Activity and Osmotic Coefficients of Dilute Potassium Chloride Solutions at 273 K

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Activities of dilute KCl solutions at 273 K were recalculated from the existing freezing-point data. It was found that the results of the most precise measurements up to a molality of 0.30 mol kg^{-1} can be predicted within experimental error by a two-parameter equation of the Hückel type. The two parameters of this Hückel equation were determined from the measured results of Scatchard and Prentiss [Scatchard, G. and Prentiss, S. S. J. Am. Chem. Soc. 55 (1933) 4355]. From this Hückel equation accurate activity and osmotic coefficients can be estimated for dilute KCl solutions at 273 K. These values, in addition to the recommended freezing-point depressions, have been tabulated at rounded molalities. The standard deviations of the estimated quantities were determined by the nonparametric jack-knife method.

It is known that the most reliable activity coefficients of dilute aqueous solutions of alkali metal halides at some temperature can be obtained from results of measurements on appropriate concentration cells with transference. In a previous study[1] it was shown that the existing experimental data of cells of this kind can successfully be predicted by using a two-parameter equation of the Hückel type for the activity coefficients. In most cases, this concentration cell method has been used only in such solutions where the molalities are less than 0.1 mol kg^{-1}. When activities of less dilute solutions of alkali metal salts have to be determined, the isopiestic method is most frequently chosen. The difficulty in applying the latter method is that one needs a reference electrolyte, and the activities of the electrolyte of interest cannot be directly determined. Another potentially accurate method for the study of the thermodynamics of less dilute salt solutions is the cryoscopic method. This method was popular at the beginning of this century, and a number of very precise cryoscopic data of solutions of various salts are available in the literature.

In comprehensive studies by Hamer and Wu[2] and by Pitzer and Mayorga[3] the activities of uni-univalent electrolytes were recalculated for aqueous solutions at 298 K. At this temperature the freezing-point data had to be omitted from the calculations. No recent studies, as far as we know, have been reported in the literature in which the activities of various uni-univalent electrolytes have been determined from the existing freezing-point data. In the present paper an analysis of this kind is performed for potassium chloride solutions.

Generally accepted activities for potassium chloride solutions at 273 K have so far not been presented. The most reliable values were obtained by Scatchard and Prentiss,[4]

based on their freezing-point determinations, and by Harned and Cook,[5] based on their measurements with potassium amalgam cells (see below). Unfortunately, the values of these two investigations do not agree with each other as well as desired. At a molality of 0.1 mol kg^{-1}, for example, Scatchard and Prentiss[4] gave the value of 0.7725 for the activity coefficient of KCl, while that of Harned and Cook is 0.768.[5]

In the present study the freezing points of the most precise cryoscopic data measured in potassium chloride solutions were correlated with the molalities by means of a Hückel equation, written to correspond to the temperature of 273 K. It was found then that these data and also the results of the other accurate freezing-point determinations in KCl solutions can be predicted almost completely by means of the resulting equation up to a molality of 0.30 mol kg^{-1}. In a previous study[6] the Hückel equation was applied with equal success to predict the freezing-point data of NaCl solutions up to a molality of 0.45 mol kg^{-1}. Only seldom has an equation with the simplicity of the Hückel one been successfully applied for molalities above 0.1 mol kg^{-1} in the literature.[1]

Calculations and results

In the present study the Hückel equation at 273 K was used, as mentioned above, for the calculation of activity coefficients of potassium chloride in aqueous solutions at the freezing point of the solutions. In a dilute solution of a uni-univalent electrolyte the equation for the mean activity coefficient at the molality scale ($\gamma_\pm$) can be presented in the form due to Pan[7] as eqn. (1). By means of the

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

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Gibbs–Duhem equation eqn. (2) can be derived from eqn. (1) for the osmotic coefficient (φ).

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

$$- (1 + \beta a^* m^{\frac{1}{2}})^{-1}] + M_1(h - 1)m \qquad (2)$$

In eqns. (1) and (2), m is the molality of the solution, M_1 is the molar mass of water ($= 0.0180\ 15$ kg mol^{-1}) and α and β are the Debye–Hückel constants, 1.1293 (kg mol^{-1})$^{\frac{1}{2}}$ and 3.245 (kg mol^{-1})$^{\frac{1}{2}}$ nm^{-1}, respectively, at 273 K and at the molality scale.[8] In the equations the two parameters that depend on the electrolyte are the ion-size parameter, a^*, and the hydration number, h.

