A Critical Comparison of the Equations Presented for Activities in Aqueous Sodium and Potassium Chloride Solutions at 298.15 K

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Eight well-known equations presented for thermodynamic activities in aqueous NaCl and KCl solutions at 298.15 K were tested with the most reliable experimental results of the isopiestic determinations reported in the literature. Usually the equations tested do not predict these data very well. Only the two-parameter Pan equation with the parameter values determined recently explains these data within experimental error up to a molality of 2.0 mol·kg^{-1}. The isopiestic results can also be predicted almost within experimental error up to the molality of the saturated KCl solution by means of a new three-parameter Glueckauf equation. The recommended values of the isopiestic ratio for this electrolyte pair have been tabulated at rounded molalities on the basis of the equations mentioned above. In addition, it was shown that activities in NaCl and KCl solutions are known considerably less accurately above than below a molality of 2.0 mol·kg^{-1}.

Introduction

The activities of sodium and potassium chlorides in aqueous solutions at 298.15 K have for a long time been the best-known reference values for the thermodynamics of electrolyte solutions. In 1945 Robinson (*1*) presented tables for the activity and osmotic coefficients in NaCl and KCl solutions from a molality of 0.1 mol·kg^{-1} to the value of the saturated solution in both cases. The values of these tables have also been often used in the determination of the activities of other electrolytes from the results of isopiestic determinations where either of these electrolytes functions as the reference electrolyte. The majority of the values of the activity and osmotic coefficients for different electrolytes in the tables of Robinson and Stokes (*2*) have been determined in this way.

Since 1970 many attempts have been made to find for each electrolyte an equation by which the activity (or osmotic) coefficients in the tables of Robinson and Stokes (*2*) can be estimated from the molality (or from some other composition variable) of the solution. Usually the equations proposed have been made electrolyte specific by several adjustable parameters. The accuracy of these formulas is often reported by means of a quantity derived from the square sum of the deviations between the observed and predicted activity coefficients. The activity coefficients of the tables, not the results of real measurements, are regarded as the observed values in these considerations.

The most accurate experimental methods to obtain activities in NaCl and KCl solutions are the electromotive force (emf) measurements on cells with a liquid junction and the isopiestic or direct vapor pressure determinations. Unfortunately, activity (or osmotic) coefficients are not easily related to the measurable quantities of the methods. Therefore, the real accuracy of the activity coefficient equations based on the tables of Robinson and Stokes (*2*) is not clearly demonstrated. In addition, the accuracy of these equations relies completely on the accuracy of the activity values in these tables.

In the present study, the activity coefficient equations presented for NaCl and KCl solutions at 298.15 K are critically tested with experimental results. The most reliable measurements for these tests are probably those of Robinson (*1*) which consist of 79 isopiestic molalities of these electrolytes from a molality of about 0.1 mol·kg^{-1} to saturated KCl solution (i.e., to about 4.8 mol·kg^{-1}). The results of this set were also one of the main sources on which the activity and osmotic coefficients in the tables of Robinson and Stokes (*2*) were based.

Results

Method of Calculations. The activity coefficient equations selected for this study are used to predict the isopiestic molalities of Robinson's set (*1*). In these calculations, NaCl is regarded as the reference electrolyte (x), and its molality m_x is thus the independent variable. The molality of the isotonic KCl solution is the dependent variable (m_y). The reverse choice was also studied in some cases, and the conclusions do not depend on the choice. For isopiestic equilibrium, the following equation holds:

$$m_y = (\varphi_x/\varphi_y)m_x = Rm_x \tag{1}$$

where φ refers to the osmotic coefficient and R is the isopiestic ratio. This equation can be used in the calculation of the predicted m_y value for each experimental point. The osmotic coefficients for this equation are calculated by the formulas tested. In the calculation of φ_y, the value of m_y is needed. Therefore, iterative calculations are required. The iterative process based on eq 1 converges rapidly, and usually about five steps are needed when the value of m_x is used in the calculation of the initial estimate of φ_y. From the measured value of m_y and the final estimate of the iterative calculations, the error for each experimental point is obtained by

$$\epsilon(m_y) = m_y(\text{obsd}) - m_y(\text{pred}) \tag{2}$$

For each activity coefficient equation tested, an error plot is drawn where the errors obtained from Robinson's set (*1*) are presented as a function of the molality m_x (see below).

Equations Tested. The activity coefficient equations used in the tests are listed below. Usually only equations are included for which the parameter values are available for both NaCl and KCl. Hence, the recent equations of Clarke and Glew (*3*) and of Archer (*4*) for NaCl solutions (these multiparameter equations cover wide ranges of temperatures and pressures) had to be omitted from the present study.

