Thermodynamic Activity Quantities in Aqueous Sodium and Potassium Chloride Solutions at 298.15 K up to a Molality of 2.0 mol kg^{-1}

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The Hückel equation used in this study to correlate the experimental activities of NaCl and KCl solutions to the molality at 298.15 K contains two parameters being electrolyte dependent: the ion-size parameter ($a*$) and the hydration number (h). In these correlations the values of $a*$ used were those previously obtained for 273 K from the freezing-point data. The value of the parameter h for NaCl was determined from the most reliable results found in the literature for concentration cells with transference. By also using the new value of h for NaCl, the corresponding value for KCl was obtained from the most accurate results of isopiestic determinations reported for this pair of electrolytes. The resulting two Hückel equations were thoroughly tested with a large number of experimental data presented in the literature on the basis of electrochemical, isopiestic and direct vapor pressure measurements. Most of these data can be predicted within experimental error by means of the Hückel equations up to a molality of 2.0 mol kg^{-1}. Reliable activity and osmotic coefficients of NaCl and KCl can therefore be calculated by these Hückel equations at any molality from 0 to 2.0 mol kg^{-1}. The values so obtained are probably the most accurate values available, and they have been tabulated at several rounded molalities. The activity and osmotic coefficients in these tables have been compared to those previously recommended by various authors. The differences between the new and previously recommended values of the two activity quantities are usually small, but often they are statistically significant.

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 in 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 later been widely accepted and used, e.g. in the analysis of isopiestic results. Both NaCl and KCl are often used as the reference electrolytes in isopiestic determinations. The activity and osmotic coefficients of Robinson's tables[1] are recommended in the well known book of Robinson and Stokes,[2] and these values were often used in the determinations of the activity tables of this book for other electrolytes from isopiestic results. 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 for

different electrolytes in their famous article[3] on the thermodynamics of single electrolytes.

In the present study it is shown that more reliable activity values for NaCl and KCl solutions at 298.15 K than those in Robinson's tables[1] can be obtained by such a simple equation as the Hückel equation up to a molality of 2.0 mol kg^{-1}. The form of the Hückel equation used in this investigation contains two parameters that are dependent on the electrolyte: the ion-size parameter ($a*$) and the hydration number (h). The values of these parameters for NaCl and KCl are obtained here in principle in the following way:

(1) The values obtained in the previous papers[4,5] for $a*$ of NaCl and KCl at 273 K are used. In those papers, the Hückel parameters were determined from the freezing-point depression data. (Our results show that, at least within the temperature range 273–298 K, $a*$ can be assumed to be independent of temperature.)

(2) The value of h for NaCl is determined from the data measured by Janz and Gordon[6] on concentration cells with transference.

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(3) The value of h for KCl is determined from the isopiestic molalities reported by Robinson[1] for NaCl and KCl solutions.

The resulting Hückel equations are then tested with all pertinent experimental data found in the literature. All tests of this study are performed so that real results of appropriate measurements are predicted by means of the Hückel equations. This method has the advantage that the prediction error can be directly compared to the experimental error. It is shown below that in these tests the Hückel equations proved to be very reliable. In most cases the measured results of these tests can be predicted within experimental error by means of these equations. Activity and osmotic coefficients are calculated using the new parameter values at several rounded molalities, and these values are tabulated as the recommended values. They are then compared to the activity values of the previous investigations (some of which, in addition to Robinson's values,[1] have achieved a wide acceptance).

Results

1) *Equations for the activity quantities.* It has been previously[7] found that it is advantageous to write the Hückel equation for the mean activity coefficient ($\gamma_\pm$) of a uni-univalent electrolyte in the form presented by Pan[8] [eqn. (1)], where m is the molality of the solution and the

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

meanings of the other symbols are explained below. From eqn. (1), eqn. (2) can be derived for the osmotic coefficient (φ) by means of the Gibbs–Duhem equation. The

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

osmotic coefficient is related to the activity of the solvent (water in this case) by the thermodynamic identity (3). In

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

the solutions considered in this study, the activity of water (a_1) is related to the vapor pressures of water over the solution (p_1) and to the vapor pressure of pure water at the temperature of the solution (p_1^*) by eqn. (4). At a temperature of 298.15 K and at a pressure of 101.325 kPa,

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

the Debye–Hückel constants α and β in eqns. (1) and (2) have the values 1.17444 $(\mathrm{kg\ mol^{-1}})^{1/2}$ and 3.2849

$(\mathrm{kg\ mol^{-1}})^{1/2}\ \mathrm{nm^{-1}}$, respectively.[9] In these equations the parameters that are dependent on the electrolyte are the ion-size parameter (a^*) and the hydration number (h). In addition, in eqns. (1)–(4) M_1 is the molar mass of water ($= 0.018\ 015\ \mathrm{kg\ mol^{-1}}$), and at 298.15 K the vapor pressure of pure water (p_1^*) is 23.766 mmHg.[10]

Hamer and Wu[11] have presented eqns. (5) and (6) for the activity and osmotic coefficient of a uni-univalent electrolyte at 298.15 K, where $A = 0.5108$ $(\mathrm{kg\ mol^{-1}})^{1/2}$

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

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

and m° ($= 1\ \mathrm{mol\ kg^{-1}}$) makes the terms containing the molality dimensionless. Hamer and Wu[11] have also presented the following values for the electrolyte parameters in these equations. NaCl: $B^* = 1.4495\ (\mathrm{kg\ mol^{-1}})^{1/2}$, $\beta = 0.020\ 442$, $C = 0.005\ 7927$ and $D = -0.000\ 288\ 60$; KCl: $B^* = 1.295\ (\mathrm{kg\ mol^{-1}})^{1/2}$, $\beta = 0.000\ 070\ 00$, $C = 0.003\ 5990$ and $D = -0.000\ 195\ 40$.

