

Traceable Mean Activity Coefficients and Osmotic Coefficients in Aqueous Calcium Chloride Solutions at 25 °C up to a Molality of 3.0 mol·kg⁻¹

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ABSTRACT: The Hückel equation used in this study to describe the thermodynamic activity quantities in dilute CaCl₂ solutions up to an ionic strength ($= I_m$) of 1.5 mol·kg⁻¹ consists of two electrolyte-dependent parameters, B and b_1 . Parameter B is linearly related to the ion-size parameter a^* in the Debye–Hückel equation, and parameter b_1 is the coefficient of the linear correction term with respect to the molality. In more concentrated solutions up to I_m of 9.0 mol·kg⁻¹, an extended Hückel equation was used. For it, the Hückel equation was supplemented with a quadratic term in molality, and the coefficient of this term is the parameter b_2 . The values of parameters B and b_1 for dilute CaCl₂ solutions were determined from the isopiestic data of Robinson for solutions of this salt against KCl solutions (*Trans. Faraday Soc.* **1940**, 36, 735–738). These parameters were successfully tested with the cell potential difference data and isopiestic data available in the literature for dilute CaCl₂ solutions. For more concentrated solutions, new values of parameters b_1 and b_2 were determined for the extended Hückel equation from the data measured by Spedding et al. (*J. Chem. Eng. Data* **1976**, 21, 341–360) for isotonic KCl and CaCl₂ solutions, but the same value of the parameter B was used as that for dilute solutions. The resulting parameter values were tested with the existing vapor pressure and isopiestic data, and these data support well the new values. Reliable thermodynamic activity quantities for CaCl₂ solutions are, therefore, obtained by using the new Hückel and extended Hückel equations. The activity coefficients, osmotic coefficients, and vapor pressures resulting from these equations are tabulated here at rounded molalities. These values were compared to those reported in the several previous tabulations.

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

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

INTRODUCTION

In 1948, Stokes¹ presented tables for activity quantities of 2:1 and 1:2 electrolytes in aqueous solution at 25 °C, and these tables have been later widely accepted and used. The suggested activity and osmotic coefficients in Stokes' tables¹ are also recommended in the well-known textbook of Robinson and Stokes.² The values of the activity and osmotic coefficients for CaCl₂ solutions in these tables have been based on the isopiestic data measured by Stokes³ for CaCl₂ solutions against NaCl or H₂SO₄ solutions, and these tables give these quantities from a molality of (0.1 to 6) mol·kg⁻¹.

It is shown here that reliable activity quantities for CaCl₂ solutions at 25 °C can also be determined using such a simple equation as the Hückel equation to an ionic strength ($= I_m$) of 1.5 mol·kg⁻¹. The Hückel equation used (see below and ref 4) to describe the thermodynamic properties of dilute solutions has two electrolyte-dependent parameters B and b_1 : the former is linearly related to the ion-size parameter a^* in the Debye–Hückel theory, and the latter is the coefficient of the linear correction term with respect to the molality. B and b_1 for dilute CaCl₂ solutions were now obtained from the isopiestic data of Robinson⁵ for KCl and CaCl₂ solutions, and the points where the CaCl₂ ionic strength is smaller than 1.6443 mol·kg⁻¹ were included in the estimation. The values of the Hückel

parameters for the reference electrolyte were taken for this determination from ref 6. The new parameter values for CaCl₂ were tested with the data used in the estimation and with the most dilute isotonic points in the set of Stokes³ measured against NaCl solutions (ref 6 also gives the Hückel parameters for NaCl solutions) and in that of Spedding et al.⁷ The latter data were measured against KCl solutions; however, the isopiestic molalities for KCl and CaCl₂ solutions are not readily available in that paper, but they have been hidden in their wide tables of isopiestic data of rare earth chlorides. They are reported, however, in detail in Table I of the review of Rard et al.⁸ where all existing isopiestic data available for CaCl₂ solutions up to the publication date against KCl,^{5,7} NaCl,^{3,9} and H₂SO₄^{3,10} solutions have been collected. The resulting parameter values for CaCl₂ solutions were also tested with the galvanic cell data measured by Lucasse,¹¹ Shedlovsky and MacInnes,¹² and McLeod and Gordon¹³ on concentration cells with transference; by Lucasse,¹¹ Fosbinder,¹⁴ Scatchard and Tefft,¹⁵ and Mussini and Pagella¹⁶ on cells with calcium amalgam electrodes; by Shatkay¹⁷ and Briggs and Lilley¹⁸ on

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cells with calcium ion sensitive membrane electrodes; and by Sahay¹⁹ on cells with lead–lead oxalate electrodes.

Additionally, it is shown here that the Hückel equation can be extended with a quadratic term in the molality, and the resulting equation explains the existing data quite well up to I_m of 9 mol·kg⁻¹. The coefficient multiplying the square of the molality in this term is parameter b_2 . The parameter values for this extended Hückel equation were determined and tested in the present study as follows:

1. The same value as that determined for dilute solutions was used for parameter B .
2. Values of b_1 and b_2 for more concentrated CaCl₂ solutions were estimated from the isopiestic data measured by Spedding et al.⁷ for KCl and CaCl₂ solutions (see above). All of the points in this set were used in the estimation, and the extended Hückel equation for KCl solutions was taken from ref 6.
3. The new values for b_1 and b_2 were tested with the data used in the estimation and with the following data measured by this method: Stokes;³ Robinson;⁵ Platford;⁹ Shul'ts et al.²⁰ (measured against NaCl solutions); Kirgintsev and Luk'yanov in 1965²¹ (NaCl), in 1966²² (KCl), and in 1967²³ (NaCl and KCl); Robinson and Bower²⁴ (NaCl); Robinson and Covington²⁵ (KCl); Rard and Miller²⁶ (NaCl and KCl); Vesala et al.²⁷ (KCl); Macaskill and Bates in 1983²⁸ (NaCl) and in 1986²⁹ (NaCl); and Rard and Archer (NaCl).³⁰ The extended Hückel equations for KCl and NaCl solutions were taken for these calculations from ref 6. Additionally, the new extended Hückel equation was tested with the direct vapor pressure data of Hepburn,³¹ Bechtold and Newton,³² Stokes,³³ Petit,³⁴ and Jakli and Van Hook³⁵ and using the vapor pressure data based on isopiestic measurements of Stokes³ and Rard and Spedding¹⁰ against H₂SO₄ solutions.

As in the previous studies,^{4,6,36–45} where the activity values in solutions of uniunivalent electrolytes were considered, all tests of the present study were carried out using the raw experimental data of appropriate measurements. The Hückel equations were observed in these tests to be very reliable. The activity coefficients of the electrolyte and the osmotic coefficients and vapor pressures of water were then obtained using the new Hückel equations and tabulated here at rounded molalities. These recommended values have also been compared with the values existing in the literature, and the activity coefficient differences between the new and literature values are presented as the cell-potential deviations for galvanic cells without a liquid junction (as in refs 4, 6, 36, and 37–45) and the osmotic coefficient differences as the vapor pressure deviations (refs 6 and 37–45).

The new activity and osmotic coefficients for CaCl₂ solutions are fully traceable and transparent because all of the parameter estimations and all sources of data are given in detail in the present study or in our previous studies. For the isopiestic method, this is possible because fully traceable activity quantities are given in ref 6 for the standard references of this method (i.e., for NaCl and KCl solutions).