When the osmotic coefficient φ is used, the relationship of eqn. (3) between the freezing point depression, ΔT_f, and the molality of the solution can be derived.

$$\Delta T_f = T_f^* - T_f = \frac{2RT_f^* M_1 m\varphi}{2RM_1 m\varphi + \Delta H_{\text{fus}}/T_f^*}$$

$$+ \frac{\Delta C_p \Delta T_f + \Delta C_p(T_f^* - \Delta T_f)\cdot\ln[(T_f^* - \Delta T_f)/T_f^*]}{2RM_1\ m\varphi + \Delta H_{\text{fus}}/T_f^*} \qquad (3)$$

In this equation T_f^* is the freezing point of pure water (i.e. 273.15 K) and T_f is that of the solution, ΔH_{fus} is the molar enthalpy of fusion of water at T_f^*, 6009.5 J mol^{-1},[9] ΔC_p is the difference between the molar heat capacities of water as a liquid and as a solid at 101.325 kPa and at T_f^*, 37.87 J K^{-1} mol^{-1}.[9,10] In the present calculations it is assumed to be independent of the temperature. R is the gas constant, 8.314 51 J K^{-1} mol^{-1}.

The parameters a^* and h in the Hückel equation were determined from the freezing-point data of Scatchard and Prentiss.[4] The method of determination was based on the minimization of the sum of squared prediction errors calculated from eqn. (4), where $e(\Delta T_f)$ is given by eqn. (5), and

$$S = \sum_{i=1}^{N} e_i(\Delta T_f)^2 \qquad (4)$$

$$e(\Delta T_f) = \Delta T_f(\text{observed}) - \Delta T_f(\text{predicted}) \qquad (5)$$

N is the number of points included in this determination. For each pair of values of a^* and h, ΔT_f(predicted) was calculated by eqn. (3) [by means of eqn. (2) for φ] from every molality included in the determination of a^* and h. For this pair of values of a^* and h, the sum of squared prediction errors was then calculated by eqn. (4). The values of a^* and h were chosen in such a way that they give the smallest value of S. During the preliminary calculations it was observed that only such points could be taken into account in the determination of a^* and h in which the molality is less than 0.3 mol kg^{-1}. The determination of this upper limit was based on studies of the randomness of the
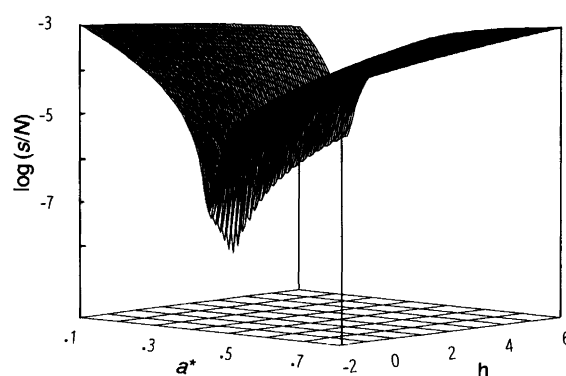

Fig. 1. Common logarithm of the quantity S/N obtained from the freezing-point depressions of Scatchard and Prentiss[4] as a function of the parameters a^* and h in the Hückel equation ($m < 0.30$ mol kg^{-1}). S is the sum of the squared prediction errors defined by eqn. (4) and N is 15.

error plots obtained from the subsets containing different numbers of points due to Scatchard and Prentiss[4] and on the corresponding values of the residual standard deviation for fit (s_0), defined by eqn. (6).

$$s_0 = [S/(N - 2)]^{\frac{1}{2}} \qquad (6)$$

For the points where the molalities are less than 0.3 mol kg^{-1}, the dependence of S in eqn. (4) on a^* and h is shown in Fig. 1. In this figure the common logarithm of the quantity S/N is presented as a function of these parameters. According to this figure S is a very sensitive function of the parameters in the Hückel equation, as has previously been observed for NaCl solutions.[6] A very deep minimum of 2.0×10^{-7} K^2 for S, corresponding to the value of 1.25×10^{-4} K for s_0, is obtained when $a^* = 0.390$ nm and $h = -0.32$. The standard deviations of these values can be obtained by the jack-knifing technique (see Appendix or Ref. 11), and the results are 0.005 nm and 0.16, respectively.