Pitzer's activity and osmotic coefficients for a uni-univalent electrolyte at 298.15 K can be calculated

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

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

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

$$B^\gamma = 2\beta^0 + 2\beta^1\{1 - e^{-\alpha m^{1/2}}$$
$$\times [1 + \alpha m^{1/2} - (1/2)\alpha^2 m]\}/(\alpha^2 m) \qquad (10)$$

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

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

by eqns. (7)–(12).[3] In these equations, $A_\varphi = 0.392$ $(\mathrm{kg\ mol^{-1}})^{1/2}$, $b = 1.2$ $(\mathrm{kg\ mol^{-1}})^{1/2}$ and $\alpha = 2.0$ $(\mathrm{kg\ mol^{-1}})^{1/2}$. Pitzer and Mayorga[3] have also 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 $C^\varphi = -0.000\ 84$.

2) *Estimation of the Hückel parameters for NaCl.* In the present study the parameters of the Hückel equation for NaCl have been determined from the results of Janz and Gordon[6] measured by concentration cells of type (13).

$$\mathrm{Ag|AgCl(s)|NaCl(aq,}\ m_1)|\mathrm{NaCl(aq,}\ m_2)|\mathrm{AgCl(s)|Ag} \qquad (13)$$
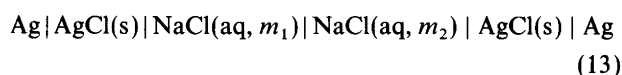
The EMF (E) of cells of type (13) depends on the molalities m_1 and m_2 according to eqn. (14), where Δt_+ is

$$E = -(2RT/F)\left(t_+(1)\ln(m_2/m_1) \right.$$

$$+ t_+(1)\ln[\gamma_\pm(2)/\gamma_\pm(1)]$$

$$\left. + \int_{m_1}^{m_2} \Delta t_+ \, dm/m + \int_{\gamma_\pm(1)}^{\gamma_\pm(2)} \Delta t_+ \, d\gamma_\pm/\gamma_\pm \right) \qquad (14)$$

$$\Delta t_+ = t_+ - t_+(1) \qquad (15)$$

given by eqn. (15). In eqns. (14) and (15) t_+ is the cationic transference number and $t_+(1)$ is its value in the solution whose molality is m_1. In a previous paper[12] the values of the parameters of several electrolytes were determined for the relationship of eqn. (16) between the molality and the transference number at 298.15 K. The

$$t_+ = t_+^\infty - A(m/m^0)^{1/2} + B(m/m^0) \qquad (16)$$

values of parameters t_+^∞, A and B in eqn. (16) are 0.396 17, 0.048 03 and 0.043 99 for NaCl, and 0.490 47, 0.003 85 and 0.006 67 for KCl, respectively.

The freezing-point depressions of dilute NaCl solutions can be predicted very accurately by a Hückel equation with $a^* = 0.43$ nm.[4] This value was accepted here for the Hückel equation for NaCl at 298.15 K. With this value for a^*, the best value of 3.01 for the parameter h was obtained from the set of Janz and Gordon.[6] This h-value was determined by minimization of the sum of squared prediction errors defined for a general variable z by eqn. (17). In this

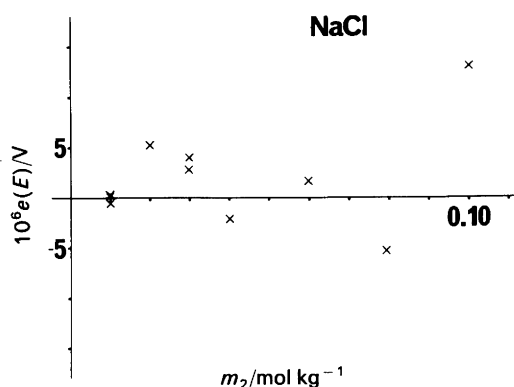$$S(z) = \sum_{i=1}^{N} e_i(z)^2 \qquad (17)$$

Fig. 1. The difference between the observed and predicted EMF values as a function of the molality m_2 in the set measured by Janz and Gordon[6] on concentration cells with transference in NaCl solutions, see cell (13) in the text. The predicted values were calculated by means of eqn. (14) using also eqns. (1) and (16). In eqn. (1) the values of $a^* = 0.43$ nm and $h = 3.01$ and in eqn. (16) the parameter values given in the text were used. In all points of this set the value of m_1 is about 0.05 mol kg^{-1} and the exact values of m_1, given in Ref. 6, were used in the calculations. A possible outlier was omitted; its coordinates are $(m_2 = 0.019\ 978\ m^0,$ $e(E) = +24.5\ \mu V)$.

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case, z represented the electromotive force E and the errors were thus calculated by eqn. (18), where E(predicted) was calculated using eqn. (14) by means of eqn. (16)

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

with the parameter values given in the text for NaCl, and by means of eqn. (1) with $a^* = 0.43$ nm and with the systematically varied values of h. In this estimation only a small weight was given for a point of $(m_1 = 0.049\ 826\ m^0,$ $m_2 = 0.019\ 978\ m^0$ and $E = 0.017\ 112$ int. V), which seems to be a slightly erroneous point. When this point is omitted, the residual standard deviation of fit, s_0, defined by eqn. (19) in which N is the number of points, is a rather sensitive function of h, as the following data

$$s_0(z) = [S(z)/(N-1)]^{1/2} \qquad (19)$$

confirm: $[h = 2.8,\ s_0(E) = 6.8\ \mu V]$, (2.9, 5.6), (3.0, 5.3), (3.1, 6.0) and (3.2, 7.5). The error plot [in which the errors of Janz and Gordon's set, the $e(E)$ values in eqn. (18), are presented as a function of m_2] is shown for the resulting Hückel equation in Fig. 1.

3) *Estimation of the Hückel parameters for KCl.* The parameter values presented above for NaCl also proved to apply for molalities much higher than those used in their estimation (see below). These values were therefore accepted for the Hückel equation of NaCl. In the same way as above for NaCl, the values of a^* for KCl can be obtained from the freezing-point results. In Ref. 5 it has been shown that a value of 0.39 nm for a^* seems to be the best one for dilute KCl solutions.

