$$

The osmotic coefficient is related to the activity of the solvent (water in this case, a_1) in pure solutions of a uniunivalent electrolyte by the following thermodynamic identity

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

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

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

For water at 25 °C, $p_1^* = 3.1686$ kPa (i.e., 23.766 mmHg; see Kell[30]).

The Hückel equation used in the present study (and also in refs 7, 24, and 25) for the activity coefficients has practically the same form as that of eq 1. It can be obtained from this equation by defining the new parameters B and b_1 by equations $B = \beta_{\mathrm{DH}}a^*$ and $b_1 = 2\,M_1(h - 1)m^\circ$, respectively, where $m^\circ = 1\ \mathrm{mol{\cdot}kg^{-1}}$. With these definitions, eqs 1 and 2 have the forms

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

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

In more concentrated solutions, the following extended Hückel equations were used here as earlier[7] for the activity and osmotic coefficients

$$\ln\gamma = -\frac{\alpha\sqrt{m}}{1 + B\sqrt{m}} + b_1(m/m^\circ) + b_2(m/m^\circ)^2 \tag{7}$$

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m^\circ) + \frac{2}{3}b_2(m/m^\circ)^2 \tag{8}$$

Hamer and Wu[22] suggested the following extended Hückel equations for the activity and osmotic coefficients of LiCl solutions at 25 °C, and these equations apply up to the saturated solution (i.e., to $m = 19.219\ \mathrm{mol{\cdot}kg^{-1}}$)

$$\log(\gamma) = -\frac{A\sqrt{m}}{1 + B^*\sqrt{m}} + \beta(m/m^\circ) + C(m/m^\circ)^2 + D(m/m^\circ)^3 + E(m/m^\circ)^4 + F(m/m^\circ)^5 + G(m/m^\circ)^6 \tag{9}$$

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

where the Debye–Hückel parameter A has a value of 0.5108 $(\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$ [$= \alpha/\ln(10)$] and the parameters being dependent on the electrolyte are: $B^* = 1.305\ (\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$, $\beta = 0.11603$, $C = -7.7726\cdot10^{-3}$, $D = 2.9279\cdot10^{-3}$, $E = -3.1953\cdot10^{-4}$, $F = 1.4068\cdot10^{-5}$, and $G = -2.2498\cdot10^{-7}$.

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[5,6] has the form

$$\ln\gamma = f^\gamma + B^\gamma(m/m^\circ) + (3/2)C^\phi(m/m^\circ)^2 \tag{11}$$

where

$$f^\gamma = -\frac{\alpha}{3}\left[\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^\circ}} + \frac{2\sqrt{m^\circ}}{1.2}\ln(1 + 1.2\sqrt{m/m^\circ})\right] \tag{12}$$

$$B^\gamma = 2\beta^0 + \frac{\beta^1 m^\circ}{2m}\left[1 - e^{-2\sqrt{m/m^\circ}}\left(1 + 2\sqrt{m/m^\circ} - 2\frac{m}{m^\circ}\right)\right] \tag{13}$$

In eqs 11 and 13, β^0, β^1, and C^ϕ are the parameters that are dependent on the electrolyte. Pitzer and Mayorga[6] have determined from Robinson and Stokes' tables[1] the following values of these parameters for LiCl at 25 °C: $\beta^0 = 0.1494$, $\beta^1 = 0.3074$, and $C^\phi = 0.00359$. Kim and Frederick[31] and Marshall et al.[32] have used the tables of Hamer and Wu[22] up to the saturated solution for the estimation of the Pitzer parameter for eq 11. In the former study,[31] the values of $\beta^0 = 0.20972$, $\beta^1 = -0.34380$, and $C^\phi = -0.00433$ were obtained, and in the latter study,[32] the values of $\beta^0 = 0.21281$, $\beta^1 = -0.26973$, and $C^\phi = -0.00451$. For osmotic coefficients of water in solutions of a uniunivalent electrolyte, the Pitzer equation has the form

$$\phi = 1 - \frac{\alpha}{3}\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^\circ}} + (\beta^0 + \beta^1 \mathrm{e}^{-2\sqrt{m/m^\circ}})(m/m^\circ) + C^\phi(m/m^\circ)^2 \tag{14}$$