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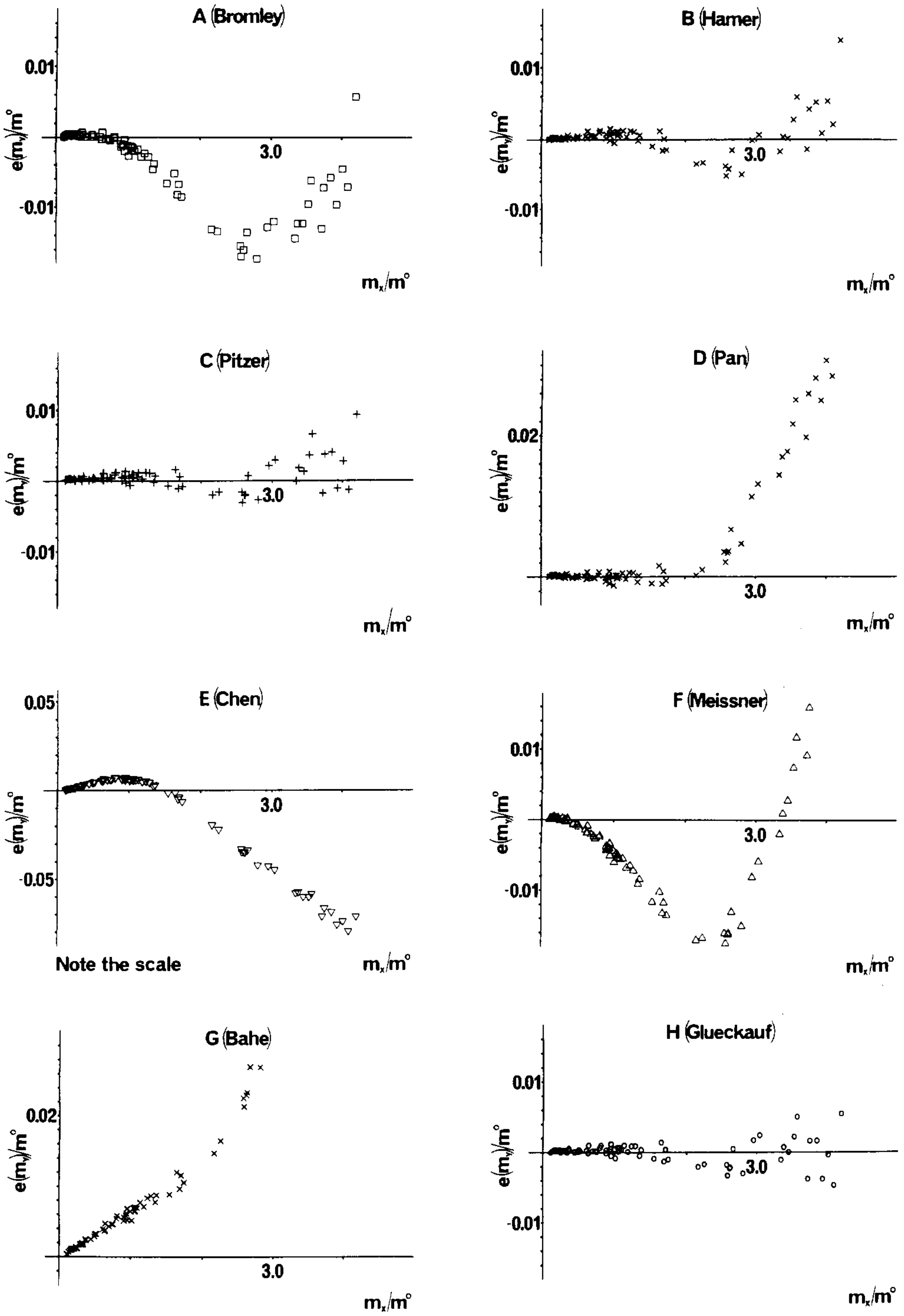

Figure 1. Difference between the measured and predicted molalities of KCl (m_y) as a function of the molality of NaCl (m_x) in the isopiestic set of Robinson (*1*). The predicted values of m_y have been calculated by the following equations: Bromley (A), Hamer and Wu (B), Pitzer and Mayorga (C), Pan (D), Chen *et al.* (E), Kusik and Meissner (F), Bahe (G) and Glueckauf (H); see text.

The equations included in the tests are presented here in the form suitable for a uni-univalent electrolyte. Also the explicit form of the corresponding osmotic coefficient equation is given in case it can be solved. The following symbols are generally used: $m^\circ = 1$ mol·kg^{-1} and $M_1 = 0.018\,015$ kg·mol^{-1}.