THEORY

In the previous studies,^{6,37–45} it was observed that the following Hückel equations explain well the thermodynamic behavior of

aqueous solutions of many uniunivalent salts at least up to a molality of 1 mol·kg⁻¹

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

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

In these equations, m is the molality; I_m is the ionic strength; γ is the mean activity coefficient on the molality scale; ϕ is the osmotic coefficient of the solvent (label 1 refers to the solvent, which is water in this case); z_+ is the charge number of the cation and z_- that of the anion; α is the Debye–Hückel parameter [its value at 25 °C and at 101.325 kPa is 1.17444 (mol·kg⁻¹)^{-1/2}, see Archer and Wang⁴⁶]; m° is 1 mol·kg⁻¹; and the parameters that depend on the electrolyte are B and b_1 . For 1:1 electrolytes, $|z_+ z_-|$ is 1 and I_m is the same as m . For 2:1 and 1:2 electrolytes, $|z_+ z_-|$ is 2 and I_m is $3m$. Generally for pure electrolyte solutions, the osmotic coefficient is defined in the following way by using the activity of water (a_1)

$$\ln a_1 = -\nu m M_1 \phi \quad (3)$$

where M_1 is the molar mass of water (= 0.018015 kg·mol⁻¹) and where for a 1:1 electrolyte the stoichiometric number ν (= $\nu_+ + \nu_-$) is 2 and for a 2:1 or 1:2 electrolyte it is 3. The activity of water is connected to the vapor pressure of water over the solution (p_1) and to that of pure water at the same temperature (p_1^*) by

$$a_1 = \frac{p_1}{p_1^*} \quad (4)$$

Strictly speaking, this equation is only an approximation, but it is useful under the studied conditions because the difference between the fugacity and vapor pressure is very small. For water at 25 °C, $p_1^* = 3.1686$ kPa (i.e., 23.766 mmHg, see Kell⁴⁷).

As earlier,^{6,37–45} in less dilute solutions of uniunivalent electrolytes, the corresponding extended Hückel equations were used here for the activity and osmotic coefficients of CaCl₂ solutions

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

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

Staples and Nuttall⁴⁸ suggested the following extended Hückel equations for these thermodynamic activity quantities of CaCl₂ solutions at 25 °C, and the equations can be used up to a molality of 10 mol·kg⁻¹

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

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

where $A_m = 1.17625 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ (i.e., an older value for the parameter α) and the parameters dependent on the electrolyte are: $B^* = 1.60002 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $C = 0.256690$, $D = 0.151052$, $E = -0.0377055$, $F = 9.90578\cdot 10^{-3}$, $G = -1.69480\cdot 10^{-3}$, $H = 1.34960\cdot 10^{-4}$, and $I = -3.94208\cdot 10^{-6}$.

For activity and osmotic coefficients of a 2:1 or 1:2 electrolyte, the Pitzer equations^{49,50} have the forms

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

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

where

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

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

where the most often used general parameter values are $b = 1.2 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $\alpha_p = 2.0 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$. In eqs 9 to 12, β^0 , β^1 , and C^ϕ are the parameters that depend on the electrolyte. Pitzer and Mayorga⁵⁰ have determined the following values of these parameters for CaCl_2 at 25 °C: $\beta^0 = 0.3159$, $\beta^1 = 1.614$, $C^\phi = -0.000339$. These values apply up to I_m of 7.5 $\text{mol}\cdot\text{kg}^{-1}$. Later using new experimental data, Phutela and Pitzer⁵¹ estimated the following values for the Pitzer parameters: $\beta^0 = 0.30534$, $\beta^1 = 1.7083$, $C^\phi = 0.002153$. These values apply up to I_m of 12.9 $\text{mol}\cdot\text{kg}^{-1}$. Ananthaswamy and Atkinson⁵² have presented the following new Pitzer equations for activity and osmotic coefficients of CaCl_2 solutions up to I_m of 10 $\text{mol}\cdot\text{kg}^{-1}$

$$\ln \gamma = 2f^\gamma + \frac{4}{3}B^\gamma(m/m^\circ) + 2^{3/2}C^\phi(m/m^\circ)^2 + \frac{32}{9}D^\phi(m/m^\circ)^3 + \frac{10 \times 2^{5/2}}{12}E^\phi(m/m^\circ)^4 + \frac{96}{15}F^\phi(m/m^\circ)^5 \quad (13)$$

$$\phi = 1 - \frac{2\alpha}{3} \frac{\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{4}{3}(\beta^0 + \beta^1 e^{-\alpha_p\sqrt{I_m}})(m/m^\circ) + \frac{2^{5/2}}{3}C^\phi(m/m^\circ)^2 + \frac{8}{3}D^\phi(m/m^\circ)^3 + \frac{2 \times 2^{5/2}}{3}E^\phi(m/m^\circ)^4 + \frac{16}{3}F^\phi(m/m^\circ)^5 \quad (14)$$

The general parameter values of b and α_p for these equations are the same as those for eqs 9 and 10, and the specific values at 25 °C for CaCl_2 solutions are $\beta^0 = 0.339701$, $\beta^1 = 1.50481$, $C^\phi = -0.0267882$, $D^\phi = 0.00841344$, $E^\phi = -936.925\cdot 10^{-6}$, and $F^\phi = 30.41\cdot 10^{-6}$. More complicated Pitzer equations for very concentrated CaCl_2 solutions have also been presented by Pitzer et al.⁵³

To apply to the whole thermodynamic data existing for aqueous CaCl_2 solutions up to I_m of 32.31 $\text{mol}\cdot\text{kg}^{-1}$, Rard and Clegg⁵⁴ had to consider the solutions as mixtures of Ca^{2+} , CaCl^+ , and Cl^- ions. (Reference 54 is a highly detailed review of the thermodynamic studies of CaCl_2 solutions at 25 °C and have been used here as the main source of the literature data.) They presented Pitzer equations for these mixtures and also for the case where CaCl_2 is a usual strong electrolyte in aqueous solution; i.e., no ion pairs of CaCl^+ exist. Because in the present study the main interest is focused on the properties of dilute CaCl_2 solutions, the latter models are only considered here. These Pitzer models for activity and osmotic coefficients are the following

$$\ln \gamma = 2f^\gamma + \frac{4}{3}B^\gamma(m/m^\circ) + \frac{8}{3}C^\gamma(m/m^\circ)^2 + \frac{4}{3}D_3(m/m^\circ)^3 + \frac{5}{4}D_4(m/m^\circ)^4 + \frac{6}{5}D_5(m/m^\circ)^5 \quad (15)$$

$$\phi = 1 - \frac{2\alpha}{3} \frac{\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{4}{3}(\beta^0 + \beta^1 e^{-\alpha_p\sqrt{I_m}})(m/m^\circ) + \frac{16}{3}(C^0 + C^1 e^{-\omega\sqrt{I_m}})(m/m^\circ)^2 + D_3(m/m^\circ)^3 + D_4(m/m^\circ)^4 + D_5(m/m^\circ)^5 \quad (16)$$

where f^γ is given in eq 11 and B^γ in eq 12 and the value of 1.4 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ is used for α_p instead of the former value of 2.0 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$. Quantity C^γ is defined by the equation

$$C^\gamma = 3C^0 + \frac{4C^1}{\omega^4 I_m^2} \left[6 - e^{-\omega\sqrt{I_m}} \left(6 + 6\omega\sqrt{I_m} + 3\omega^2 I_m + \omega^3 I_m^{3/2} - \frac{\omega^4}{2} I_m^2 \right) \right] \quad (17)$$

where the general parameter ω has a value of 1.0 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$. Rard and Clegg⁵⁴ presented for eqs 15 and 16 two sets of parameter values. From the first set [i.e., in the model of RC(1)], the parameters D_3 , D_4 , and D_5 were omitted, and the remaining parameters have the following values: $\beta^0 = -0.29865$, $\beta^1 = 2.17867$, $C^0 = 0.022524$, and $C^1 = 0.54082$. In the other set [i.e., in the model of RC(2)], these parameters were included, and all estimated parameter values are $\beta^0 = -0.95125$, $\beta^1 = 3.0670$, $C^0 = -0.06228$, $C^1 = 1.6884$, $D_3 = 0.03036$, $D_4 = -0.001959$, and $D_5 = 47.1\cdot 10^{-6}$. Both of these sets of values will be considered below in addition to the