The most reliable value for the parameter h of KCl can probably be determined from the isopiestic results of Robinson.[1] In this determination, NaCl can be regarded as the reference electrolyte (x) because the activities in the solutions of this salt are known (see above). In the present calculations, the molality of NaCl was therefore used as the independent variable (m_x), and the molality of the isotonic KCl solution was the response variable (m_y). Afterwards, the reverse choice was also studied, and the results obtained do not appreciably depend on the choice. In the isopiestic equilibrium with these symbols, eqn. (20) can be written. The value of h for KCl $(=h_y)$

$$m_y = (\varphi_x/\varphi_y)\, m_x \qquad (20)$$

was chosen which gives the minimum for the sum of squared prediction errors defined by eqn. (17), where now z represents the quantity m_y. The errors are thus calculated by eqn. (21), where m_y(predicted) was computed for each experimental point using eqns. (2) and (20).
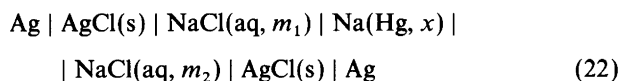
$$e(m_y) = m_y(\text{observed}) - m_y(\text{predicted}) \qquad (21)$$

The determination of m_y(predicted) requires iterative calculations. It has been verified that about five iterative steps are usually a sufficient number. During the estima-

tion of the h_y-value, it was observed that only 58 [N in eqn. (17)] out of the 79 points forming Robinson's set (i.e. only those points where $m_x < 2.2$ mol kg^{-1}) could be included in the determination of h_y.

By the method described above, a value of 1.42 was determined for the Hückel parameter h of KCl. As mentioned in the previous paragraph, this value and the corresponding value of NaCl (3.01) apply up to molalities slightly above 2 mol kg^{-1}. In the estimation of the h_y-value it was observed that the residual standard deviation of fit, eqn. (19), is a sensitive function of h_y, as the following results indicate: ($h_y = 1.39$, $s_0(m_y) = 0.000\ 94\ m^\circ$), (1.40, 0.000 71), (1.41, 0.000 54), (1.42, 0.000 47), (1.43, 0.000 56), (1.44, 0.000 75) and (1.45, 0.000 98). The error plot in which the errors of Robinson's set, the $e(m_y)$ values in eqn. (21), are presented as a function of the molality m_x is shown in Fig. 2.

4) *Tests of the resulting Hückel equations.* The new parameter values of the Hückel equation can be tested with the existing experimental data obtained by various methods. Reliable electrochemical measurements in NaCl and KCl solutions at 298.15 K have been made on concentration cells of the type (13) and on cells of types (22) and (23), which also can be written correspondingly for

Ag | AgCl(s) | NaCl(aq, m_1) | Na(Hg, x) |

| NaCl(aq, m_2) | AgCl(s) | Ag   (22)

Na(Hg, x) | NaCl(aq, m) | AgCl(s) | Ag   (23)

KCl solutions. For these tests, results of some isopiestic studies in NaCl and KCl solutions and results of several direct vapour pressure determinations in solutions of either of these electrolytes are also available in the literature.

Measurements on the concentration cells of type (13) have been made by in addition to Janz and Gordon (see
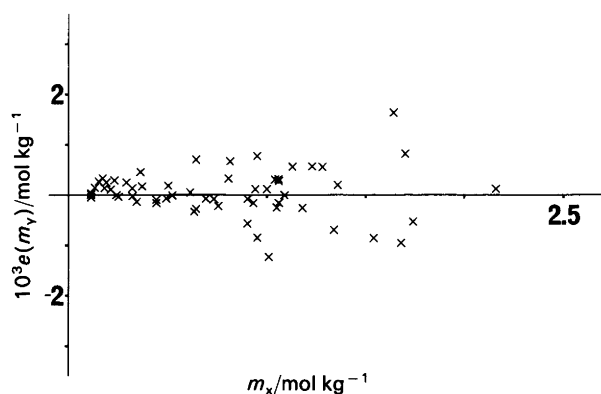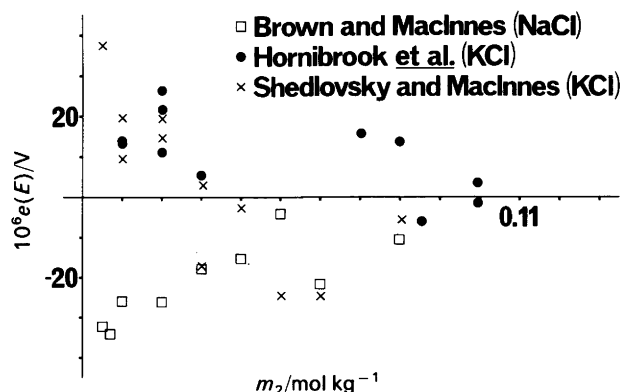

Fig. 3. The difference between the observed and predicted EMF values as a function of the molality m_2 in the sets measured by Brown and MacInnes,[13] Shedlovsky and MacInnes[14] and Hornibrook et al.[15] on concentration cells with transference, see cell (13). The predicted EMF values were calculated as described in the text. In the set of Brown and MacInnes the molality m_1 is always 0.100 00 mol kg^{-1}, in that of Shedlovsky and MacInnes it is 0.100 57 mol kg^{-1}, and in the set of Hornibrook et al. it varies slightly from one point to another around a value of 0.05 mol kg^{-1}. (The exact values given in the original paper[15] were used in the calculations.) The concentrations of the KCl solutions reported by Shedlovsky and MacInnes were converted into the molalities by means of the following equation for the density (ρ) of KCl solutions at 298.15 K (Ref. 12): $\rho/(\text{g cm}^{-3}) = 0.997\ 07 + 0.047\ 383\ (c/\text{mol dm}^{-3}) - 0.002\ 7181\ (c/\text{mol dm}^{-3})^2$.

above), Brown and MacInnes (NaCl),[13] Shedlovsky and MacInnes (KCl)[14] and Hornibrook et al. (KCl).[15] The test results obtained from these data are presented in Fig. 3. They are shown in this figure as error plots in the same way as the results of Fig. 1.