The validity of the parameter values of $a^* = 0.390$ nm and $h = -0.32$ was then tested by using all existing thermodynamical data measured in KCl solutions at the vicinity of 273 K. In these tests the existing experimental data were predicted by means of eqns. (1) or (2) applying the derived values of the two parameters. The error plots of this Hückel equation obtained from the cryoscopic sets are shown in graphs A and B in Fig. 2. Only such sets are included in these graphs which contain points measured at molalities above 0.1 mol kg^{-1}. The important results by Adams,[12] Brown and Prue[13] and Garnsey and Prue[14] are therefore not included in Fig. 2. The reason for the exclusion of these data sets is that the ΔT_f values of the dilute solutions in these sets can be predicted equally well by the best activity coefficient equations at 298 K.[15] The errors arrived at by these equations do not differ significantly from the errors obtained by the present Hückel equation.

During the determination of the most reliable values for a^* and h it was observed that all data points due to
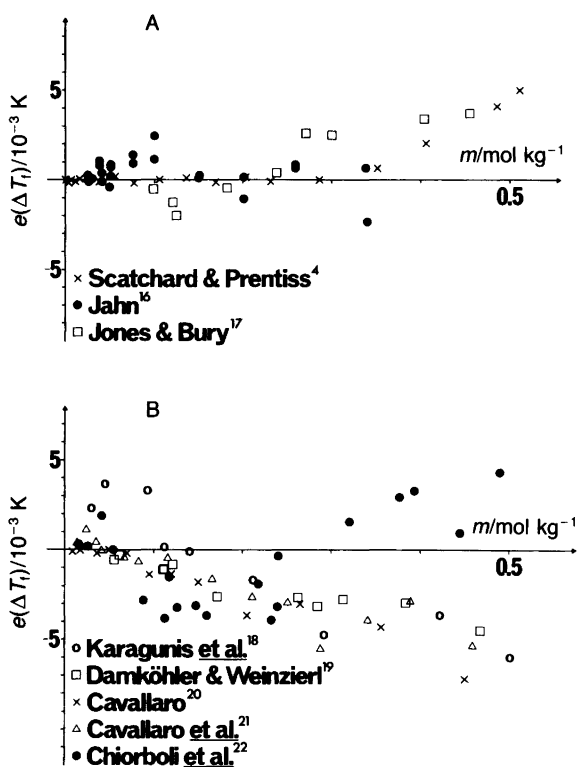
A

$e(\Delta T_f)/10^{-3}$ K

m/mol kg^{-1}

0.5

-5

× Scatchard & Prentiss[4]
• Jahn[16]
□ Jones & Bury[17]

B

$e(\Delta T_f)/10^{-3}$ K

m/mol kg^{-1}

0.5

-5

○ Karagunis et al.[18]
□ Damköhler & Weinzierl[19]
× Cavallaro[20]
△ Cavallaro et al.[21]
• Chiorboli et al.[22]

Fig. 2. The difference, $e(\Delta T_f)$, between the experimental freezing point depressions and those predicted by means of the Hückel equation with $a^* = 0.390$ nm and $h = -0.32$ as a function of the molality.

Scatchard and Prentiss[4] could be predicted quite satisfactorily by means of an equation of the Hückel type. In an attempt to increase the practical applicability limits, another Hückel equation was determined by the above-described method from all points of this study. The fit contained in this case points up to a molality of 1.25 mol kg^{-1}, and the minimum of 5.4×10^{-4} K for s_0 was obtained when $a^* = 0.368$ nm and $h = 0.42$. The error plots obtained by means of this Hückel equation from three different sets are shown in Fig. 3.

$e(\Delta T_f)/10^{-3}$ K

m/mol kg^{-1}

1.5

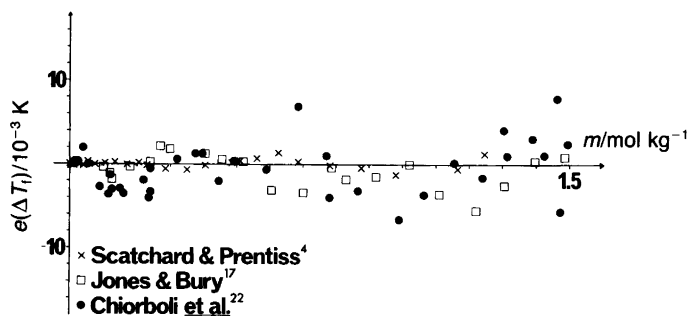× Scatchard & Prentiss[4]
□ Jones & Bury[17]
• Chiorboli et al.[22]