Table 1. Results from the Parameter Estimation for the Hückel Equation (Equations 1 and 2) and for the Extended Hückel Equation (Equations 5 and 6) with $B = 1.55 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$ for Calcium Chloride Solutions at 25 °C by the Least-Squares Fitting Using Equations 18 and 38, Respectively, with Various Sources of Isopiestic Data against KCl or NaCl Solutions

source of data	b_2	b_1	$s(b_1)^a$	N^b	$(m_{\max}/m^o)^c$	$(s_0/\text{Pa})^d$	ref (and eq)
Robinson	0	0.377 ^e	0.005	9	0.5481	0.14	5 (18)
Spedding et al.	0.0667 ^e	0.3486 ^e	0.0003	78	2.1694	0.3	7 (38)
Robinson	0.0671	0.3430	0.0008	25	1.921	0.4	5 (38)
Stokes ^f	0.0631	0.3596	0.0006	29	2.981	0.6	3 (38)
Robinson and Bower ^f	0.0647	0.3566	0.0004	16	2.850	0.3	24 (38)
Robinson and Covington	0.0644	0.3568	0.0008	9	2.1195	0.3	25 (38)
Rard and Miller ^f	0.0651	0.3538	0.0009	20	2.9772	0.6	26 (38)

^aThe standard deviation of parameter b_1 . ^bNumber of points included in the estimation. ^cThe maximum molality included in the estimation ($m^o = 1 \text{ mol} \cdot \text{kg}^{-1}$). ^dStandard error between the vapor pressures of water over the tested and reference solutions (see eq 19). ^eRecommended value. ^fThe reference electrolyte is NaCl.

activity and osmotic coefficients tabulated by Rard and Clegg on the basis of the most complicated model containing the ion pair CaCl^+ .

RESULTS AND DISCUSSION

Determination of Parameters B and b_1 for Dilute Solutions and Tests of the Resulting Values Using Isopiestic Data. In ref 6, the parameter values of $B = 1.3 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$ and $b_1 = 0.011$ were suggested for the Hückel equation of KCl solutions, and these values can be used up to a molality of $1.5 \text{ mol} \cdot \text{kg}^{-1}$. They were applied now to the determination of the Hückel parameters for dilute CaCl_2 solutions from the isopiestic set of Robinson⁵ where this salt was measured against KCl solutions. Nine points where the ionic strength of the CaCl_2 solution is smaller than $1.65 \text{ mol} \cdot \text{kg}^{-1}$ were included from this set in the determination. This set is in the literature the only one which contains sufficient points for this estimation. The other two isopiestic sets containing points from these dilute solutions are that of Spedding et al.⁷ and Stokes³ where three and six points, respectively, are so dilute that $I_m(\text{CaCl}_2)$ is less than the limit of $1.65 \text{ mol} \cdot \text{kg}^{-1}$. The most precise data^{12,13} from concentration cells with transference (see below) are only for very dilute solutions ($I_m < 0.3 \text{ mol} \cdot \text{kg}^{-1}$), and the other galvanic cell data^{11,14–19} are less accurate. Therefore, these data are used below only in the tests of the resulting Hückel equation. The following equation was used in the estimation of the parameters of this equation from the isopiestic data⁵ for these dilute CaCl_2 solutions

$$\begin{aligned}
 f_1 &= \ln a_{1,x} + 3M_1m_y - \frac{2\alpha M_1}{B_y^3} \left[(1 + B_y \sqrt{I_{m,y}}) \right. \\
 &\quad \left. - 2 \ln(1 + B_y \sqrt{I_{m,y}}) - \frac{1}{1 + B_y \sqrt{I_{m,y}}} \right] \\
 &= f_0 - 3b_{1,y}M_1(m_y^2/2m^o) \\
 &= f_0 + k_1m_y^2
 \end{aligned} \quad (18)$$

where $k_1 = -3b_{1,y}M_1/(2m^o)$. In this estimation, KCl was the reference electrolyte (x) because the activities in solutions of this salt are known. CaCl_2 was the tested electrolyte (y). The details of the estimations are described, e.g., in ref 41 (see eq 13 in that study). The following results were obtained by the least-squares fitting using eq 18: $B_y = 1.55 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$ and $b_{1,y} = 0.377$. The standard deviation of parameter b_1 and the standard

error s_0 of the resulting model for this isopiestic set, defined by the equation

$$s_0 = \sqrt{\sum_{i=1}^N (p_{x,i} - p_{y,i})^2 / (N - P)} \quad (19)$$

where N is the number of the points included and P the number of the estimated parameters (now 2), are given in Table 1. The vapor pressures of both solutions x and y were calculated using eqs 2 to 4 with the suggested Hückel parameters.

The estimated parameters were first tested by calculating the vapor pressures of water over the isotonic CaCl_2 and KCl solutions in the set of Robinson⁵ and comparing the resulting

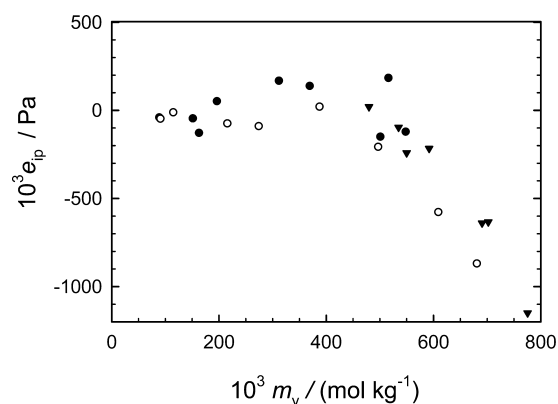


Figure 1. Plot of e_{ip} (eq 20), the difference between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic solutions of KCl or NaCl (x) and CaCl_2 (y) measured by Robinson⁵ (x = KCl, symbol ●), Stokes³ (NaCl, ○), and Spedding et al.⁷ (KCl, ▼). The vapor pressures were calculated by eqs 3 and 4 using eq 2 with $B_{\text{NaCl}} = 1.4 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$, $b_{1,\text{NaCl}} = 0.072$, $B_{\text{KCl}} = 1.3 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$, $b_{1,\text{KCl}} = 0.011$, $B_{\text{CaCl}_2} = 1.55 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$, and $b_{1,\text{CaCl}_2} = 0.377$.

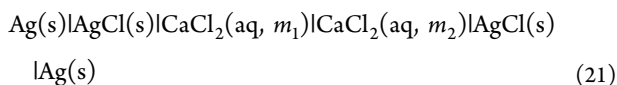
values. The results are shown in Figure 1 where the isopiestic vapor pressure error (e_{ip}) defined by

$$e_{ip} = p_x - p_y \quad (20)$$

is presented versus the molality m_y . For all of the solutions used in the estimation, the largest absolute error in these tests is less than 0.2 Pa, and thus the data support well the parameter values

obtained. This figure also shows the errors for the isopiestic points measured by Stokes³ and by Spedding et al.⁷ for dilute CaCl_2 solutions. For the NaCl points,³ the values of $B = 1.4 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.072$ were used for NaCl solutions.⁶ The points up to I_m of $1.7 \text{ mol}\cdot\text{kg}^{-1}$ support in this figure well the new Hückel parameters.