(A) Bromley Equation. Bromley's equation (*5*) for the mean activity coefficients ($\gamma_\pm$) has the form

$$\log \gamma_\pm = -A_\gamma m^{1/2}/(1 + \rho m^{1/2}) + Bm + [0.06(m^\circ)^{-1} + 0.6(B)]m/(1 + am)^2 \quad (3)$$

This equation contains only one parameter (B) that is dependent on the electrolyte. From this equation, the following equation can be derived for the osmotic coefficient:

$$\varphi = 1 - [A_\gamma \ln(10)/(\rho^3 m)][(1 + \rho m^{1/2}) - 2\ln(1 + \rho m^{1/2}) - 1/(1 + \rho m^{1/2})] + \ln(10)[0.06(m^\circ)^{-1} + 0.6B][(1 + 2am)/(1 + am)^2 - \ln(1 + am)/am]/a + \ln(10)Bm/2 \quad (4)$$

In eqs 3 and 4, $A_\gamma = 0.511$ (kg·mol^{-1})$^{1/2}$, $\rho = 1.0$ (kg·mol^{-1})$^{1/2}$, $a = 1.5$ kg·mol^{-1}, and B is 0.0574 kg·mol^{-1} for NaCl and 0.0240 kg·mol^{-1} for KCl. The error plot for the equation of Bromley is presented in graph A of Figure 1.

(*B*) *Hamer Equation.* Hamer and Wu's equations (*6*) for the activity and osmotic coefficient of NaCl and KCl are the following:

$$\log \gamma_\pm = -Am^{1/2}/(1 + B^*m^{1/2}) + \beta(m/m^\circ) + C(m/m^\circ)^2 + D(m/m^\circ)^3 \quad (5)$$

and

$$\varphi = 1 - \ln(10)\{\mathrm{A}[(1 + B^*m^{1/2}) - 2\ln(1 + B^*m^{1/2}) - (1 + B^*m^{1/2})^{-1}]/((B^*)^3m) - (1/2)\beta(m/m^\circ) - (2/3)\mathrm{C}(m/m^\circ)^2 - (3/4)D(m/m^\circ)^3\} \quad (6)$$

where $A = 0.5108$ (kg·mol^{-1})$^{1/2}$ and $m^\circ = 1$ mol·kg^{-1}. The following values for the electrolyte parameters of this equation were presented by these researchers: NaCl, $B^* = 1.4495$ (kg·mol^{-1})$^{1/2}$, $\beta = 0.020\,442$, $C = 0.005\,792\,7$, and $D = -0.000\,288\,60$; KCl, $B^* = 1.295$ (kg·mol^{-1})$^{1/2}$, $\beta = 0.000\,070\,00$, $C = 0.003\,599\,0$, and $D = -0.000\,195\,40$. The error plot of the equation of Hamer and Wu is presented in graph B of Figure 1.

(*C*) *Pitzer Equation.* Pitzer's activity and osmotic coefficients can be calculated by the following equations (*7*):

$$\ln \gamma_\pm = f^\gamma + B^\gamma(m/m^\circ) + C^\gamma(m/m^\circ)^2 \quad (7)$$

and

$$\varphi = 1 - A_\varphi m^{1/2}/(1 + bm^{1/2}) + B^\varphi(m/m^\circ) + C^\varphi(m/m^\circ)^2 \quad (8)$$

where

$$f^\gamma = -A_\varphi[m^{1/2}/(1 + bm^{1/2}) + 2\ln(1 + bm^{1/2})/b] \quad (9)$$

$$B^\gamma = 2\beta^\circ + 2\beta^1\{1 - \mathrm{e}^{-\alpha m^{1/2}}[1 + \alpha m^{1/2} - (1/2)\alpha^2 m]\}/(\alpha^2 m) \quad (10)$$

$$C^\gamma = (3/2)C^\varphi \quad (11)$$

and

$$B^\varphi = \beta^0 + \beta^1\mathrm{e}^{-\alpha m^{1/2}} \quad (12)$$

In these equations, $A_\varphi = 0.392$ (kg·mol^{-1})$^{1/2}$, $b = 1.2$ (kg·mol^{-1})$^{1/2}$, and $\alpha = 2.0$ (kg·mol^{-1})$^{1/2}$. Pitzer and Mayorga (*7*) presented the following values for the electrolyte parameters: NaCl, $\beta^0 = 0.0765$, $\beta^1 = 0.2664$, and $C^\varphi = 0.001\,27$; KCl, $\beta^0 = 0.048\,35$, $\beta^1 = 0.2122$, and $C^\varphi = -0.000\,84$. The error plot for the Pitzer equation is presented in graph C of Figure 1.