Results and Discussion

Determination of Parameters B and b_1 for Dilute Solutions. The parameter values suggested in ref 7 for the Hückel equation of NaCl and KCl seem to apply well up to a molality of about 1.0 mol·kg^{-1}, and these values can now be used to determine the activity parameters for the Hückel equation of LiCl in dilute solutions. The isopiestic set of Robinson and Sinclair[3] was used in this estimation. This set, where LiCl solutions were measured against KCl solutions, contains 23 points (out of 51) where the molality of KCl is less than 1.0 mol·kg^{-1}. In this determination, KCl can be regarded as the reference electrolyte (x) because the activities in the solutions of this salt are known. The activity of water in dilute KCl solutions can be calculated from the isopiestic molality of the KCl solution (m_x) using eqs 3 and 6 with the values of B [$= 1.3\ (\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$] and b_1 ($= 0.011$) suggested in ref 7. LiCl is now the tested electrolyte (y), and the molality of the isotonic LiCl solution is thus regarded as the response variable (m_y). In isopiestic equilibrium, the condition that $a_{1,x} = a_{1,y}$ is valid, and thus the following equation can be derived with eqs 3 and 6 for the determination of B and b_1 for LiCl solutions (see ref 7)

$$f_1 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] = f_0 - b_{1,y}M_1(m_y^2/m^\circ) = f_0 + k_1 m_y^2 \tag{15}$$

where $k_1 = -b_{1,y}M_1/m^\circ$. When parameter B_y has been fixed, eq 15 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 now be determined so that the value of intercept f_0 is zero.

In the determination of the Hückel parameters for LiCl, the points where the KCl molality is less than 1.5 mol·kg^{-1} could be included. This means that 32 points in the set of Robinson and Sinclair[3] were taken into account in the least-squares fitting

Table 1. Intercept with f_1 Axis ($= f_0$) as a Function of Parameter B_{LiCl} ($= B_y$) in the Regression Analysis Obtained by Equation 15 from the Isopiestic Data of Robinson and Sinclair[3] for KCl and LiCl Solutions up to a LiCl Molality of 1.227 mol·kg^{-1}

B_{LiCl}									
(mol·kg^{-1})$^{-1/2}$	1.3	1.35	1.4	1.45	1.5	1.55	1.6	1.65	1.7
$10^6 f_0$	−70	−53	−36	−19	−3	12	27	42	56

with eq 15. The following results were obtained: $B_y = 1.5$ (mol·kg^{-1})$^{-1/2}$ and $b_{1,y} = 0.2208 \pm 0.0011$ where the standard deviation is also given. The details of the determination of the value of B_y are shown in Table 1. The estimated parameters can first be tested by predicting the vapor pressures of water over these isotonic lithium and potassium chloride solutions. The vapor pressures of both solutions were calculated by using eqs 3, 4, and 6 with the suggested activity parameters. The results are shown in Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{ip} = p_x - p_y \tag{16}$$

and presented as a function of the molality m_y. For the solutions where $m_{\mathrm{LiCl}} < 1.3$ mol·kg^{-1}, the largest absolute error in these tests is less than 0.5 Pa (= 0.004 mmHg), and the errors form a random pattern. Thus, the results of the dilute solutions of Robinson and Sinclair's set[3] support very well the suggested parameter values. In this figure are also included the errors of the two points measured by Robinson[4] in dilute NaCl and LiCl solutions. In the calculation of these points, the parameter values $B = 1.4$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.072$ were used for NaCl,[7] and these two points also support well the suggested parameter values for LiCl.

Tests of the New Hückel Equation with Concentration Cell Data. The most reliable technique to determine activity coefficients for LiCl (as well as for the other alkali metal chlorides) in very dilute aqueous solutions is to measure appropriate concentration cells with transference. The precision of the data measured by using this technique can be in the best cases as high as 0.001 mV. However, the calculation of activity coefficients from the cell potential difference (= cpd) data obtained on concentration cells of this kind requires that the transference numbers (t_+ or $t_- = 1 - t_+$) of ions in the electrolyte solutions be known. The most reliable transference numbers for these calculations are obtained using the moving boundary method (see, for example, ref 26).

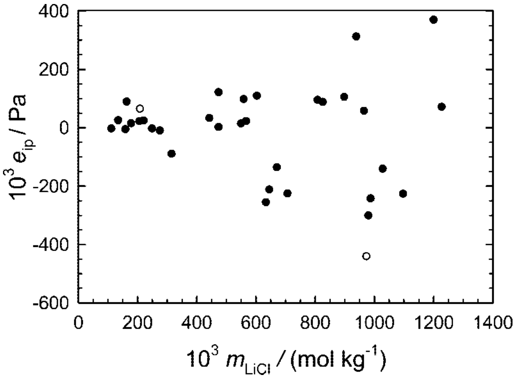

Figure 1. Difference, e_{ip}, in eq 16, between the vapor pressure of water over the tested solution (y) and that over the reference solution (x) as a function of the molality of the tested solution (m_{LiCl}) in the isotonic KCl (x) and LiCl (y) solutions of Robinson and Sinclair[3] (●) and in the isotonic NaCl (x) and LiCl (y) solutions of Robinson[4] (○). The vapor pressures have been calculated by eqs 3 and 4 using the Hückel equation (eq 6) with the suggested parameter values.