Fig. 3. The difference, $e(\Delta T_f)$, between the experimental freezing-point depressions and those predicted by means of the Hückel equation with $a^* = 0.368$ nm and $h = 0.42$ as a function of the molality.
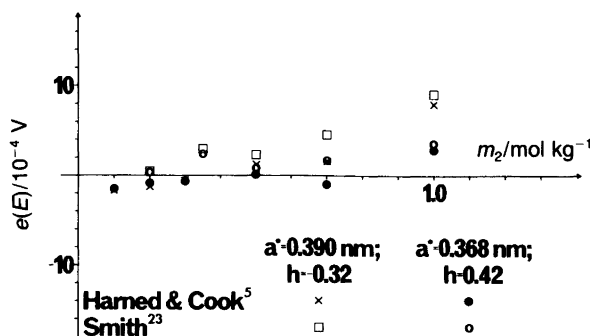
$e(E)/10^{-4}$ V

m_2/mol kg^{-1}

1.0

Harned & Cook[5]	a·0.390 nm; h·-0.32	a·0.368 nm; h·0.42
Harned & Cook[5]	×	•
Smith[23]	□	○

Fig. 4. The difference, $e(E)$, between the experimental electromotive forces of amalgam cells [cell (7) in the text] and those predicted by using the Hückel equations obtained in this study. The molality m_2 in eqn. (8) is presented on the molality axis and m_1 is 0.1 mol kg^{-1} in Smith's data set and 0.05 mol kg^{-1} in that of Harned and Cook.

The two Hückel equations determined above can also be tested with the results from electrochemical measurements. In dilute KCl solutions at 273 K Smith[23] and Harned and Cook[5] have performed experiments on potassium amalgam cells of the type shown in cell (7). The electromotive force

$$Ag(s)|AgCl(s)|KCl(aq,m_1)|K(Hg,x)|KCl(aq,m_2)|AgCl(s)|Ag(s) \tag{7}$$
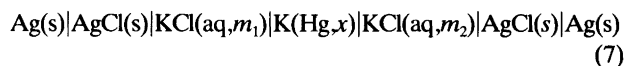
(E) of cells of this kind depends on the molalities m_1 and m_2 according to eqn. (8). In our tests, we predicted the experi-

$$E = -\frac{2RT}{F} \ln \frac{\gamma_\pm(2)m_2}{\gamma_\pm(1)m_1} \tag{8}$$

mental EMF values of these sets with eqn. (8), for which the activity coefficients were calculated by eqn. (1) with the two pairs of the parameter values determined above. The results are shown in Fig. 4.

Discussion

According to Fig. 2A, all experimental ΔT_f values included in the determination of the Hückel parameters a^* and h can be predicted within 0.0003 K by means of the resulting Hückel equation. According to this graph the results obtained by Jahn[16] and by Jones and Bury[17] are less precise than those of Scatchard and Prentiss.[4] However, the measured freezing-point depressions of these two sets also probably agree, within their precision, with the predicted values which were calculated by means of the Hückel equation with the parameter values of $a^* = 0.390$ nm and $h = -0.32$.

In Fig. 2B the set containing the most precise experimental data is probably the one measured by Damköhler and Weinzierl.[19] The points from this study seem to be as reproducible as the ΔT_f values of Scatchard and Prentiss.[4] Unfortunately, the errors obtained by the Hückel equation from that set do not satisfactorily support this equation.

Additionally, according to this graph, the errors of the sets obtained by Karagunis *et al.*,[18] Cavallaro[20] and Cavallaro *et al.*[21] form almost the same pattern as the errors of Damköhler and Weinzierl.[19] Therefore, the experimental points of these four sets agree with each other but disagree with the points of Scatchard and Prentiss.[4] The question therefore arises, as to whether it is possible to determine more reliable values for a^* and h from the set of Damköhler and Weinzierl[19] than the values obtained from the set of Scatchard and Prentiss.[4] In order to study this possibility, the values of these parameters were also determined from the set of Damköhler and Weinzierl.[19] In the corresponding fit, however, the value of s_0 is more than twice the value obtained above from the set of Scatchard and Prentiss.[4] In addition, the Hückel equation determined from the set of Damköhler and Weinzierl[19] does not predict the experimental ΔT_f values of the dilute sets of Adams,[12] Brown and Prue[13] and Garnsey and Prue,[14] as well as the Hückel equation determined above. One may therefore conclude that the experimental results of Damköhler and Weinzierl[19] are probably not as reliable as originally believed.