(*D*) *Pan Equation.* Pan (*8*) used the following simple modification of the Stokes–Robinson equation (*9*) for the activity coefficients of uni-univalent electrolytes:

$$\ln \gamma_\pm = -\frac{\alpha m^{1/2}}{1 + \beta a^* m^{1/2}} + 2M_1(\mathrm{h} - 1)m \quad (13)$$

The corresponding equation for the osmotic coefficients is

$$\varphi = 1 - [\alpha/(\beta a^*)^3 m][(1 + \beta a^* m^{1/2}) - 2\ln(1 + \beta a^* m^{1/2}) - (1 + \beta a^* m^{1/2})^{-1}] + M_1(h - 1)m \quad (14)$$

In these equations, $\alpha = 1.174\,44$ (kg·mol^{-1})$^{1/2}$ and $\beta = 3.2849$ (kg·mol^{-1})$^{1/2}$ nm^{-1}. The parameters that are dependent on the electrolyte are the ion-size parameter (a^*) and the hydration number (h). In a previous paper (*10*), the following values for the parameters of the Pan equation were determined: NaCl, $a^* = 0.43$ nm and $h = 3.01$; KCl, $a^* = 0.39$ nm and $h = 1.42$. In the present tests these values are used. The error plot of the Pan equation with the parameter values mentioned above is presented in graph D of Figure 1.

(*E*) *Chen Equation.* Chen *et al.* (*11*) presented the following equations for the mean activity coefficient of a uni-univalent electrolyte:

$$\ln \gamma_\pm = (\ln \gamma_{\mathrm{x,c}} + \ln \gamma_{\mathrm{x,a}})/2 - \ln(1 + 2M_1 m) \quad (15)$$

$$\ln \gamma_{\mathrm{x,c}} = \ln \gamma_{\mathrm{x,a}} = \ln \gamma_i^{\mathrm{pdh}} + \ln \gamma_i^{\mathrm{lc}} \quad (16)$$

$$\ln \gamma_i^{\mathrm{pdh}} = -[\mathrm{A}_\varphi/(M_1)^{1/2}][2\ln(1 + \rho I_{\mathrm{x}}{}^{1/2})/\rho + (I_{\mathrm{x}}{}^{1/2} - 2I_{\mathrm{x}}I_{\mathrm{x}}{}^{1/2})/(1 + \rho I_{\mathrm{x}}{}^{1/2})] \quad (17)$$

$$I_{\mathrm{x}} = (x_{\mathrm{c}} + x_{\mathrm{a}})/2 = x \quad (18)$$

$$\ln \gamma_i^{\mathrm{lc}} = \mathrm{x}_1{}^2\tau_1\mathrm{e}^{-\alpha\tau_1}/(2x\mathrm{e}^{-\alpha\tau_1} + x_1)^2 - xx_1\tau_2\mathrm{e}^{-\alpha\tau_2}/(x + x_1\mathrm{e}^{-\alpha\tau_2})^2 + x_1\tau_2\mathrm{e}^{-\alpha\tau_2}/(x + x_1\mathrm{e}^{-\alpha\tau_2}) - \tau_2 - \tau_1\mathrm{e}^{-\alpha\tau_1} \quad (19)$$

The corresponding equations for the osmotic coefficients are the following:

$$\varphi = -(\ln \gamma_1^{\mathrm{pdh}} + \ln \gamma_1^{\mathrm{lc}} + \ln x_1)/(2M_1 m) \quad (20)$$

$$\ln \gamma_1^{\mathrm{pdh}} = [2A_\varphi/(M_1)^{1/2}][I_{\mathrm{x}}I_{\mathrm{x}}{}^{1/2}/(1 + \rho I_{\mathrm{x}}{}^{1/2})] \quad (21)$$

$$\ln \gamma_1^{\mathrm{lc}} = -2xx_1\tau_1\mathrm{e}^{-\alpha\tau_1}/(2\mathrm{x}\mathrm{e}^{-\alpha\tau_1} + \mathrm{x}_1)^2 + 2x\tau_1\mathrm{e}^{-\alpha\tau_1}/(2\mathrm{x}\mathrm{e}^{-\alpha\tau_1} + x_1) + 2x^2\tau_2\mathrm{e}^{-\alpha\tau_2}/(x + x_1\mathrm{e}^{-\alpha\tau_2})^2 \quad (22)$$

In the equations of Chen *et al.* (*11*), $A_\varphi = 0.392$ (kg·mol^{-1})$^{1/2}$, $\rho = 14.9$, $\alpha = 0.2$, and x_{a}, x_{c}, and x_1 refer to the mole fractions of the cation, anion, and solvent (water in this case), respectively, and in this case $x_{\mathrm{c}} = x_{\mathrm{a}} = x$. Chen and Evans (*12*) presented the following values for the electrolyte parameters of these equations: NaCl, $\tau_1 = \tau_{\mathrm{ca,w}} = -4.5916$ and $\tau_2 = \tau_{\mathrm{w,ca}} = 9.0234$; KCl, $\tau_1 = -4.1341$ and $\tau_2 = 8.1354$. The error plot obtained from Robinson's isopiestic results by means of the equation of Chen *et al.* (*11*) is presented in graph E of Figure 1.