Table 2. Cell Potential Differences (E in Int. mV[a]) Measured by MacInnes and Beattie[14] on Concentration Cells of Types 17 and 24 for LiCl Solutions and the Errors (e_E, See Equation 23) Obtained for the Suggested Hückel Equation from These Data

m_1 mol·kg^{-1}	m_2 mol·kg^{-1}	E(cell 17) mV	[e_E(17)/mV][b]	E(cell 24) mV	[e_E(24)/mV][b]
0.01	0.001	39.074	0.931	113.8	−1.16
		39.039	0.896	114	−0.96
0.03	0.003	37.595	0.336	112.7	−0.65
		37.615	0.356	112.8	−0.55
0.1	0.01	35.885	−0.218	110.53	−1.08
		35.893	−0.210	110.55	−1.06
				110.57	−1.04
0.3	0.03	35.210	−0.154	111.18	−0.32
		35.211	−0.153	111.16	−0.34
0.3	0.1	16.420	−0.352	53.67	0.17
		16.401	−0.371	53.73	0.23
1.0	0.1			116.48	−0.82
				116.52	−0.78

[a] 1 Int. V = 1.00034 V. [b] $e_E = E$(observed) − E(predicted), and the latter value was calculated from eq 20 (for cell 17) or eq 25 (for cell 24) with eq 5 with $B = 1.5$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2208$.

Table 3. Cell Potential Differences (E) Measured by Kelley and Lilley[13] on Concentration Cells of Type 17 for LiCl Solutions and the Errors (e_E, See Equation 23) Obtained for the Suggested Hückel Equation from These Data

m_1 mol·kg^{-1}	m_2 mol·kg^{-1}	E mV	[e_E/mV][a]
0.100267	0.0051453	46.861	−0.135
	0.020302	24.679	−0.124
	0.060020	7.803	−0.057
	0.079350	3.546	−0.028
0.095736	0.0094510	36.253	−0.120
	0.028629	18.579	−0.090
	0.047039	10.854	−0.066
	0.067220	5.357	−0.055

[a] Calculated from eqs 20, 22, and 23 with the activity coefficients obtained from eq 5 with $B = 1.5$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2208$.

In the literature are available two studies[13,14] measured on concentration cells with transference in dilute solutions of LiCl at 25 °C, i.e., on cells of the following type

$$\mathrm{Ag(s)|AgCl(s)|LiCl(aq,}m_1\mathrm{)|LiCl(aq,}m_2\mathrm{)|AgCl(s)|Ag(s)} \tag{17}$$

In the data sets measured with cell 17 for the determination of activity coefficients, the molality of solution 1 ($= m_1$) is often exactly or almost constant within each set, and the molality m_2 is varied (see the corresponding cells in ref 7). In the LiCl study of MacInnes and Beattie,[14] m_1 was not constant from one point to another, and in that of Kelley and Lilley[13] two different reference LiCl solutions (molality m_1) were used. The experimental data from these studies are shown here in Tables 2 and 3, respectively. Theoretically, the cpd of this cell (E) can be expressed by the following equation

$$E = -\frac{2RT}{F}\int_1^2 t_+ \mathrm{d}\ln(\gamma m/m^{\mathrm{o}}) \tag{18}$$

where t_+ is the transference number of the cation (Li$^+$). In the subsequent calculations, the treatment of Longsworth (see, e.g., ref 26) is followed. Transference number t_+ is first divided into two parts

$$t_+ = t_{+,1} + \Delta t_+ \tag{19}$$

where $t_{+,1}$ is the transference number of Li$^+$ at molality m_1. To test the suggested Hückel parameters of $B = 1.5$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2208$, the data in Tables 2 and 3 were predicted by means of these values. The equation used to predict the cpd values has the following form

$$E = -\frac{2RTt_{+,1}}{F}\ln(m_2/m_1) - \frac{2RTt_{+,1}}{F}\ln(\gamma_2/\gamma_1) - \frac{2RT}{F}\int_{m_1}^{m_2}\Delta t_+(\mathrm{d}m/m) - \frac{2RT}{F}\int_{\ln\gamma_1}^{\ln\gamma_2}\Delta t_+\mathrm{d}[\ln(\gamma)] \quad (20)$$