The most extensive measurements on concentration cells of type (22) in both NaCl and KCl solutions have been made by Harned et al.[16,17] Caramazza[18] has also

Fig. 2. The difference between the observed and predicted molality 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 were calculated using eqn. (20) by means of eqn. (2) with $a_x^* = 0.43$ nm, $h_x = 3.01$, $a_y^* = 0.39$ nm and $h_y = 1.42$; for details see text.
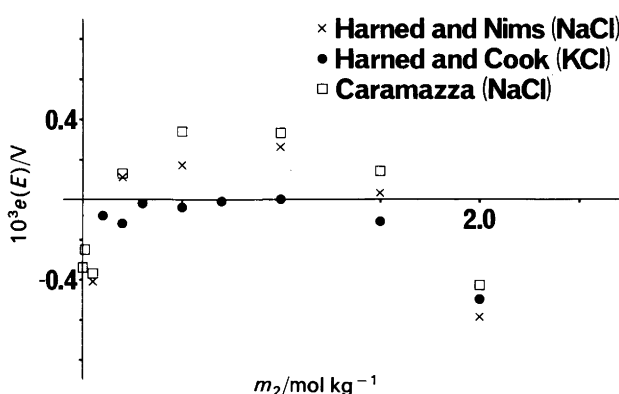

Fig. 4. The difference between the observed and predicted EMF values as a function of the molality in the sets measured by Harned and Nims,[16] Harned and Cook[17] and Caramazza[18] on concentration cells without transference, see cell (22). The predicted EMF values were calculated as described in the text. In the sets of Harned and Nims and of Caramazza the molality m_1 is 0.1 mol kg^{-1}, and in that of Harned and Cook it is 0.05 mol kg^{-1}.

measured several points by cells of this type in NaCl solutions. The electromotive force (E) of the amalgam cells of this kind depends on the molalities m_1 and m_2 according to eqn. (24). In the tests of the Hückel equations, the

$$E = -(2RT/F)\ln[\gamma_\pm(2)\,m_2/(\gamma_\pm(1)\,m_1)]\qquad(24)$$

activity coefficients for eqn. (24) have been calculated by eqn. (1) with the new parameter values. The predicted EMF values are then compared to the observed ones. The results of the comparison are presented as error plots in Fig. 4.

Sodium amalgam–silver chloride cells of type (23) and the corresponding potassium amalgam cells were used by Mussini and coworkers.[19,20] In these studies, a series of EMF values have been measured at several mole fractions (x) of alkali metal in the amalgam electrode. The electromotive force of a cell of this kind depends on the molality (m) according to eqn. (25), where $E^0(x)$ is the

$$E = E^0(x) - (2RT/F)\ln(\gamma_\pm m/m^0)\qquad(25)$$

standard value of the electromotive force for the series of measurements made with such a cell where the mole fraction of alkali metal in the amalgam electrode has a value of x.

The series of the measurements made by Mussini et al.[19] in NaCl solutions and Giordano et al.[20] in KCl solutions at different mole fractions can be used to test the Hückel equations in the following way. The EMF value at a fixed mole fraction and at a fixed molality can be predicted by eqn. (25) when the activity coefficient is first calculated by eqn. (1) with the new values of a^* and h. For a series of measurements at a fixed mole fraction of alkali metal in the amalgam, the value of $E^0(x)$ can be determined so that the sum of all errors [the error is defined in eqn. (18)] in this series is zero. The results of the tests of the Hückel equations with these electrochemical data are presented in the four graphs of Fig. 5. Again in these graphs, the errors are presented as a function of the molality in the different mole fraction series.

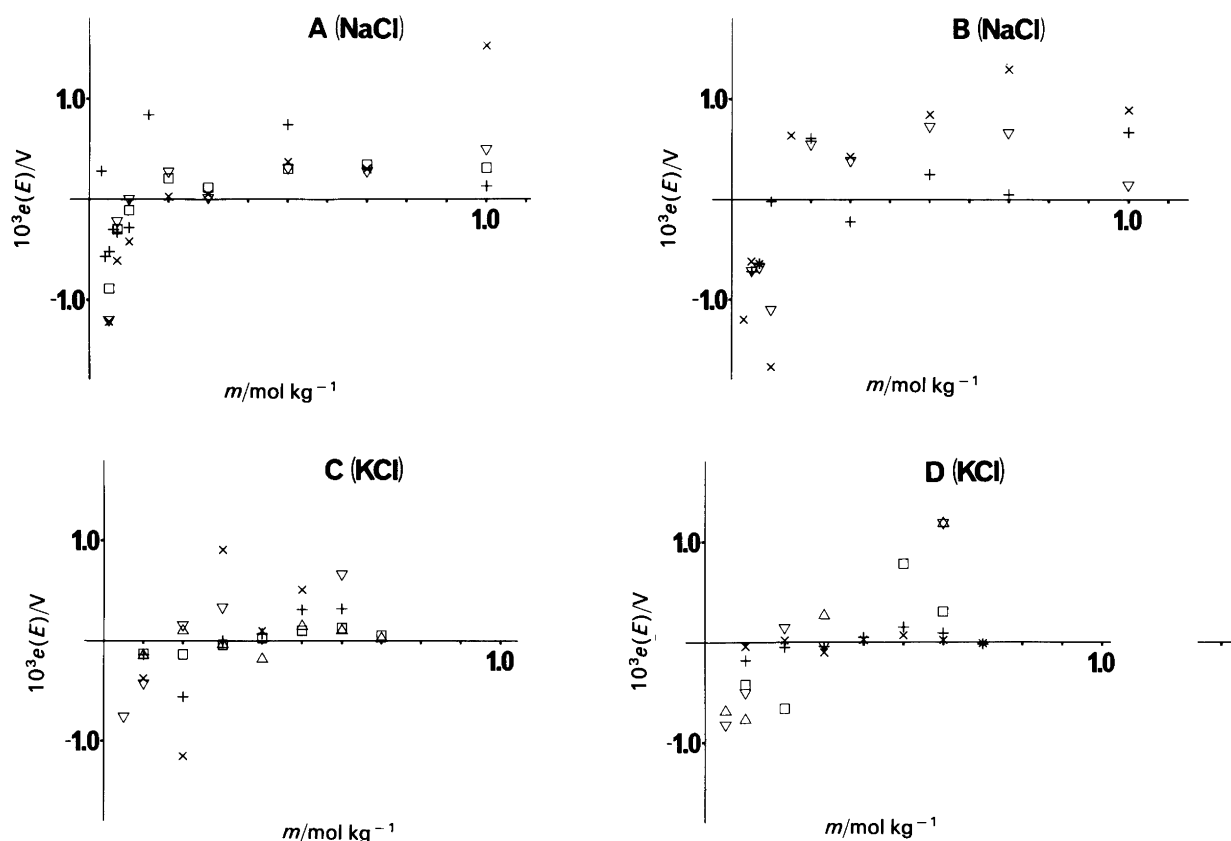Isopiestically the electrolyte pair NaCl–KCl in aqueous solutions at 298.15 K has been studied by Robinson,[1]