(*F*) *Meissner Equation.* The following equation was presented for the activity coefficient by Kusik and Meissner (*13*):

$$\gamma_\pm = \{1 + B[1 + 0.1(m/m^\circ)]^q - B\}\gamma^* \quad (23)$$

where

$$B = 0.75 - 0.065q \quad (24)$$

$$\log \gamma^* = -\mathrm{A}_\gamma m^{1/2}/[1 + C(m/m^\circ)^{1/2}] \quad (25)$$

$$C = 1 + 0.055q\mathrm{e}^{-0.023(m/m^\circ)^3} \quad (26)$$

In eq 25 $A_\gamma = 0.5107$ (kg·mol^{-1})$^{1/2}$. The electrolyte parameter in this equation is q, and these researchers presented the values of 2.23 and 0.92 for this parameter in NaCl and KCl solutions, respectively. The determination of an analytic expression for the osmotic coefficient from the equations above is difficult (or perhaps impossible). However, the osmotic coefficient can be calculated numerically with computers by means of these equations using the thermodynamic identity

$$\varphi = 1 + (1/m)\int_0^{\ln\gamma_\pm} m\, d(\ln \gamma_\pm) \qquad (27)$$

The error plot for the equation of Kusik and Meissner was obtained with the numerical calculations of this kind, and it is presented in graph F of Figure 1.

(G) Bahe Equation. Bahe (*14*) presented the following equation for the activity coefficients:

$$\log \gamma_\pm = -A(c/c°)^{1/3} + B(c/c°) - \log(1 + 2M_1 m) \qquad (28)$$

where $c°$ is 1 mol·dm^{-3} and A is a constant (at 298.15 K, its value is 0.288 94). B is the parameter that is dependent on the electrolyte, and its values for NaCl and KCl are 0.0970 and 0.0680, respectively. c is the concentration of the electrolyte, and it can be calculated from the molality by using the following equation presented by Harned and Owen (*15*):

$$(cm°)/(mc°) = \rho_1 - a(m/m°) + b(m/m°)^2 \qquad (29)$$

where $\rho_1 = 0.997$ and $a = 0.0183$ and $b = 0$ for NaCl and $a = 0.0284$ and $b = 0.0003$ for KCl. The adequacy of eq 29 for the present purpose was checked by several density results found in the literature. In the tests of the equation of Bahe (*14*), the osmotic coefficients were calculated numerically by using eq 27. The test results are presented as an error plot in graph G of Figure 1.

(H) Glueckauf Equation. The equations presented by Glueckauf (*16*) for the activity and osmotic coefficients were used here in the following forms:

$$\ln \gamma_\pm = -\alpha m^{1/2}/(1 + \beta a^* m^{1/2}) + M_1 rm(r + h_c - 2)/[2(1 + M_1 rm)] + [(h_c - 2)/2] \ln(1 + M_1 rm) - (h_c/2) \ln(1 - M_1 h_c m) \qquad (30)$$

and

$$\varphi = -\alpha[(1 + \beta a^* m^{1/2}) - 2 \ln(1 + \beta a^* m^{1/2}) - (1 + \beta a^* m^{1/2})^{-1}]/[(\beta a^*)^3 m] - \ln[(1 - M_1 h_c m)/(1 + M_1 rm)]/(2M_1 m) - (h_c + r - 2)/[2(1 + M_1 rm)] \qquad (31)$$

where $\alpha = 1.174\,44$ (kg·mol^{-1})$^{1/2}$ and $\beta = 3.2849$ (kg·mol^{-1})$^{1/2}$ nm^{-1}. These equations contain three parameters that are dependent on the electrolyte, and two of these parameters (i.e., a^* and h_c) were determined from the activity data. The r parameter is defined by

$$r = V_{m,2}^{\infty}/V_{m,1}° \qquad (32)$$

where $V_{m,2}^{\infty}$ is the partial molar volume of the electrolyte at infinite dilution and $V_{m,1}°$ is the molar volume of pure water. With the $V_{m,2}^{\infty}$ values given by Harned and Owen (*15*) a value of 0.91 for r of NaCl and a value of 1.47 for r of KCl are obtained. For NaCl, Glueckauf presented the values of 0.422 nm and 2.50 for a^* and h_c, respectively. For the present tests, the h_c value of Glueckauf was accepted but the value of the best Pan equation for a^*, 0.43 nm, was used instead of the Glueckauf value. Since Glueckauf presented no values of a^* and h_c for KCl, they had to be estimated. For a^* the value of the Pan equation, 0.39 nm, was again taken. The value of h_c was then determined from Robinson's data (*1*). The best fit with these results is obtained when the value of h_c for KCl is 1.31. The error plot for the new Glueckauf equations is shown in graph H of Figure 1.