The relationship $t_+ = t_+(m)$ for eq 20 was determined from the moving boundary results of Longsworth.[33] The transference number data have been reported on the concentration (molarity, c) scale. For the conversion of the data on the molality (m) scale, the following equation (given by Harned and Owen[34]) was used

$$\frac{cm^{\circ}}{mc^{\circ}} = \rho_0 - A\frac{m}{m^{\circ}} \quad (21)$$

where for LiCl the value of parameter A is 0.0182 and the general parameter ρ_0 is 0.997 and $c^{\circ} = 1\ \mathrm{mol\cdot dm^{-3}}$. The following equation has been previously estimated for t_+ from the moving boundary data of Longsworth[33] for LiCl solutions at 25 °C

$$t_+ = 0.33646 - 0.08292\sqrt{m/m^{\circ}} + 0.06577(m/m^{\circ}) \quad (22)$$

The functional form of this equation is partially the same one as that used by Longsworth[33] and exactly the same one as that used in refs 25 and 26. The experimental data of Longsworth covered the concentration range from (0.01 to 0.1) $\mathrm{mol\cdot dm^{-3}}$, and the transference numbers are reported in these data with four digits. Equation 22 predicts the reported values always within 0.0004. The integral in the last term on the right-hand side of eq 20 (i.e., in the second activity coefficient term) must be evaluated numerically. The cpd errors are defined by the equation

$$e_E = E(\text{observed}) - E(\text{predicted}) \quad (23)$$

and are shown in Tables 2 and 3. They are quite small. Thus, the data support satisfactorily the suggested Hückel equation. It seems, in addition, that the data set of Kelley and Lilley[13] in Table 3 is not as accurate as the corresponding NaCl and KCl sets measured on concentration cells with transference (see ref 7), or the transference numbers of Longsworth[33] are not completely correct for LiCl solutions. The older experimental data of MacInnes and Beattie[14] on cell 17 in Table 2 are even less accurate than those of Kelley and Lilley.

MacInnes and Beattie[14] measured also the following concentration cell without transference

$$\mathrm{Ag(s)|AgCl(s)|LiCl(aq,}m_1\mathrm{)|Li(Hg)|LiCl(aq,}m_2\mathrm{)} \times |\mathrm{AgCl(s)|Ag(s)} \quad (24)$$

where Li(Hg) refers to the lithium amalgam electrode. The cpd of this cell is given by

$$E = -\frac{2RT}{F}\ln(m_2/m_1) - \frac{2RT}{F}\ln(\gamma_2/\gamma_1) \quad (25)$$

and the experimental data are given in Table 2. These data were predicted by means of the suggested Hückel equation for LiCl, and the results are shown as cpd errors (see eq 23) in this table. Measurements on cells with an amalgam electrode are not usually as precise as those on cells with transference. Therefore, the amalgam data support satisfactorily the suggested model up to a molality of 1.0 $\mathrm{mol\cdot kg^{-1}}$.

Determination of Parameters b_1 and b_2 for More Concentrated Solutions. The most reliable values of parameters b_1 and b_2 for LiCl can then be determined from all isopiestic results of Robinson[4] for NaCl and LiCl solutions. In this determination, NaCl must now be regarded as the reference electrolyte (x) because the activities in the solutions of this salt are known. The activity of water in NaCl solutions can be calculated from the isopiestic molality of the NaCl solution (m_x) from eqs 3 and 8 with the suggested parameter values[7] of $B = 1.4\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$. The molality of the isotonic LiCl solution is the response variable (m_y). Again in isopiestic equilibrium, the condition that $a_{1,x} = a_{1,y}$ is valid, and the value of parameter B is known [it is $1.5\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$] for LiCl. Thus, the following equation can be derived for the determination of b_1 and b_2 for LiCl

$$f_2 = \ln a_{1,x} + 2M_1m_y - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \frac{4M_1b_{2,y}m_y^3}{3(m^{\circ})^2} = f_0 - b_{1,y}M_1(m_y^2/m^{\circ}) = f_0 + k_2m_y^2 \quad (26)$$

where $k_2 = -b_{1,y}M_1/m^{\circ}$. When parameter $b_{2,y}$ has been fixed, eq 26 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.