Tests of the New Hückel Equation Using Galvanic Cell Data. The most reliable way to obtain activity coefficients for CaCl_2 (as well as for the alkali metal or ammonium chlorides or bromides, see, e.g., ref 6) in very dilute aqueous solutions is to make measurements on appropriate concentration cells with transference. For CaCl_2 solutions at 25°C , two important high-precision sets have been measured by this technique, i.e., by using the cells of type



The former is that of Shedlovsky and MacInnes,¹² and the latter is that of McLeod and Gordon.¹³ In the former set, the concentrations were reported on the molarity scale, and in the latter the molality scale was used. The molalities of the solutions in the former set¹² can be obtained by using the equations

$$\frac{\rho}{\text{kg}\cdot\text{dm}^{-3}} = 0.99707 + 0.0924(c/c^\circ) - 0.0042(c/c^\circ)^{3/2} \quad (22)$$

$$m = \frac{c}{\rho - cM_2} \quad (23)$$

where ρ and c are the density and the concentration (molarity) of the solution, respectively; M_2 is the molar mass of CaCl_2 ($= 0.11099 \text{ kg}\cdot\text{mol}^{-1}$); and c° is $1 \text{ mol}\cdot\text{dm}^{-3}$. Equation 22 was given by Shedlovsky and MacInnes.¹² In the data sets measured using cells of type 21, the molality of solution 1 is often kept in a constant value within each set, and the molality m_2 is varied. In the CaCl_2 study of Shedlovsky and MacInnes,¹² m_1 was in a constant value of $0.050196 \text{ mol}\cdot\text{kg}^{-1}$, and in the study of McLeod and Gordon,¹³ it varied slightly around a value of $0.025 \text{ mol}\cdot\text{kg}^{-1}$ in all experiment points except that it was $0.028796 \text{ mol}\cdot\text{kg}^{-1}$ in one point (see below). Theoretically, the cell potential difference (cpd = E) of this cell is given by the following equation

$$E = -\frac{3RT}{2F} \int_1^2 t_+ d \ln(\gamma m/m^\circ) \quad (24)$$

where t_+ is the transference number of the cation (Ca^{2+}). In the following calculations, the treatment of Longworth (see, e.g., refs 6 and 55) is accepted: Transference number t_+ is first divided into two parts

$$t_+ = t_{+,1} + \Delta t_+ \quad (25)$$

where $t_{+,1}$ is the value of t_+ at the molality m_1 . To test the Hückel equation where $B = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.377$, the data in these sets^{12,13} were predicted with these parameter values. The equation used to predict the cpd values was obtained from eq 24 and has the following form

$$E = -\frac{3RT_{+,1}}{2F} \ln(m_2/m_1) - \frac{3RT_{+,1}}{2F} \ln(\gamma_2/\gamma_1) - \frac{3RT}{2F} \int_{m_1}^{m_2} \Delta t_+ (dm/m) - \frac{3RT}{2F} \int_{\ln \gamma_1}^{\ln \gamma_2} \Delta t_+ d \ln \gamma \quad (26)$$

The relationship $t_+ = t_+(m)$ for eq 26 could now be obtained from the moving boundary data measured either by Longworth⁵⁶ or by Keenan et al.⁵⁷ The experimental transference numbers were reported on the concentration (molarity, c) scale, and eqs 22 and 23 were used for the conversion of these t_+ values into the molality (m) scale. The subsequent equations were determined here for t_+ from the moving boundary data of Longworth⁵⁶ and Keenan et al.⁵⁷ for CaCl_2 solutions at 25°C , respectively

$$t_+ = 0.43837 - 0.1771\sqrt{m/m^\circ} + 0.1443(m/m^\circ) \quad (27)$$

$$t_+ = 0.43992 - 0.1810\sqrt{m/m^\circ} + 0.1548(m/m^\circ) \quad (28)$$

The functional form in these equations is the same as that suggested by Longworth.⁵⁵ The 9 data points from Longworth⁵⁶ and 22 points from Keenan et al.⁵⁷ covered approximately the same concentration range from $(0.0045 \text{ to } 0.0500) \text{ mol}\cdot\text{dm}^{-3}$, and the t_+ values are given in these data sets with four digits. Equation 27 reproduces the reported values of Longworth always within 0.0004 and eq 28 those of Keenan et al. within 0.0003. Unfortunately, the transference numbers from eqs 27 and 28 do not agree well. For all of the experimental concentrations, the absolute difference between the predictions of these equations is larger than 0.0012 but smaller than 0.00135. Therefore, the new Hückel equation must be tested with both eq 27 and 28. These equations were directly used in the evaluation of integral in the third term on the right-hand side of eq 26, but the values of the integral in the fourth term had to be determined by numerical methods. The cpd errors for the sets of Shedlovsky and MacInnes¹² and McLeod and Gordon¹³ were calculated from

$$e_E = E(\text{observed}) - E(\text{predicted}) \quad (29)$$

and are described in Figure 2 as a function of the molality m_2 . The cpd data support excellently the new Hückel equation for CaCl_2 solutions in the case where eq 28 was used for the transference numbers. Thus, it is probable that the transference numbers from the data of Keenan et al.⁵⁷ are more correct than those of Longworth,⁵⁶ and therefore, the former values⁵⁷ are only considered here in the other tests. Also, the new Hückel equation for CaCl_2 seems to be very reliable because almost all of the absolute errors from these high-precision electrochemical data in Figure 2 are smaller than 0.01 mV. In the same way as for NaCl and KCl solutions in ref 6, the Hückel parameters for CaCl_2 solutions are very strongly supported by the results of the most accurate electrochemical measurements available in the literature for dilute solutions.

The new Hückel parameters were also tested with the galvanic cell data obtained by Lucasse¹¹ on cell types 21 where the reference molality m_1 was $0.01 \text{ mol}\cdot\text{kg}^{-1}$. These data are not so precise as the other data^{12,13} measured on these cells. The errors for the set of Lucasse were calculated similarly as for the other two sets obtained with cell 21, and they are shown in Figure 2. These results support at least satisfactorily the new Hückel equation. Lucasse¹¹ measured also the following concentration cells without transference

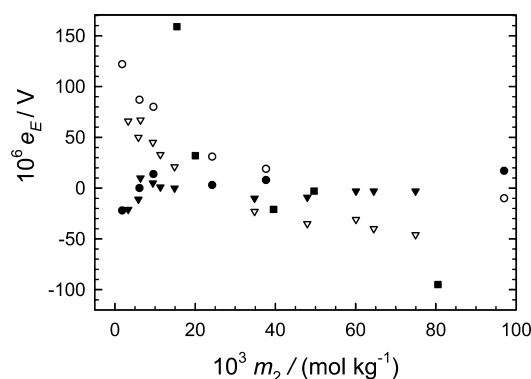
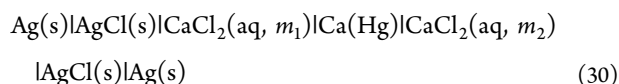


Figure 2. Plot of e_E (eq 29), the deviation between the observed and predicted cell potential difference (cpd) from the concentration cell data measured on cell 21 by Shedlovsky and MacInnes¹² ($m_1 = 0.050196 \text{ mol}\cdot\text{kg}^{-1}$), McLeod and Gordon¹³ [m_1 varied slightly around a value of $0.025 \text{ mol}\cdot\text{kg}^{-1}$ in all other points than the point ($m_1 = 0.028796 \text{ mol}\cdot\text{kg}^{-1}$, $m_2 = 0.060084 \text{ mol}\cdot\text{kg}^{-1}$, $E = -9.784 \text{ int. mV}$)], and Lucasse¹¹ ($m_1 = 0.01 \text{ mol}\cdot\text{kg}^{-1}$) in dilute CaCl_2 solutions as a function of molality m_2 . The predicted cpd was calculated by using eq 26 where eq 1 with $B = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.377$ was used for the activity coefficients and eqs 27 and 28 were used for the transference numbers (for the details see text). Symbols: ●, Shedlovsky and MacInnes,¹² t_+ from eq 28; ○, Shedlovsky and MacInnes,¹² eq 27; ▼, McLeod and Gordon,¹³ eq 28; ▽, McLeod and Gordon,¹³ eq 27; ■, Lucasse,¹¹ eq 28.