Discussion

According to graph D of Figure 1, the isopiestic molalities of Robinson can be predicted within experimental error up to a molality of 2.0 mol·kg^{-1} with the Pan equations for NaCl and KCl. In this case, the absolute errors are usually less than 0.0005 mol·kg^{-1} and form a completely random pattern. In the previous paper (*10*) it is presented, in addition, that these equations predict very accurately up to this limit almost all reliable thermodynamic data measured in solutions of these electrolytes at 298.15 K. Therefore, we have good reason to believe that the activity quantities obtained by these equations are not far from the real values. As a consequence, the thermodynamical data of various experimental methods can be reproduced almost as accurately as they can be measured by means of these simple equations. In the previous paper (*10*), a new table of the activity and osmotic coefficients for NaCl and KCl solutions is presented, and this table was based on the Pan equations. It contains, according to our understanding, the most reliable values available.

According to graph H of Figure 1, the equation of Glueckauf (*16*) explains the isopiestic data almost within experimental error up to the molality of the saturated KCl solution. Because of the good predictive ability of this simple equation, it is interesting to see how well this equation applies to experimental data of other sources, especially how well this equation works above the molality of 2.0 mol·kg^{-1} (the upper limit for the Pan equation, see above). For the concentrated NaCl solutions in the literature are available accurate results of the direct vapor pressure determinations by Negus [see Robinson (*1*)], Olynyk and Gordon (*17*), Gibbard *et al.* (*18*), and Pepela and Dunlop (*19*). For the present tests the experimental vapor pressure were first scaled, as presented in ref 10, with the value of 23.766 mmHg (=3.1686 kPa) for p_1^* (i.e., for the vapor pressure of pure water at 298.15 K); see Kell (*20*). The predicted values are then obtained by

$$p_1 = p_1^* e^{-2mM_1\varphi} \qquad (33)$$

The error plots from the four vapor pressure sets are then drawn so that the errors defined by

$$\epsilon(p_1) = p_1(\text{obsd}) - p_1\,(\text{pred}) \qquad (34)$$

are presented as a function of the molality in each set. The vapor pressure error plot of the Glueckauf equation is presented in graph A of Figure 2. According to this graph, the Glueckauf equation does not predict even satisfactorily the experimental vapor pressures of NaCl solutions above a molality of 2.0 mol·kg^{-1}.

Although eq 31 does not explain the vapor pressures of NaCl solutions, the following extended version of it turned out to be sufficient:

$$\varphi = \varphi(\text{eq } 31) + d(m/m°)^2 \qquad (35)$$

From the set of Negus (see ref 1) and that of Olynyk and Gordon (*17*) a value of 0.0030 can be obtained by curve fitting for the d parameter of this equation. The errors obtained from the four vapor pressure sets mentioned above by eq 35 are shown as error plots in graph B of Figure 2. According to this graph, the extended equation predicts the observed vapor pressures nearly within experimental error. [Below the molality of 2.0 mol·kg^{-1}, however, the osmotic coefficients