The following results were obtained from Robinson's data[4] for eq 8 of LiCl from regression analysis with eq 26: $b_{2,y} = 0.0117$ and $b_{1,y} = 0.2028 \pm 0.0005$ where the standard deviation is also given. The details of the determination of the value of $b_{2,y}$ are shown in Table 4. The estimated parameters can again be first tested by predicting the vapor pressures of this data set (see above). The vapor pressures of both solutions can be calculated using eqs 3, 4, and 8 with the suggested activity parameters. The results are shown in Figure 2 where the isopiestic vapor pressure error (defined by eq 16) is presented as function of the molality m_y. The largest error in these tests is about 1.3 Pa (= 0.01 mmHg), and the small trends observed in the plot are approximately of the same order as the precision of the measurements in the concentrated solutions. Thus, the results of Robinson's set[4] support well the suggested parameters. The suggested parameter values of $B = 1.5\ (\mathrm{mol\cdot\ kg^{-1}})^{-1/2}$, $b_1 = 0.2028$, and $b_2 = 0.0117$ were then tested in the same way with the isopiestic data of Robinson and Sinclair,[3] of Kirgintsev and Luk'yanov,[15] and of Frolov et al.[16] For the KCl solutions in the set of ref 3, the following parameter values[7] were used: $B = 1.3\ (\mathrm{mol\cdot kg^{-1}})^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$. These results are also shown in Figure 2 and support quite well the suggested parameter values.

Tests of the New Extended Hückel Equation for LiCl with Other Thermodynamic Data. The LiCl parameters can additionally be tested with the following vapor pressure data for LiCl solutions: Gibbard and Scatchard,[17] Pearce and Nelson,[18] and Kangro and Groeneveld.[19] For the first[17] of these sets, the vapor pressures were calculated from the reported osmotic coefficients using eqs 3 and 4. The vapor pressures of these sets were the predicted using eqs 3, 4, and 8. For the latter

Table 4. Intercept with f_2 Axis ($= f_0$) as a Function of Parameter $b_{2,\mathrm{LiCl}}$ ($= b_{2,y}$) in the Regression Analysis Obtained by Equation 26 from the Isopiestic Data of Robinson[4] for NaCl and LiCl Solutions up to LiCl Molality of 4.883 mol·kg^{-1}

$b_{2,\mathrm{LiCl}}$	0.0109	0.0111	0.0113	0.0115	0.0117	0.0119	0.0121	0.0123	0.0125
$10^6 f_0$	255	194	134	74	14	−47	−107	−167	−227

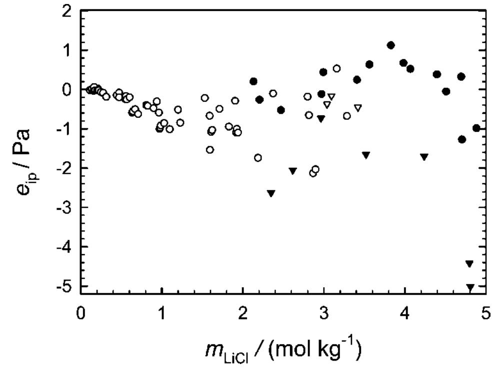

Figure 2. Difference, e_{ip} in eq 16, between the vapor pressure of water over the tested solution (y) and that over the reference solution (x) as a function of the molality of the tested solution (m_{LiCl}) in the isotonic NaCl (x) and LiCl (y) solutions reported ●, by Robinson;[4] ▼, by Kirgintsev and Luk'yanov;[15] and ▽, by Frolov et al.[16] and in the isotonic KCl (x) and LiCl (y) solutions reported ○, by Robinson and Sinclair.[3] The vapor pressures have been calculated by eqs 3 and 4 using the extended Hückel equations (eq 8) with the suggested parameter values.

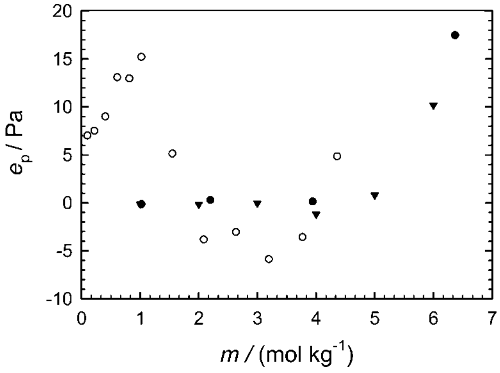

Figure 3. Difference, e_p in eq 27, between the observed and predicted vapor pressure of water over the LiCl solution as a function of the molality m of the solution. The vapor pressures have been predicted by eqs 3 and 4 using the extended Hückel equation (eq 8) with $B = 1.5\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.2028$, and $b_2 = 0.0117$. The following data were used (see text): ●, Gibbard and Scatchard;[17] ○, Pearce and Nelson;[18] ▼, and Kangro and Groeneveld.[19]