Fig. 5. The difference between the observed and predicted EMF values as a function of the molality in the sets measured by Mussini et al.[19] and by Giordano et al.[20] on alkali metal amalgam–silver chloride cells, see cell (23). The predicted EMF values were calculated as described in the text. The following values for $E^0(x)$ in eqn. (25) were used in the calculation of the predicted EMF values. The symbols of the different subsets are also denoted. NaCl: $x = 0.001\,291$, $E^0(x) = 2.012\,18$ V (graph A, ×); 0.002 020, 2.024 80 (A, ▽); 0.003 630, 2.040 57 (A, +); 0.004 268, 2.045 99 (A, □); 0.005 880, 2.055 63 (B, ×); 0.007 950, 2.066 17 (B, ▽); 0.012 51, 2.081 03 (B, +). KCl: 0.001 433, 2.034 04 (C, ×); 0.003 279, 2.056 48 (C, ▽); 0.004 148, 2.064 31 (C, +); 0.007 648, 2.088 60 (D, □); 0.011 72, 2.104 17 (D, △); 0.014 69, 2.115 46 (D, ×); 0.018 30, 2.128 56 (D, ▽); 0.019 25, 2.131 71 (D, +); 0.029 19, 2.158 86 (C, □); 0.040 14, 2.186 47 (C, △). In the list above, x refers to the mole fraction of the alkali metal in the amalgam electrode.

Robinson and Sinclair,[21] Janis and Ferguson[22] and Scatchard et al.[23] The experimental data of Robinson[1] were used above in the parameter estimation. The experimental results of the three other studies can be used to test the Hückel equations in the same way as the measured points of Robinson[1] were used above. The results of these tests are presented in Fig. 6.

Accurate vapor-pressure measurements in NaCl solutions at 298.15 K have been performed by Negus (see Robinson[1]), Pearce and Nelson,[24] Olynyk and Gordon,[25] Pepela and Dunlop[26] and Gibbard et al.[27] These data can be used to test the Hückel equation for NaCl. For the tests of the corresponding equation for KCl, the following vapor-pressure data exist in the literature: Pearce and Nelson,[24] Brown and MacGregor Delaney[28] and Lovelace et al.[29] The last mentioned set has been measured at 293.15 K, but, nevertheless, the points of this set have been used in the present tests without any calorimetric corrections. The experimental vapor pressures are reported in the papers listed above in different ways. The vapor-pressure data of these sources were used here as follows. The reported vapor pressures were first converted into the activities of water by eqn. (3). The reported activities of water and the activities obtained from the reported vapor pressures or osmotic coefficients were converted the activities of water by eqn. (3). The reported activities of water and the activities obtained from the reported vapor pressures or osmotic coefficients were converted into the vapor pressures by eqn. (4) with the value of 23.766 mmHg for p_1^* (see above). In the analysis of the data of Lovelace et al.[29] measured at 293.15 K, the value of 17.539 mmHg was used for p_1^* (see Kell[10]). The p(observed) values so obtained were then compared to those predicted by means of eqns. (2)-(4) with the new parameter values. The results of the tests with these data are compiled in Fig. 7, where the errors of the individual
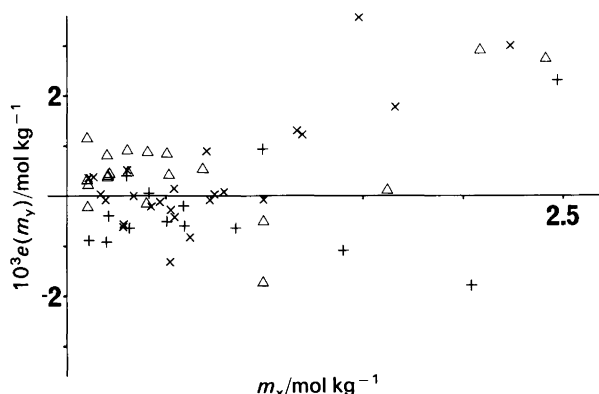