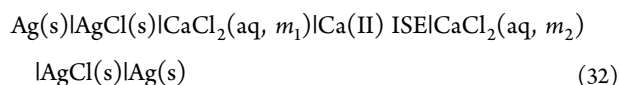


where Ca(Hg) refers to the calcium amalgam electrode; the reference molality m_1 was $0.01 \text{ mol}\cdot\text{kg}^{-1}$; and 13 molalities m_2 were studied from $(0.03504 \text{ to } 3.502) \text{ mol}\cdot\text{kg}^{-1}$. Additionally, Fosbinder¹⁴ measured cells of this type, and this set contains 11 points. The reference molality of m_1 was $0.0099 \text{ mol}\cdot\text{kg}^{-1}$, and molality m_2 varied from $(0.0435 \text{ to } 3.2702) \text{ mol}\cdot\text{kg}^{-1}$. The third study in the literature measured on cells of this type is the one of Scatchard and Tefft¹⁵ where the molality m_1 varied slightly around a value $0.1 \text{ mol}\cdot\text{kg}^{-1}$ from one point to another, the molality m_2 varied from $(0.009921 \text{ to } 0.9301 \text{ mol}\cdot\text{kg}^{-1})$, and the set contains nine points. All of these amalgam cell studies were used here in testing of the new Hückel parameters. The cpd of the cells of this type is given by

$$E = -\frac{3RT}{2F} \ln(m_2/m_1) - \frac{3RT}{2F} \ln(\gamma_2/\gamma_1) \quad (31)$$

These data were predicted using the new Hückel parameters, and the results are illustrated as cell potential difference errors (see eq 29) in Figure 3. Measurements on cells containing a dilute amalgam electrode are usually not as accurate as those obtained on cells with transference. Therefore, also these amalgam data can be predicted at least satisfactorily using the recommended Hückel equation up to I_m of $0.3 \text{ mol}\cdot\text{kg}^{-1}$.

Briggs and Lilley¹⁸ measured the following concentration cell without transference



where Ca(II) ISE refers to the calcium ion “selective” electrode (see also refs 48 and 54). The value of $0.0010275 \text{ mol}\cdot\text{kg}^{-1}$ can be regarded as the reference molality m_1 in this cell, and the

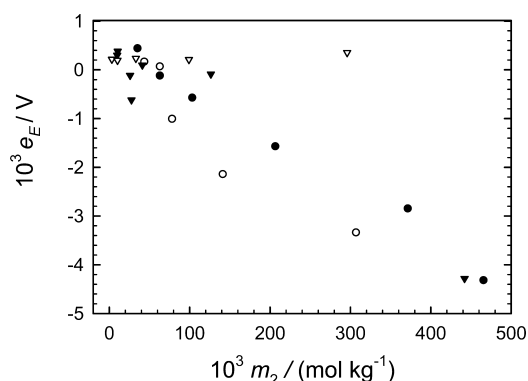
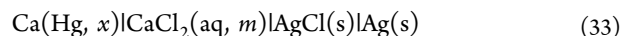


Figure 3. Plot of e_E (eq 29), the deviation between the observed and predicted cell potential difference (cpd) from the concentration cell data measured on cell 30 by Lucasse¹¹ ($m_1 = 0.01 \text{ mol}\cdot\text{kg}^{-1}$, symbol ●), Fosbinder¹⁴ ($m_1 = 0.0099 \text{ mol}\cdot\text{kg}^{-1}$, ○), and Scatchard and Tefft¹⁵ (m_1 varied slightly around a value of $0.1 \text{ mol}\cdot\text{kg}^{-1}$, ▼) and on cell 32 by Briggs and Lilley¹⁸ ($m_1 = 0.0010275 \text{ mol}\cdot\text{kg}^{-1}$, see text, symbol ▽) in dilute CaCl_2 solutions as a function of molality m_2 . The predicted cpd was calculated by using eq 31 where eq 1 with $B = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.377$ was used for the activity coefficients. The result from the probably erroneous point of ($m_2 = 0.0897 \text{ mol}\cdot\text{kg}^{-1}$, $E = -66.85 \text{ int. mV}$) in the set of Fosbinder¹⁴ was omitted.

following molalities m_2 were measured against this reference solution: 0.0032519 , 0.010165 , 0.033081 , 0.099104 , and $0.295890 \text{ mol}\cdot\text{kg}^{-1}$. The resulting cpd values (E values) are -41.09 , -80.45 , -119.50 , -155.18 , and -192.14 mV , respectively (see ref 48). The cpd of cell 32 can be calculated from eq 31. These data were reproduced using the new Hückel equation, and the results are given as cpd errors (see eq 29) in Figure 3. Additionally, Briggs and Lilley¹⁸ measured on cell 32 the following point: ($m_1 = 0.033081 \text{ mol}\cdot\text{kg}^{-1}$, $m_2 = 0.29589 \text{ mol}\cdot\text{kg}^{-1}$, and $E = -72.66 \text{ mV}$). The error for the new Hückel equation for this point is $+0.099 \text{ mV}$. Therefore, all of these calcium-selective electrode data support well the new Hückel equation up to I_m of $1.5 \text{ mol}\cdot\text{kg}^{-1}$.

The cpd data measured by Mussini and Pagella¹⁶ on direct amalgam cells of the following type were also used in the tests of the estimated Hückel parameters for CaCl_2



where $\text{Ca(Hg}, x)$ refers to a calcium amalgam electrode and x is the mole fraction of calcium in the amalgam. It was in a constant value of 0.00321 in the measurements where the molality of CaCl_2 (m) varied from $(0.005828 \text{ to } 0.09680) \text{ mol}\cdot\text{kg}^{-1}$. The cpd was calculated in this case from the following equation

$$E = E^\circ - \frac{3RT}{2F} \ln(4^{1/3} \gamma m / m^\circ) \quad (34)$$

where E° is the standard value of the cpd, and it depends on x . In the tests, these data were calculated with the new Hückel equation for CaCl_2 solutions; the measured values were compared to the predictions; and the resulting error plot is presented in Figure 4. In it, the cpd errors were calculated using eq 29 and are shown versus the molality. The best value of $E^\circ = 2.14594 \text{ V}$ in eq 34 was used in the calculation of the predictions, and these data support well the suggested Hückel equation. In the tests of the estimated Hückel parameters for CaCl_2 solutions, also the cpd data measured by Shatkey¹⁷ on

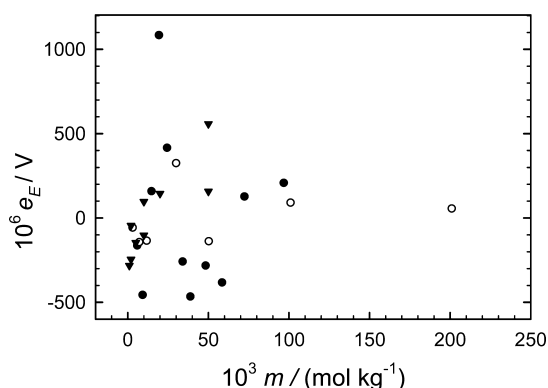
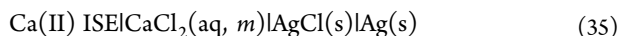
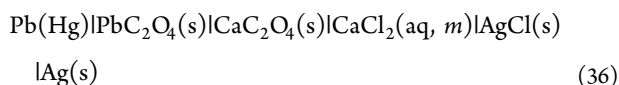


Figure 4. Plot of ϵ_E (eq 29), the deviation between the observed and predicted cell potential difference (cpd) from the galvanic cell data measured on cell 33 by Mussini and Pagella¹⁶ ($E^\circ = 2.14594$ V, symbol \bullet), on cell 35 by Shatkay¹⁷ ($E^\circ = -0.17966$ V, symbol \circ), and on cell 36 by Sahay¹⁹ ($E^\circ = 0.31452$ V, symbol \blacktriangledown) in dilute CaCl_2 solutions as a function of molality m . The predicted cpd was calculated by using eq 34 where eq 1 with $B = 1.55$ ($\text{mol}\cdot\text{kg}^{-1}$)^{-1/2} and $b_1 = 0.377$ was used for the activity coefficients. The error of the point ($m = 0.507$ $\text{mol}\cdot\text{kg}^{-1}$, $E = -141.5$ mV) of Shatkay¹⁷ is -1.18 mV.