two sets, the older values of 3.1667 kPa (= 23.752 mmHg[18]) and 3.1672 kPa (= 23.756 mmHg[19]) were used for the vapor pressure of pure water (i.e., the same values as those in the original papers). The results are shown in Figure 3 where the vapor pressure error (e_p) is defined by

$$e_p = p(\text{observed}) - p(\text{predicted}) \tag{27}$$

and presented as function of the molality m. The data of Gibbard and Scatchard[17] and of Kangro and Groeneveld[19] can be predicted well with the new extended Hückel equation up to a molality of 5 mol·kg^{-1}. The data of Pearce and Nelson[18] are not in this case sufficiently accurate for the use in evaluation of validity of the suggested Hückel parameters.

The suggested Hückel parameters for more concentrated LiCl solutions can also be tested with the cpd data measured by Harned[20] and Caramazza.[21] These data were measured on cells of type 24, and the molality of reference solution 1 (= m_1) was 0.1 mol·kg^{-1} in both sets. These data were predicted with the new extended Hückel equation by using eq 25. The results are shown in Figure 4, and the cpd errors support in this figure quite well the suggested model but only up to a molality of 2.0 mol·kg^{-1} (probably because of the problems of the lithium−amalgam electrode in concentrated solutions).

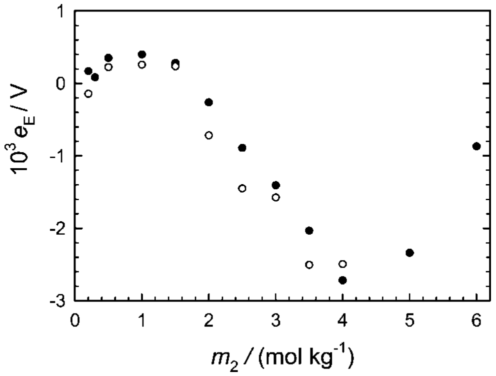

Figure 4. Deviation, e_E in eq 23, between the observed and predicted cell potential difference (cpd) from the data measured by ●, Caramazza[21] and ○, Harned[20] in LiCl solutions on cell 24 (in both sets $m_1 = 0.1$ mol·kg^{-1}) as a function of molality m_2. The predicted cpd was calculated by using eq 25 where the extended Hückel equation (eq 7) with $B = 1.5\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.2028$, and $b_2 = 0.0117$ was used for the activity coefficients.

Table 5. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Lithium Chloride Solutions at 25 °C as a Function of Molality (m)[a]

m mol·kg^{-1}	γ	ϕ	p kPa
0.1	0.793(0.795)	0.942(0.943)	3.1579
0.2	0.761(0.763)	0.941(0.943)	3.1472
0.3	0.747(0.751)	0.946(0.948)	3.1364(3.1363)
0.4	0.742(0.746)	0.954(0.956)	3.1253(3.1252)
0.5	0.742(0.746)	0.963(0.965)	3.1141(3.1140)
0.6	0.745(0.750)	0.972(0.975)	3.1027(3.1025)
0.7	0.750(0.755)	0.983(0.985)	3.0910(3.0908)
0.8	0.757(0.762)	0.994(0.996)	3.0791(3.0790)
0.9	0.765(0.770)	1.005(1.006)	3.0670(3.0669)
1.0	0.775(0.780)	1.016(1.017)	3.0547(3.0546)
1.2	0.797	1.040	3.0293
1.4	0.824	1.064	3.0030
1.6	0.854	1.090	2.9756
1.8	0.887	1.116	2.9474
2.0	0.923	1.143	2.9181
2.5	1.030	1.213	2.8407
3.0	1.160	1.286	2.7573
3.5	1.318	1.364	2.6679
4.0	1.509	1.445	2.5728
4.5	1.740	1.531	2.4722
5.0	2.021	1.620	2.3667
5.5	2.362	1.713	2.2567
6.0	2.780	1.809	2.1429

[a] See text.

Recommended Activity and Osmotic Coefficients for LiCl at 25 °C. Because of the experimental evidence indicated in the tests of the present study (see Figures 1 to 4), the suggested Hückel equations are reliable, and new tables for the activity and osmotic coefficients have been calculated on the basis of these equations. These activity quantities are shown in Table 5. Also the vapor pressures of water are included in this table. The values of all activity quantities have been calculated for this table by using the parameter values for the extended Hückel equation. In dilute solutions (i.e., when $m \leq 1$ mol·kg^{-1}), the values obtained with the suggested Hückel equation are given in parentheses when they differ significantly from those presented in the table. The absolute difference between these two values is always quite small (less than about 0.005 for γ and 0.003 for ϕ). It is important to emphasize, however, that we cannot at the moment say surely which of the values from these two equations are more reliable at molalities less than 1.0 mol·kg^{-1} because no high-precision activity coefficient data are available for dilute LiCl solutions (see above) to test thoroughly the new suggested Hückel equation.