Fig. 6. The difference between the measured and predicted molalities of the KCl solutions (m_y) as a function of the molality of the NaCl solutions (m_x) in the isopiestic set of Robinson and Sinclair[21] (x), Janis and Ferguson[22] (+) and Scatchard et al.[23] (△). The predicted values of m_y were calculated as described in the text. The following errors in the set of Robinson and Sinclair are outside the ranges of the figure: ($m_x = 2.004$ m°, $e(m_y) = 0.0043$ m°); (2.144, 0.0071) and (2.464, 0.0061).
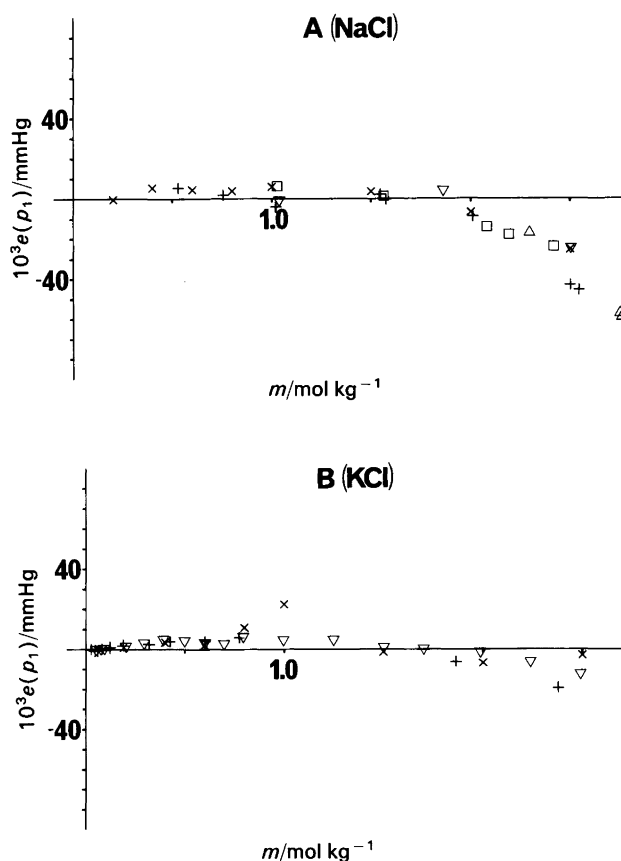

Fig. 7. The difference between the observed and predicted vapor pressures of water in NaCl (graph A) and in KCl solutions (B) as a function of the molality of the solutions. For NaCl solutions, the observed values were obtained by Negus (see Robinson,[1] symbol □), Pearce and Nelson[24] (x), Olynyk and Gordon[25] (△), Pepela and Dunlop[26] (+) and Gibbard et al.[27] (▽). For KCl solutions they were obtained by Lovelace et al.[29] (▽), Pearce and Nelson[24] (x) and Brown and MacGregor Delaney[28] (+). The errors were calculated as described in the text.

points are presented as a function of the molality. The errors have been calculated as before, i.e. by eqn. (26).

$$e(p_1) = p_1(\text{observed}) - p_1(\text{predicted}) \qquad (26)$$

Discussion

The h-parameters for the Hückel equations were determined above from the concentration cell set of Janz and Gordon[6] and the isopiestic set of Robinson.[1] According to Figs. 1 and 2, the experimental data of these two sets can be excellently predicted by means of the resulting equations.

The results of the other sets obtained by cells with transference are shown in Fig. 3. All errors in the plots of these sets, containing only dilute solutions, are very small, but they do not form a random pattern in the sets of Brown and MacInnes (NaCl) and Shedlovsky and

MacInnes (KCl). The experimental points of these two sets do not therefore support the Hückel equations perfectly.

The results of the concentration cells without transference are shown in Fig. 4. The errors in this figure are approximately ten times larger than the errors in the sets measured on cells with transference (see also Figs. 1 and 3). Therefore, the experimental data measured by the amalgam cells are probably not as precise as those determined by cells with transference in dilute solutions. According to Fig. 4, the results measured by Harned and Cook[17] can be predicted within their precision by means of the Hückel equation for KCl up to a molality of 1.5 mol kg^{-1}. Unfortunately, the experimental points of Harned and Nims[16] and of Caramazza[18] do not completely support the Hückel equation for NaCl.

According to the four graphs of Fig. 5, the experimental data determined by Mussini and coworkers on cells containing an alkali-metal amalgam electrode are usually even less precise than the data measured on concentration cells without transference (see also Fig. 4). According to graphs C and D, however, the measurements of Giordano et al.[20] succeeded excellently at the following four mole fraction of potassium in the amalgam: 0.014 69, 0.019 25, 0.029 19 and 0.040 14. In these cases the experimental data are internally at least as consistent as the best data obtained by concentration cells with an amalgam electrode. Strong evidence in support of the Hückel equation for KCl is the fact that the results of these four precise sets can be predicted very well by means of this equation. The less precise data of Giordano et al.[20] and the data of Mussini et al.[19] for NaCl (see graphs A and B) do not support the new Hückel equations as well as desired. In NaCl solutions above 0.1 mol kg^{-1}, however, the measured EMF values probably agree with the predicted ones within their precision (if a correctly adjusted value of E^{0} is used in each set).

Fig. 6 contains the test results obtained from other isopiestic sets than that of Robinson (whose results are presented in Fig. 2). The error plots in Fig. 6 need only a few comments. The results of the experimental data of the three isopiestic sets illustrated in this figure support well the Hückel equations for NaCl and KCl up to a molality of 2.0 mol kg^{-1}.

Graphs A and B in Fig. 7 contain the test results of the sets consisting of the vapor pressures of NaCl and KCl solutions. According to graph A, the vapor pressure data of the different workers support well the Hückel equation for NaCl up to a molality of 2.0 mol kg^{-1}. In graph B, the errors of the different sets are also small, but in this case a tiny trend can, perhaps, be recognized in the error plots. A slight trend in the error plot of the set measured by Lovelace et al.[29] is expected because of the temperature differences (see above). The two large errors in the error plot of the set of Pearce and Nelson[24] probably originate from the fact that these points are not completely reliable.

Because the experimental evidence indicated in Figs. 1–7 strongly supports the Hückel equations deter-

mined above, very reliable activities in NaCl and KCl solutions at 298.15 K can be calculated by these equations at any molality below 2.0 mol kg^{-1}. The recommended activity and osmotic coefficients at several rounded molalities are presented for NaCl and KCl in Table 1. The values of this table have been calculated by eqn. (1) or (2) with the parameter values determined above, i.e. with $a^{*} = 0.43$ nm and $h = 3.01$ for NaCl, and $a^{*} = 0.39$ nm and $h = 1.42$ for KCl.