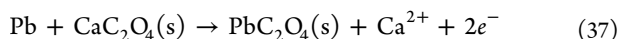
direct ion-selective electrode cells of the following type were used



where Ca(II) ISE refers again to the calcium ion “selective” electrode (see also ref 54). In these measurements, the molality of CaCl_2 (m) varied from $(0.00001 \text{ to } 3.11)$ $\text{mol}\cdot\text{kg}^{-1}$, but only molalities from 0.003 $\text{mol}\cdot\text{kg}^{-1}$ are considered here (as in ref 54). The cpd for this cell can be obtained from eq 34, but the E° is not in this case a usual standard cpd (such as that in electrochemical cells). Nevertheless, it can remain in a constant value from one point to another. These data were predicted using the new Hückel parameters, and the error plot for this case is given in Figure 4. The best value of $E^\circ = -0.17966$ V in eq 34 was used in the calculation of the predictions, and the upper limit for I_m of the points included in its determination was 0.603 $\text{mol}\cdot\text{kg}^{-1}$. According to the error plot, these data support well the new Hückel equation up to I_m of 1.521 $\text{mol}\cdot\text{kg}^{-1}$ (see also the caption of this figure). Finally, the estimated Hückel parameters for CaCl_2 solutions were evaluated with galvanic cell data measured by Sahay¹⁹ on the following cells of the third kind



where Pb(Hg) refers to the lead amalgam electrode, and the electrode reaction for this electrode is



It behaves, according to Sahay,¹⁹ reversibly with respect to Ca^{2+} ions. Eleven points are given in this set from a molality of $(0.001 \text{ to } 0.05)$ $\text{mol}\cdot\text{kg}^{-1}$. The cpd of this cell is given by eq 34, and the resulting error plot is described in Figure 4. The best value of $E^\circ = 0.31452$ V was used in the tests of the predicted cpd values, and the errors support well the new Hückel parameters.

Determination of Parameters b_1 and b_2 in More Concentrated Solutions. In more concentrated solutions, the most reliable parameter values for the extended Hückel

equation of CaCl_2 can be determined using all of the isopiestic results of Spedding et al.⁷ for KCl and CaCl_2 solutions. These data contain as much as 78 points. In this determination, KCl is again regarded as the reference electrolyte (x). The activity of water in KCl solutions was obtained from the isotonic molality of the KCl solution (m_x) using eqs 3 and 6 with the recommended values⁶ of $B = 1.3$ ($\text{mol}\cdot\text{kg}^{-1}$)^{-1/2}, $b_1 = 0.01324$, and $b_2 = 0.0036$. The molality of the isotonic CaCl_2 solution is the response variable (m_y), and the value of parameter B_y is 1.55 ($\text{mol}\cdot\text{kg}^{-1}$)^{-1/2} based on the above dilute solutions. The following equation was derived for the determination of b_1 and b_2 for CaCl_2 solutions

$$\begin{aligned} f_2 = \ln a_{1,x} + 3M_1m_y - \frac{2\alpha M_1}{B_y} \left[(1 + B_y\sqrt{I_{m,y}}) \right. \\ \left. - 2 \ln(1 + B_y\sqrt{I_{m,y}}) - \frac{1}{1 + B_y\sqrt{I_{m,y}}} \right] \\ + \frac{2M_1b_{2,y}m_y^3}{(m^\circ)^2} \\ = f_0 - 3b_{1,y}M_1(m_y^2/2m^\circ) \\ = f_0 + k_2m_y^2 \end{aligned} \quad (38)$$

where $k_2 = -3b_{1,y}M_1/2m^\circ$. The details of the estimations are presented in ref 41 (see eq 25 in that study). The following results were obtained in this regression analysis: $b_{2,y} = 0.0667$ and $b_{1,y} = 0.3486 \pm 0.0003$ where the standard deviation is additionally given. These parameter values are compared in Table 1 to the values obtained in the same way from the other important isopiestic data sets containing sufficient points for this determination. For NaCl solutions in these estimations, the following parameter values⁶ were used: $B = 1.4$ ($\text{mol}\cdot\text{kg}^{-1}$)^{-1/2}, $b_1 = 0.0699$, and $b_2 = 0.0062$. The data from direct vapor pressure measurements are usually not as accurate as those from the isopiestic method, and therefore, these data are not used in this comparison. The standard errors s_0 in Table 1 for the isopiestic sets were calculated using eq 19. The resulting parameter values agree well in this table with each other, and thus the recommended values seem to be reliable. These values were further tested by predicting the vapor pressures in the set used in the estimation⁷ (see above). At each point, the vapor pressures of both KCl and CaCl_2 solutions were calculated using eqs 3, 4, and 6 with the extended Hückel equations suggested. The results are illustrated in graph A of Figure 5 where the isopiestic vapor pressure error (eq 20) is presented versus the molality m_y . Almost all errors in this test are smaller than 0.7 Pa, and no trends are observed in the error plot. Thus, the results support well the new extended Hückel equation.

The obtained parameter values for CaCl_2 solutions were then tested in the same way with all of the isopiestic data of Robinson⁵ and Stokes³ (see above). These results are also included in graph B of Figure 5, and they support quite well the new parameter values. In Figure 5 are presented, in addition, the results of the tests with the isopiestic data of Platford⁹ (4 points, graph A), Shul'ts et al.²⁰ (3, B), Kirgintsev and Luk'yanov in 1965²¹ (5, B), in 1966²² (6, A), and in 1967²³ (8, B), Robinson and Bower²⁴ (16, A), Robinson and Covington²⁵ (9, A), Rard and Miller²⁶ (22, A), Vesala et al.²⁷ (11, B), Macaskill and Bates in 1983²⁸ (4, B) and in 1986²⁹ (2, B), and Rard and Archer³⁰ (4, B). All of these data seem to verify the