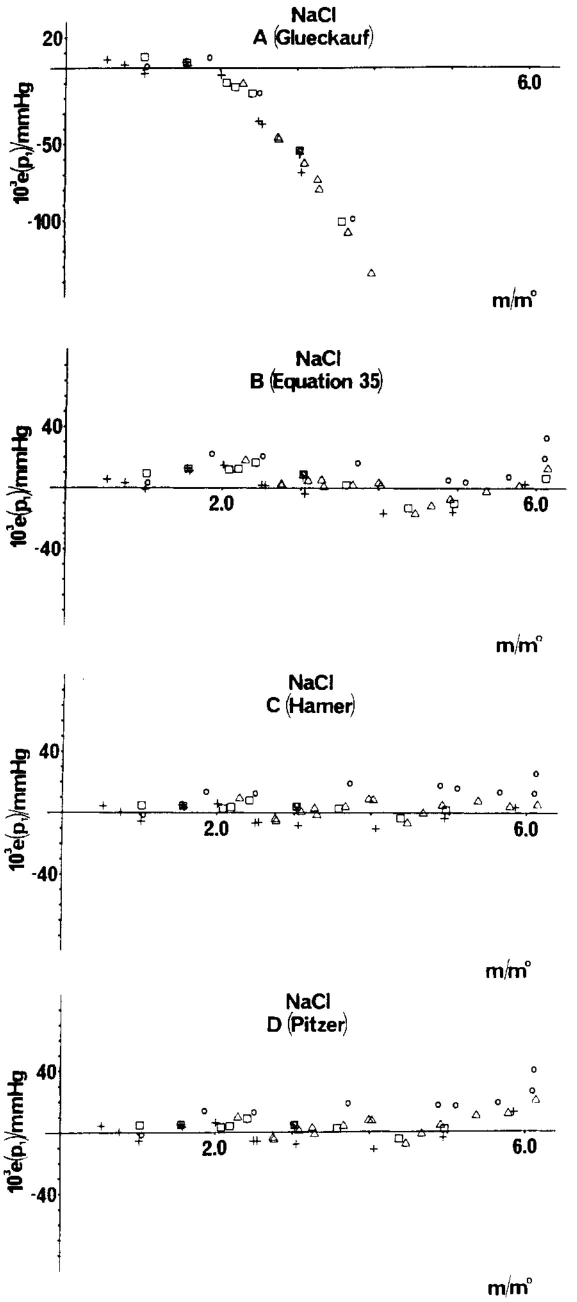

Figure 2. Difference between the observed and predicted vapor pressures of water in NaCl solutions. The observed values have been obtained by Negus [see Robinson (*1*), symbol □], Olynyk and Gordon (*17*), (△), Gibbard *et al.* (*18*) (○), and Pepela and Dunlop (*19*) (+). The predicted values have been calculated by eq 33 with eq 31 (graph A), eq 35 (B), eq 6 (C), or eq 8 (D); see text.

of eq 35 are considerably less accurate than those of eq 14 or 31.]

According to Figure 1, both the equation of Pitzer and that of Hamer and Wu describe also satisfactorily all experimental data reported by Robinson (*1*). The other four equations, whose error plots are presented in this figure, reproduce these data so that the error plot cannot be regarded as random. With the vapor pressure data used above also the equations of Pitzer and Hamer are tested further. The results of these tests are shown in graphs C and D of Figure 2. According to these graphs, the equations tested predict probably within experimental error the vapor pressures of NaCl solutions.

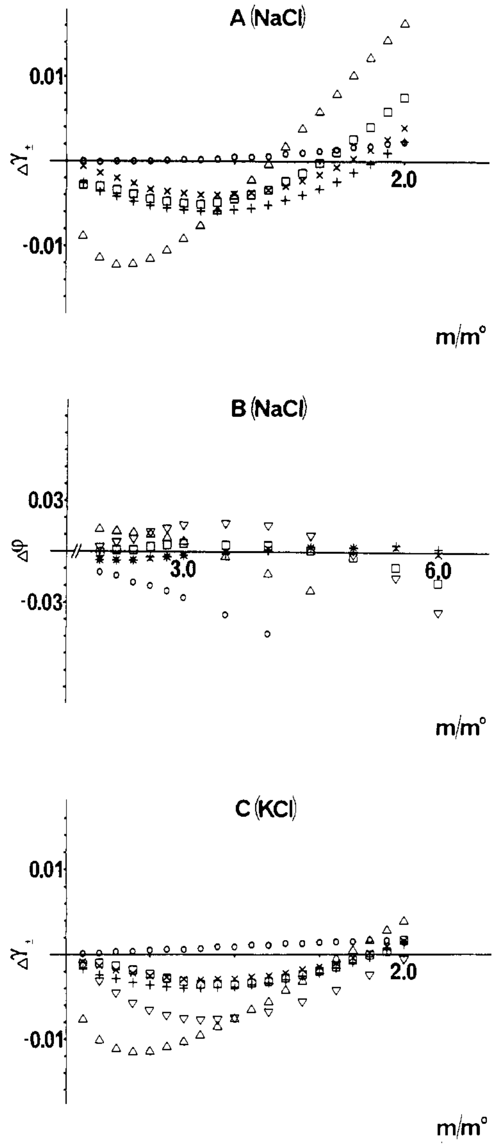

Figure 3. Difference between the activity or osmotic coefficients calculated by the different models and those calculated by eq 13 (activity coefficient) or eq 35 (osmotic coefficient). Graph A contains the results of dilute NaCl solutions, graph B those of concentrated NaCl solutions, and graph C those of dilute KCl solutions. The symbols of the models are the following: Hamer and Wu (*6*) (×), Pitzer and Mayorga (*7*) (+), Glueckauf (*16*) (○), Bromley (*5*) (□), Kusik and Meissner (*13*) (△), and Chen *et al.* (*11*) (▽).