The activity and osmotic coefficients recommended in Table 1 can be compared to the many values presented in the earlier literature. The results of such a comparison are shown in Figs. 8–10. The two graphs of Fig. 8 contain the results of the comparison of the activity coefficients presented for dilute solutions, i.e. up to a molality of 0.1 mol kg^{-1}. The results of the activity coefficient comparison in less dilute solutions, i.e. between the molality range 0.1 and 2.0 mol kg^{-1}, are then presented in the two graphs of Fig. 9. In Figs. 8 and 9 the quantity $\Delta\gamma_{\pm}$, defined by eqn. (27), is presented as a function of the

$$\Delta\gamma_{\pm} = \gamma_{\pm}(\text{literature value}) - \gamma_{\pm}(\text{value in Table 1}) \quad (27)$$
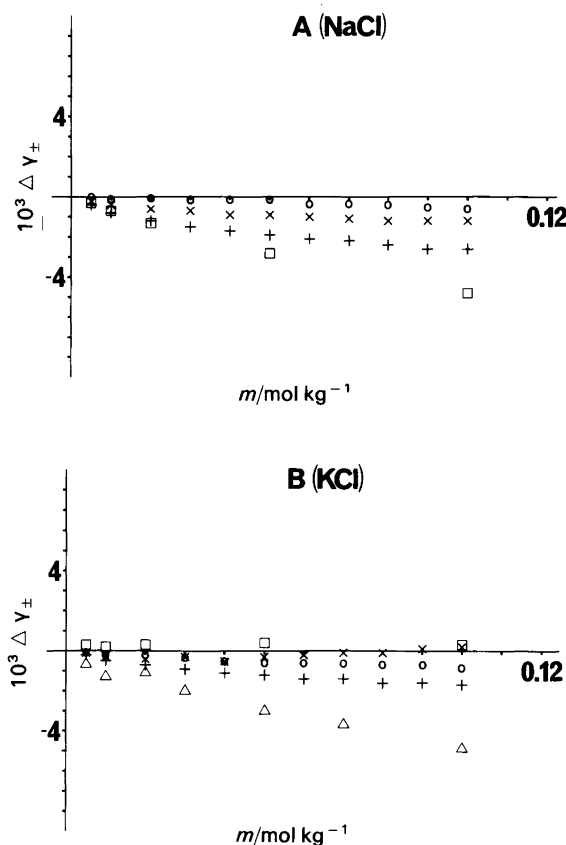

Fig. 8. The difference between the literature values of the activity coefficient and the values recommended in Table 1 as a function of the molality in dilute solutions. Graph A contains the results of the NaCl solutions and graph B those of the KCl solutions. List of symbols: Hamer and Wu[11] (O, A and B), Pitzer and Mayorga[3] (+, A and B), Shedlovsky[30] (□, A and B), Partanen[7] (×, A and B) and Giordano et al.[20] (△, B).

molality. The activity coefficients of Hamer and Wu[11] for Figs. 8 and 9 have been calculated by eqn. (5) and those of Pitzer and Mayorga[3] by eqn. (7).

The two graphs of Fig. 10 contain the results of the comparison of the osmotic coefficients presented for NaCl and KCl solutions. In this figure the quantity $\Delta\varphi$, defined by eqn. (28), is presented as a function of the molality.
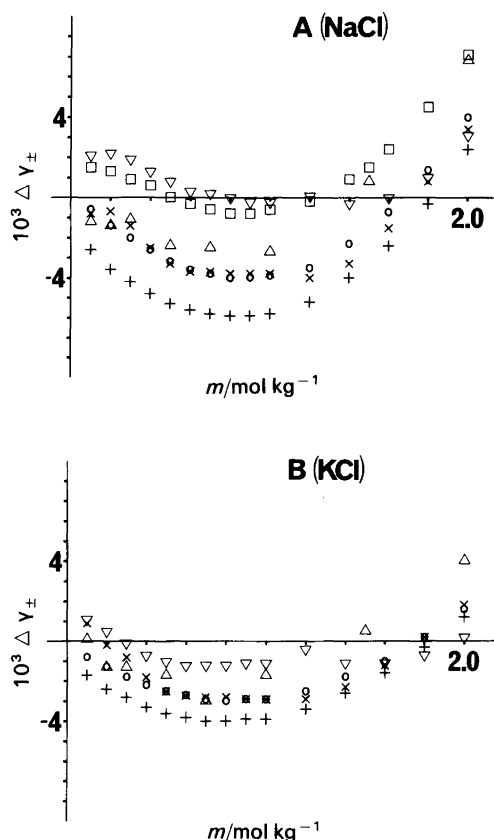
$$\Delta\varphi = \varphi(\text{literature value}) - \varphi(\text{value in Table 1}) \qquad (28)$$

For this figure, the osmotic coefficients of Hamer and Wu[11] have been calculated by eqn. (6) and those of Pitzer and Mayorga[3] by eqn. (8).

According to graph A in Fig. 8, the activity coefficients recommended in Table 1 for dilute NaCl solutions agree quite well with the values presented by Hamer and Wu.[11] The previous values presented in our laboratory for this quantity[7] are slightly higher than the values recommended here. The reason for this disagreement is due to the fact that the previous activity coefficients were based on the measurements of Brown and MacInnes[13] on cells with transference, and those data do not support the Hückel equation determined here very well (Fig. 3). On the other hand, the activity coefficients obtained previously in our laboratory[7] agree very well, according to graph B in Fig. 8, with the values recommended in Table 1 for dilute KCl solutions. Also, the values suggested by Shedlovsky[30] on the basis of the measurements by Shedlovsky and MacInnes[14] on cells with transference, are close to the values in Table 1.