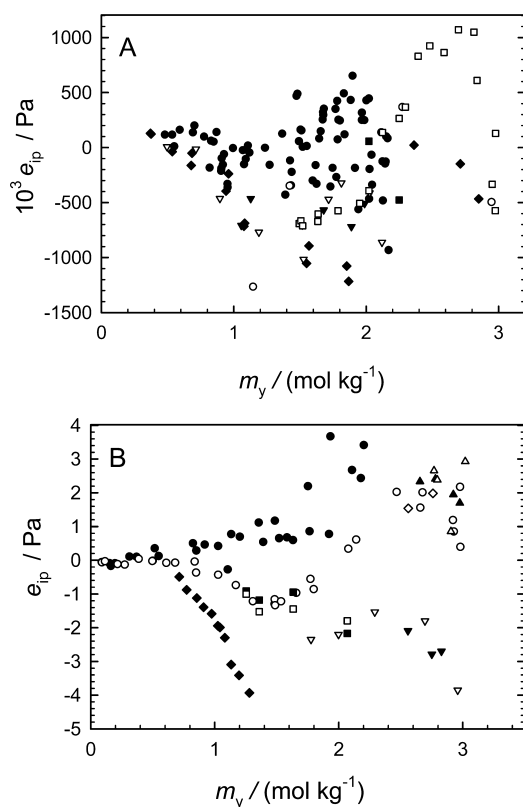


Figure 5. Plot of e_p (eq 20), the difference between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic solutions of KCl or NaCl (x) and CaCl_2 (y) solutions measured by Spedding et al.⁷ (x = KCl, graph A, symbol ●), Robinson⁵ (KCl, B, ●), Platford⁹ (NaCl, A, ○), Stokes³ (NaCl, B, ○), Kirgintsev and Luk'yanov²² (KCl, A, ▼), Shult's et al.²⁰ (NaCl, B, ▼), Robinson and Covington²⁵ (KCl, A, ▽), Kirgintsev and Luk'yanov²¹ (NaCl, B, ▽), Rard and Miller²⁶ (KCl, A, ■), Kirgintsev and Luk'yanov²³ (KCl, B, ■), Rard and Miller²⁶ (NaCl, A, □), Kirgintsev and Luk'yanov²³ (NaCl, B, □), Robinson and Bower²⁴ (NaCl, A, ◆), Vesala et al.²⁷ (KCl, B, ◆), Macaskill and Bates in 1986²⁹ (NaCl, B, ◇) and in 1983²⁸ (NaCl, B, ▲), and Rard and Archer³⁰ (NaCl, B, △). The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B_{\text{NaCl}} = 1.4 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_{1,\text{NaCl}} = 0.0699$, $b_{2,\text{NaCl}} = 0.0062$, $B_{\text{KCl}} = 1.3 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_{1,\text{KCl}} = 0.01324$, $b_{2,\text{KCl}} = 0.0036$, $B_{\text{CaCl}_2} = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_{1,\text{CaCl}_2} = 0.3486$, and $b_{2,\text{CaCl}_2} = 0.0667$.

validity of the new extended Hückel equation excluding the data of Vesala et al.²⁷ which seem to be erroneous.

The new Hückel parameters for CaCl_2 solutions were additionally evaluated with the following vapor pressure data for solutions of this salt: Hepburn,³¹ Bechtold and Newton,³² Stokes,³³ Petit,³⁴ and Jakli and Van Hook.³⁵ The predictions of the vapor pressures were calculated using eqs 3, 4, and 6. For the set of Petit, the older value of 23.756 mmHg was used for the vapor pressure of pure water (i.e., the same as that in the original paper³⁴). Figure 6 shows the results, and in this figure the vapor pressure error (e_p) is defined by

$$e_p = p(\text{observed}) - p(\text{predicted}) \quad (39)$$

and presented as a function of molality m . The CaCl_2 parameters were finally tested with the osmotic coefficients reported by Rard and Spedding¹⁰ for concentrated CaCl_2 solutions based on isopiestic measurements against H_2SO_4 solutions. These "experimental" osmotic coefficients have

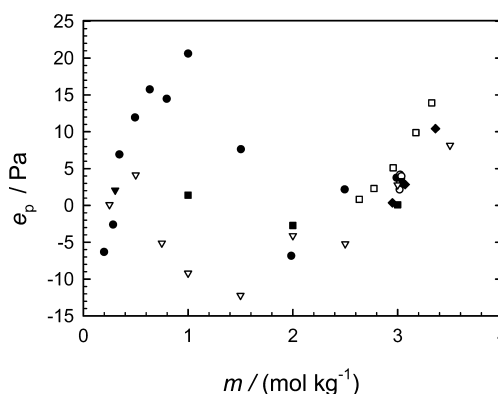


Figure 6. Plot of e_p (in eq 39), the difference between the reported and predicted vapor pressure of water over CaCl_2 solutions as a function of molality m . The reported vapor pressures were obtained from the data measured by Hepburn³¹ (symbol ●), Stokes³³ (○), Bechtold and Newton³² (▼), Petit³⁴ (▽), and Jakli and Van Hook³⁵ (■) and from the osmotic coefficients that resulted from the isopiestic data measured by Rard and Spedding¹⁰ (□) and Stokes³ (◆), the ϕ values are given in ref 8) for CaCl_2 and H_2SO_4 solutions. The vapor pressures have been predicted by eqs 3 and 4 using eq 6 with $B = 1.55 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3486$, and $b_2 = 0.0667$.

been calculated using the osmotic coefficients reported in the review of Rard et al.³⁸ for H_2SO_4 solutions. Also, some osmotic coefficients obtained in the same way by Rard et al.⁸ from Stokes' data³ for CaCl_2 and H_2SO_4 solutions were included in this figure. For these data,^{8,10} the vapor pressures were first calculated using eqs 3 and 4, and then the resulting values were predicted using eqs 3, 4, and 6 with the new extended Hückel equation. The errors are shown in Figure 6. All of the vapor pressure data described in this figure support at least satisfactorily the suggested parameter values up to I_m of about $9 \text{ mol}\cdot\text{kg}^{-1}$.

Recommended Activity and Osmotic Coefficients. On the basis of the experimental evidence provided by the tests of the present investigation (Figures 1 to 6), the Hückel equation and the extended Hückel equation apply well to the experimental data presented in the literature for calcium chloride solutions. A new table (Table 2) of the thermodynamic activity quantities in solutions of this salt at 25 °C was calculated using these equations. The activity coefficients of the CaCl_2 and the osmotic coefficients and vapor pressures of water are included in this table at rounded molalities.

The values of all activity quantities in Table 2 have been calculated by using the extended Hückel equation. In dilute solutions (i.e., when $m \leq 0.7 \text{ mol}\cdot\text{kg}^{-1}$), the values obtained with the two-parameter Hückel equation are given in parentheses in case they are different from those presented in the table. The absolute difference between these two values is always quite small. It is less than 0.5 mV for the galvanic cell deviation for γ (the definition is given in the table) and less than 1.3 Pa for the vapor pressure deviation for ϕ .

Comparison of the New Activity Values to Those Presented in the Literature. The thermodynamic activity values in Table 2 were compared to the activity and osmotic coefficients recommended by Stokes¹ and by Rard and Clegg.⁵⁴ Additionally, in these comparisons are included the values calculated by the equations of Pitzer and Mayorga⁵⁰ (eqs 9 and 10), Phutela and Pitzer⁵¹ (eqs 9 and 10), Ananthaswamy and Atkinson⁵² (eqs 13 and 14), Rard and Clegg⁵⁴ (eqs 15 and 16; the two models RC1 and RC2 used are introduced in the

Table 2. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Calcium Chloride Solutions at 25 °C as Functions of the Molality (m)^a

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p/kPa
0.01	0.728	0.907	3.1670
0.02	0.664	0.886	3.1656
0.05	0.576(0.577)	0.861(0.862)	3.1612
0.1	0.517(0.518)	0.852(0.853)	3.1540
0.2	0.470(0.472)	0.859(0.860)	3.1393
0.3	0.453(0.454)	0.876(0.877)	3.1239
0.4	0.448	0.897(0.896)	3.1078
0.5	0.449(0.448)	0.920(0.916)	3.0908(3.0912)
0.6	0.454(0.451, -0.26^b)	0.944(0.936)	3.0731(3.0739)
0.7	0.462(0.456, -0.48^b)	0.969(0.957)	3.0546(3.0559)
0.8	0.473	0.995	3.0352
0.9	0.487	1.022	3.0150
1.0	0.502	1.050	2.9939
1.2	0.540	1.108	2.9489
1.4	0.586	1.169	2.9003
1.6	0.643	1.234	2.8479
1.8	0.710	1.302	2.7916
2.0	0.790	1.374	2.7314
2.5	1.064	1.567	2.5639
3.0	1.490	1.782	2.3734