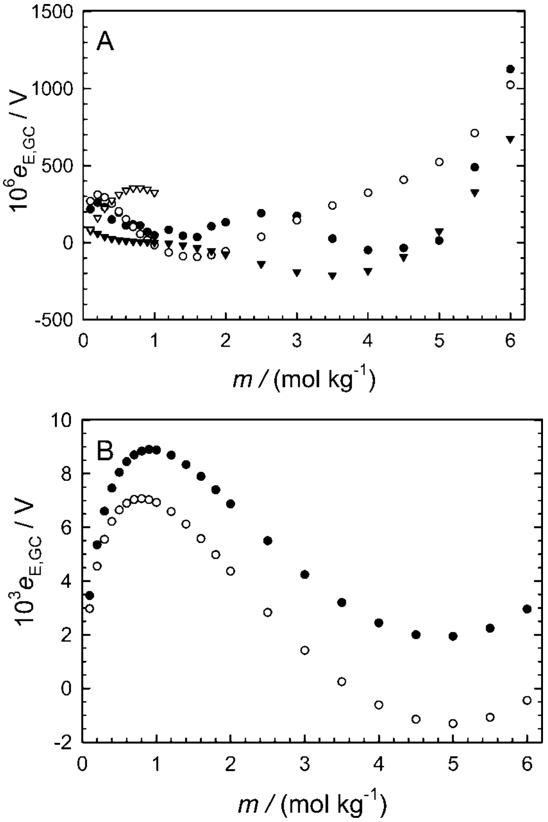

Figure 5. Deviation, expressed as galvanic cell errors $e_{E,GC}$ in eq 28, between the literature activity coefficients ●, of Robinson and Stokes[1] (graph A); ○, of Hamer and Wu[22] (eq 9, A); and of the Pitzer equation (eq 11) with the parameter values ▼, of Pitzer and Mayorga[6] (A); ●, of Kim and Frederick[31] (B); and ○, of Marshall et al.[32] (B) and those obtained in this study using the extended Hückel equation (eq 7, see Table 5) and deviation, expressed in the same way, between the activity coefficients from eq 7 (symbol ▽, A) and those from the recommended Hückel equation (eq 5, see Table 5) as a function of the molality m in LiCl solutions.

Comparison of the Recommended Activity Values to the Literature Values. The values in Table 5 were compared to the activity and osmotic coefficients presented by Robinson,[1] Hamer and Wu,[22] Pitzer and Mayorga,[6] Kim and Frederick,[31] Marshall et al.,[32] and Partanen.[25,27] The comparison of the activity coefficients with the literature values is shown in the two graphs of Figure 5. Graph A shows the results from the activity coefficients of Robinson, Hamer and Wu, and Pitzer and Mayorga, and graph B the results from those of Kim and Frederick and Marshall et al. The quantity presented on the y axis in these graphs is the cell potential difference error [$e_{E,GC}$ where GC refers to the appropriate galvanic cell without a liquid junction containing electrodes reversible to the cation (Li^+ in this case) and anion (Cl^-) of the electrolyte (see ref 24)] 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 Table 5. Thus, $e_{E,GC}$ is defined by

$$e_{E,GC} = -\frac{2RT}{F} \ln \frac{\gamma(\text{literature})}{\gamma(\text{recd})} \qquad (28)$$

For the recommended values, the values obtained from eq 7 were used.

The comparison of the osmotic coefficients in Table 5 with the literature values is shown in the same way in the two graphs of Figure 6. The quantity presented on the y axis in these graphs is the vapor pressure error [$e_{p,VPW}$ 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., to ϕ(recd)] shown in Table 5. 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 errors in Figure 6 by using the following equation:

$$e_{p,VPW} = p(\text{literature}) - p(\text{recd}) \qquad (29)$$

For the recommended values, the values obtained from eq 8 were used.