Table 1. Recommended mean activity coefficients ($\gamma_\pm$) and osmotic coefficients (φ) in aqueous NaCl and KCl solutions at 298.15 K.

m/mol kg^{-1}	$\gamma_\pm$(NaCl)	φ(NaCl)	$\gamma_\pm$(KCl)	φ(KCl)
0.005	0.9276	0.9762	0.9267	0.9757
0.01	0.9029	0.9683	0.9013	0.9674
0.02	0.8720	0.9587	0.8691	0.9571
0.03	0.8511	0.9524	0.8470	0.9502
0.04	0.8351	0.9478	0.8300	0.9449
0.05	0.8220	0.9441	0.8160	0.9407
0.06	0.8111	0.9412	0.8041	0.9371
0.07	0.8016	0.9387	0.7937	0.9341
0.08	0.7933	0.9366	0.7846	0.9315
0.09	0.7859	0.9348	0.7763	0.9291
0.1	0.7792	0.9332	0.7689	0.9271
0.2	0.7354	0.9247	0.7183	0.9141
0.3	0.7111	0.9223	0.6883	0.9077
0.4	0.6953	0.9223	0.6675	0.9040
0.5	0.6844	0.9236	0.6517	0.9018
0.6	0.6764	0.9257	0.6392	0.9005
0.7	0.6705	0.9282	0.6290	0.8997
0.8	0.6662	0.9311	0.6204	0.8994
0.9	0.6630	0.9343	0.6130	0.8994
1.0	0.6607	0.9376	0.6067	0.8995
1.2	0.6583	0.9446	0.5962	0.9004
1.4	0.6578	0.9519	0.5879	0.9016
1.5	0.6582	0.9557	0.5844	0.9023
1.6	0.6589	0.9594	0.5812	0.9031
1.8	0.6611	0.9671	0.5756	0.9048
2.0	0.6642	0.9748	0.5710	0.9066

Fig. 9. The difference between the literature values of the activity coefficient and the values recommended in Table 1 as a function of the molality. Graph A contains the results of the NaCl solutions and graph B those of the KCl solutions. List of symbols: Robinson[1] (×, A and B), Hamer and Wu[11] (0, A and B), Pitzer and Mayorga[3] (+, A and B), Robinson and Harned[31] ($\triangle$, A and B), Scatchard et al.[23] ($\triangledown$, A and B), and Gibbard et al.[27] ($\square$, A).

Above the molality of 0.1 mol kg^{-1}, the values suggested by various authors for the activity and osmotic coefficients in NaCl and KCl solutions at 298.15 K are not, according to Figs. 9 and 10, in good agreement with each other. The values recommended in Table 1 for these quantities are usually not very far from the values suggested by Scatchard et al.[23] The activities given by Robinson[1] are often regarded as the most reliable values available, and therefore they have been widely used (see above). These values do not agree within their precision with the activity and osmotic coefficients recommended in the present study. In all graphs of Figs. 9 and 10, the deviations between Robinson's values and the values recommended here form a non-random pattern. The highest deviation of this set is in the activity coefficient plot as high as about 0.004 (Fig. 9), and in the osmotic coefficient plot it is even higher, i.e. about 0.008 (Fig. 10). Because of the strong experimental evidence presented in Figs. 1–7, it seems probable that the activity values in Table 1 are more reliable than those suggested by Robinson.[1]
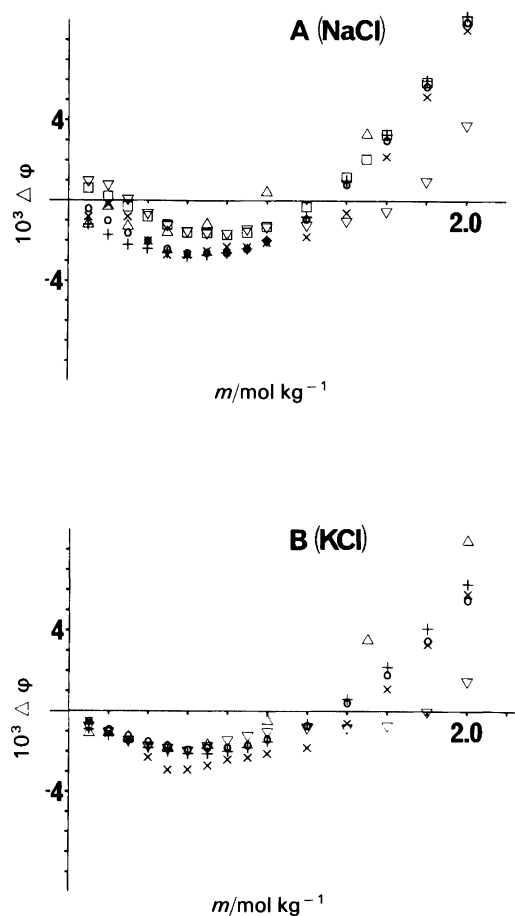
Fig. 10. The difference between the literature values of the osmotic coefficient and the values recommended in Table 1 as a function of the molality. Graph A contains the results of the NaCl solutions and graph B those of the KCl solutions. List of symbols: Robinson[1] (×, A and B), Hamer and Wu[11] (O, A and B), Pitzer and Mayorga[3] (+, A and B), Robinson and Harned[31] (△, A and B), Scatchard et al.[23] (▽, A and B) and Gibbard et al.[27] (□, A).

The activity quantities obtained by the Hückel equations determined above for sodium and potassium chloride solutions are probably the best values available. As explained above, they are supported by a great number of experimental data obtained by various methods. Because of the diversity of the methods producing data predictable by the Hückel equations, it seems probable that the measured results which do not fully support these equations are not completely reliable. Because the Hückel equations explain in many cases the measured results within experimental error, the predictions obtained by means of these equations reproduce the experimental data almost completely. Therefore it seems probable that in theoretical studies in this field interest can now be focused on the activity quantities obtained by these equations

instead of on the large amount of experimental data measured thermodynamically in NaCl and KCl solutions at 298.15 K.

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