^aThe activity values in parentheses were calculated using the Hückel equation with $B = 1.55 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.377$, and the other activity values using the extended Hückel equation with $B = 1.55 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3486$, and $b_2 = 0.0667$. ^bGalvanic cell error in mV that has been calculated from equation $e_{\text{E,GC}} = -(3RT)/(2F)\ln(\gamma(\text{eq } 5))/(\gamma(\text{eq } 1))$.

connection of these equations), and Stables and Nuttall⁴⁸ (eqs 7 and 8). The results of the comparison of the activity coefficients with the literature values are shown in two graphs of Figure 7. Graph A shows the results from the activity coefficients recommended by Stokes³ and by Rard and Clegg⁵⁴ and those from eq 7 and graph B the other results. The quantity presented on the y axis in graphs A and B is the cell potential deviation, $e_{\text{E,GC}}$, where GC refers to the appropriate galvanic cell without a liquid junction containing electrodes reversible to the cation (Ca^{2+} in this case) and anion (Cl^-) of the electrolyte (see ref 6) that resulted from the use of the literature activity coefficients from various sources [i.e., $\gamma(\text{literature})$] when compared to the recommended ones [i.e., $\gamma(\text{recd})$] shown in Table 2. Therefore, the definition of $e_{\text{E,GC}}$ is

$$e_{\text{E,GC}} = -\frac{3RT}{2F} \ln \frac{\gamma(\text{literature})}{\gamma(\text{recd})} \quad (40)$$

In this equation, the values calculated from eq 5 were used for the recommended values.

The results of the comparison of the osmotic coefficients in Table 2 to the literature values are presented in the same way in two graphs of Figure 8. In this case, the quantity presented on the y axis in the graphs is the vapor pressure deviation [$e_{\text{p,VPW}}$ where VPW refers to the vapor pressure of water] that resulted from the use of the literature osmotic coefficients [i.e., $\phi(\text{literature})$] when compared to the recommended values [i.e., to $\phi(\text{recd})$] shown in Table 2. Literature vapor pressure $p(\text{literature})$ and the recommended one $p(\text{recd})$ were obtained from the osmotic coefficients using eqs 3 and 4 and the errors in Figure 8 using the following equation

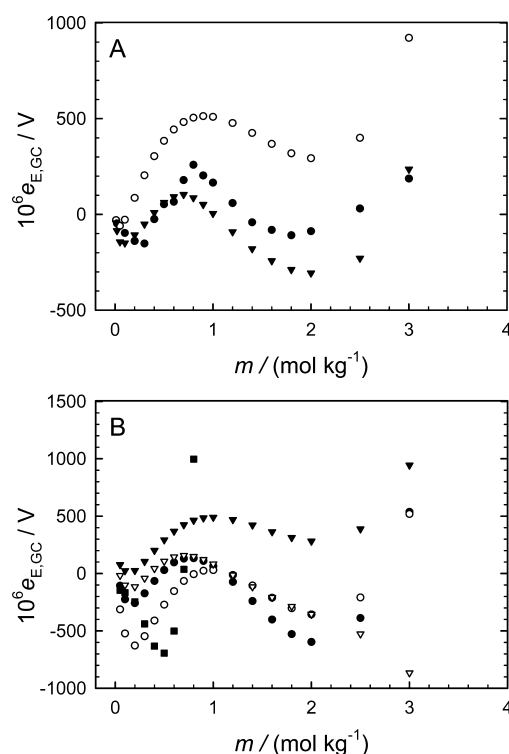


Figure 7. Deviation, expressed as galvanic cell error $e_{\text{E,GC}}$ (eq 40), between the literature activity coefficients of Stokes¹ (symbol ●, graph A), Stables and Nuttall⁴⁸ (eq 7, ○, A), Rard and Clegg (recommended values in Table 11 of ref 54, ▼, A), Pitzer and Mayorga⁵⁰ (eq 9, ●, B), Phutela and Pitzer⁵¹ (eq 9, ○, B), Ananthaswamy and Atkinson⁵² (eq 13, ▼, B), and Rard and Clegg⁵⁴ [eq 15 with model RC(1) in text, ▽, B; and eq 15 with model RC(2) in text, ■, B] and those obtained in this study using eq 5 with $B = 1.55 (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3486$, and $b_2 = 0.0667$ (Table 2) as a function of molality m .

$$e_{\text{p,VPW}} = p(\text{literature}) - p(\text{recd}) \quad (41)$$

The values obtained from eq 6 were used for the recommended values.

In general, the activity coefficients recommended by Stokes¹ and Rard and Clegg⁵⁴ agree well with those suggested here, but the values from Stables and Nuttall (eq 7) are slightly different (see Figure 7A). The osmotic coefficients in Figure 8A agree well otherwise, but the value of Rard and Clegg at 3 $\text{mol}\cdot\text{kg}^{-1}$ is considerably different. In Figures 7B and 8B, the best agreement with the new values up to 2.5 $\text{mol}\cdot\text{kg}^{-1}$ is obtained by the model RC(1) equations of Rard and Clegg.⁵⁴ On the other hand, the more complicated model RC(2) does not agree well with the new activity and osmotic coefficients. It seems that the parameters in this model cannot be used without the CaCl^+ ion parameters. The agreement of the new activity coefficients with those obtained by the parameter values of Pitzer and Mayorga⁵⁰ is best in dilute solutions ($m < 1.5 \text{ mol}\cdot\text{kg}^{-1}$), and that with those obtained by the parameter values of Phutela and Pitzer⁵¹ is best in less dilute solutions ($0.8 \text{ mol}\cdot\text{kg}^{-1} < m < 3 \text{ mol}\cdot\text{kg}^{-1}$). The equations presented by Ananthaswamy and Atkinson⁵² (eqs 13 and 14) do not predict the activity and osmotic coefficients as well as the original Pitzer equation (eqs 9 and 10)^{49,50} at the molalities considered in the figures.

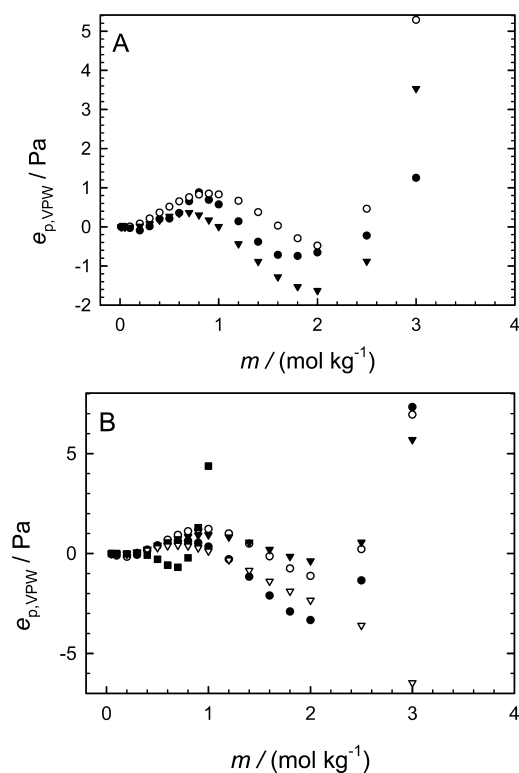


Figure 8. Deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 41), between the literature osmotic coefficients of Stokes¹ (symbol ●, graph A), Stables and Nuttall⁴⁸ (eq 8, ○, A), Rard and Clegg (recommended values in Table 11 of ref 54, ▼, A), Pitzer and Mayorga⁵⁰ (eq 10, ●, B), Phutela and Pitzer⁵¹ (eq 10, ○, B), Ananthaswamy and Atkinson⁵² (eq 14, ▼, B), and Rard and Clegg⁵⁴ [eq 16 with model RC(1) in text, ▽, B; and eq 16 with model RC(2) in text, ■, B] and those obtained in this study using eq 6 with $B = 1.55$ ($\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.3486$, and $b_2 = 0.0667$ (Table 2) as a function of molality m .

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