The results of the comparison of the activity quantities of the different equations are presented in Figure 3. In this figure the quantity of $\Delta\gamma_{\pm}$ defined by

$$\Delta\gamma_{\pm} = \gamma_{\pm}(\text{eq tested}) - \gamma_{\pm}(\text{eq } 13) \qquad (36)$$

or the quantity defined by

$$\Delta\varphi = \varphi(\text{eq tested}) - \varphi(\text{eq } 35) \qquad (37)$$

is presented as a function of the molality. In this comparison below the molality of 2.0 mol·kg^{-1}, eq 36 was used and the latter activity coefficient term was calculated by eq 13; above this limit, eq 37 was used and the latter osmotic coefficient term was calculated by eq 35. For KCl solutions, only the molalities below 2.0 mol·kg^{-1} are included (owing to the lack of the reliable vapor pressure results; see ref 10). The results of NaCl solutions are presented in graphs A ($m < 2.0$ mol·kg^{-1}) and B ($m > 2.0$ mol·kg^{-1}) of Figure 3, and those of KCl solutions in graph C of this figure. The activity and osmotic coefficients

Table 1. Recommended Isopiestic Ratios (*R* Values in Eq 1) for NaCl and KCl Solutions at 298.15 K as a Function of the Molality of NaCl

m(NaCl)/(mol·kg^{-1})	R	m(NaCl)/(mol·kg^{-1})	R
0.1	1.0068	1.2	1.0487
0.2	1.0118	1.4	1.0551
0.3	1.0163	1.5	1.0583
0.4	1.0205	1.6	1.0614
0.5	1.0244	1.8	1.0675
0.6	1.0282	2.0	1.074
0.7	1.0318	2.5	1.090
0.8	1.0353	3.0	1.106
0.9	1.0388	3.5	1.122
1.0	1.0421	4.0	1.137

of the Bahe equation (see eq 28) are omitted from all the graphs and the activity coefficients of the Chen equation (eq 15) from graph A because the $\Delta\gamma_\pm$ and $\Delta\varphi$ values in those cases lay usually outside the scales of the graphs. According to graphs A and C of Figure 3, the activity coefficients of the different equations included in these graphs usually agree within 0.01. The activity coefficients of the Glueckauf equation agree very well with the recommended values of ref 10 (the largest deviation between these values is about 0.002). Of the equations containing only one electrolyte parameter, the best one seems to be that of Bromley; see also Figure 1.

Above the molality of 2.0 mol·kg^{-1}, the osmotic coefficients are not yet known as accurately as below this limit. Sensitivity analysis, carried out by rounding the osmotic coefficients of the different equations, showed that the accuracy of φ needed to explain even the best vapor pressure data is less than 0.001. According to graph B of Figure 3, the osmotic coefficients for NaCl solutions predicted by the different equations included in this graph (eq 31 is an exception; see above) agree usually with each other almost within the accuracy that can be obtained from the vapor pressure determinations.

Vapor pressure measurements are the most reliable method to obtain absolute osmotic (and activity) coefficients in NaCl or KCl solutions at 298.15 K when the emf measurements by cells with transference are missing (i.e., after about 0.1 mol·kg^{-1}). The accuracy of the experimental osmotic coefficient obtained by this method depends on the molality, and it is at its best in concentrated solutions. As mentioned above even in this case it is less than 0.001. Therefore, we believe that the activity and osmotic coefficients given, e.g., in the tables of Robinson and Stokes (*2*), with a precision of 0.0001 contain too many digits. The use of these tables in the parameter estimation of the activity equations (dealt with above) can be a significant reason why many of these equations do not explain well the experimental results of more accurate methods (see Figure 1).

The isopiestic ratios (i.e., the *R* values in eq 1) for NaCl and KCl solutions are known better than the absolute osmotic coefficients up to the molality of the saturated KCl solution (see Figure 1). The suggested values for the isopiestic ratio are tabulated in Table 1 at several rounded molalities of NaCl solutions. The values of this table have been calculated by the Pan equation up to a molality of 1.8 mol·kg^{-1} and by the Glueckauf equation above this molality limit. For the absolute activity and osmotic coefficients of NaCl and KCl above 2.0 mol·kg^{-1}, for example, the Hamer values (see eqs 5 and 6) can be at the moment recommended. The accuracy of these values is, however, not much better than 0.01.

Acknowledgment

The authors want to thank Mrs. Marja-Liisa Varpenius for her technical assistance in preparing the figures of this study.

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Received for review June 10, 1993. Revised November 24, 1993. Accepted April 4, 1994.® J.I.P. is indebted to the Research Foundation of Lappeenranta University of Technology (the Lahja and Lauri Hotinen's Fund) for financial support.

® Abstract published in *Advance ACS Abstracts,* June 1, 1994.