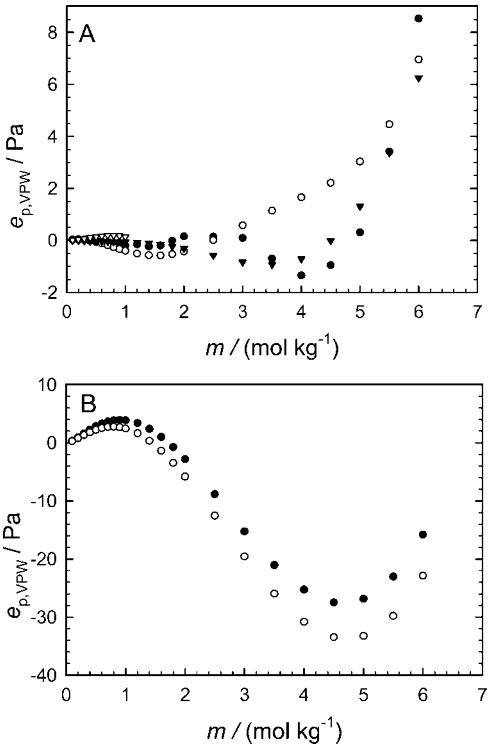

Figure 6. Deviation, expressed as vapor pressure errors $e_{p,VPW}$ in eq 29, between the literature osmotic coefficients ●, of Robinson and Stokes[1] (graph A); ○, of Hamer and Wu[22] (eq 10); and of the Pitzer equation (eq 14) with the parameter values ▼, of Pitzer and Mayorga[6] (A); ●, of Kim and Frederick[31] (B); and ○, of Marshall et al.[32] (B) and those obtained in this study using the extended Hückel equations (eq 8, see Table 5) and deviation, expressed in the same way, between the osmotic coefficients from eq 8 (symbol ▽) and those from recommended Hückel equation (eq 6, see Table 5) as a function of the molality m in LiCl solutions.

The activity and osmotic coefficients suggested by Robinson and Stokes[1] and those obtained from the equations of Pitzer and Mayorga[6] are practically the same as those suggested in the present study up to a molality of about 5.0 mol·kg^{-1}. The largest activity coefficient error in Figure 5A is in this case about 0.2 mV, and the largest osmotic coefficient error in Figure 6A is less than 1.3 Pa (= 0.01 mmHg). Up to a molality of 0.5 mol·kg^{-1}, the values from the equations of Pitzer and Mayorga[6] seem to agree slightly better than those of Robinson and Stokes[1] with those recommended in Table 5. The equations of Hamer and Wu[22] seem to predict well the activity and osmotic coefficients in Table 5 up to a molality of about 3.5 mol·kg^{-1}. On the other hand, the Pitzer parameters of Kim and Frederick[31] and of Marshall et al.[32] do not predict well the recommended activity and osmotic coefficients in Table 5. For activity coefficients in Figure 5B, the largest absolute error with these parameter values is about 9 mV, and for the osmotic coefficients in Figure 6B it is about 33 Pa (= 0.250 mmHg). It is clear that the Pitzer equations with these parameter values for LiCl solutions are not high-precision equations in less concentrated solutions despite being useful at molalities from (6 to 19.2) $\text{mol}\cdot\text{kg}^{-1}$ where the precision of data is probably not as good.

The errors that resulted from the use of the extended Hückel equation for dilute LiCl solutions at molalities less than or about 1 $\text{mol}\cdot\text{kg}^{-1}$ are also shown in graphs A of Figures 5 and 6. These errors have been calculated by the equations

$$e_{\text{E,GC}} = -\frac{2RT}{F}\ln\frac{\gamma(\text{eq 7})}{\gamma(\text{eq 5})} \quad (30)$$

$$e_{\text{p,VPW}} = p(\text{eq 8}) - p(\text{eq 6}) \quad (31)$$

For osmotic coefficients, this error is small [it is always smaller than 0.2 Pa (= 0.0015 mmHg)], but for the activity coefficients it is more significant (the largest value is about 0.4 mV). In these dilute solutions, however, it is not possible to say whether the activity coefficients from eq 5 are more reliable than those from eq 7 (see above).

The parameter values of $B = 1.58\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.101$ (see equations in the vicinity of eqs 5 and 6 for these calculations) were determined in ref 27 and the parameter values of $B = 1.6\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.086$ in ref 25 for eq 5 of LiCl from the cell potential difference data of Kelley and Lilley[13] (see Table 3). These parameter values give almost identical activity coefficients for LiCl up to a molality of 0.1 $\text{mol}\cdot\text{kg}^{-1}$, but the activity coefficients obtained with these values differ slightly from those obtained by using the Hückel or the extended Hückel equation determined in this study (see Table 5). At a molality of 0.1 $\text{mol}\cdot\text{kg}^{-1}$, the galvanic cell error (see above) between these models has the maximum value and it is about 0.45 mV or 0.33 mV, respectively.

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