In Fig. 3 it can be seen that the Hückel equation obtained from all points of Scatchard and Prentiss[4] accords satisfactorily with the experimental ΔT_f values up to a molality of about 1.5 mol kg^{-1}. For these higher concentrations, however, the Hückel equation seems to be incapable of predicting the most precise measured results within experimental error. Presumably, the pattern of the errors in the set of Scatchard and Prentiss[4] is not a random one. On the other hand, the results from freezing point measurements
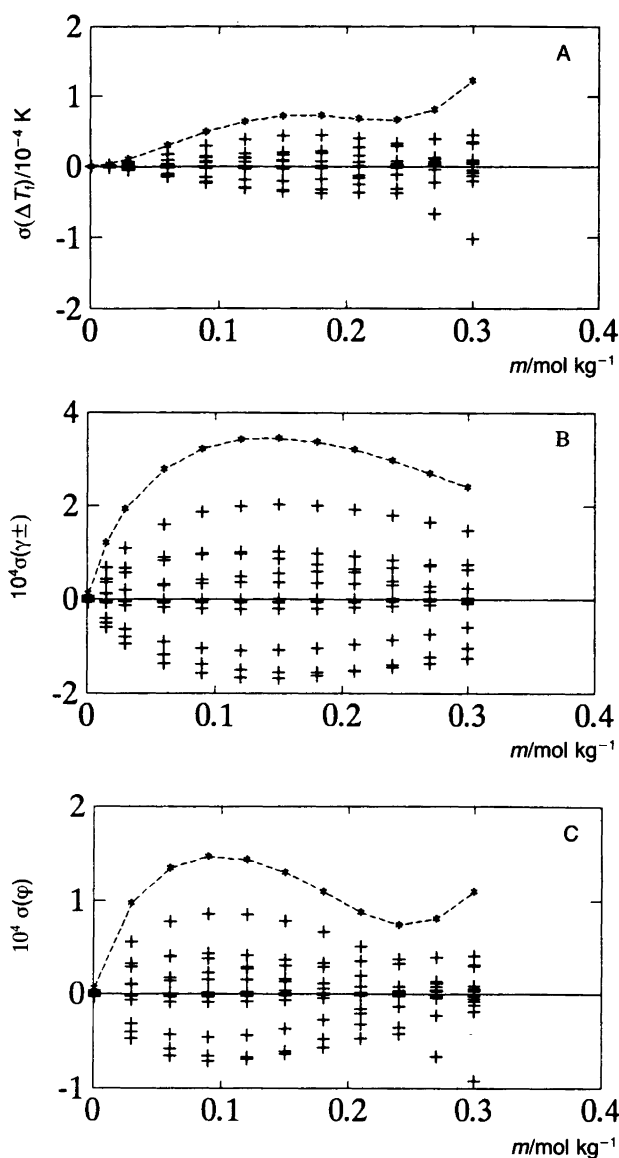

Fig. 5. Jack-knife standard deviation estimates for the freezing-point depressions (A), activity coefficients (B) and osmotic coefficients (C) obtained by using the Hückel equation with $a^* = 0.390$ nm and $h = -0.32$. + denotes the difference $\theta_i - \bar{\theta}$ in the Appendix and (— —*— —) denotes the value of $\sigma(\theta)$ in the equation presented in the Appendix.

Table 1. Recommended freezing-point depressions of KCl solutions at rounded molalities.

m/mol kg^{-1}	ΔT_f/K	m/mol kg^{-1}	ΔT_f/K
0.01	0.0360	0.25	0.8416
0.02	0.0713	0.26	0.8744
0.03	0.1061	0.27	0.9071
0.04	0.1407	0.28	0.9398
0.05	0.1750	0.29	0.9724
0.06	0.2092	0.30	1.0051
0.07	0.2432	0.35	1.169
0.08	0.2771	0.40	1.332
0.09	0.3108	0.45	1.494
0.10	0.3445	0.50	1.657
0.11	0.3781	0.55	1.818
0.12	0.4116	0.60	1.980
0.13	0.4450	0.65	2.141
0.14	0.4783	0.70	2.302
0.15	0.5116	0.75	2.463
0.16	0.5448	0.80	2.623
0.17	0.5780	0.85	2.784
0.18	0.6111	0.90	2.944
0.19	0.6442	0.95	3.104
0.20	0.6772	1.00	3.264
0.21	0.7101	1.10	3.583
0.22	0.7431	1.20	3.902
0.23	0.7759	1.30	4.220
0.24	0.8088	1.40	4.537

of different workers in less dilute KCl solutions are not consistent, as shown in Figs. 2 and 3. Therefore, we believe that the Hückel equation, for which the results are reported in Fig. 3, also has some general value. According to this figure, the experimental freezing points can in most cases be predicted within 0.002 K when applying this equation. When evaluating this prediction ability it is important to emphasise that, for example, the freezing points of Jones and Bury[17] have been given with an accuracy of 0.001 K.

According to Fig. 4, the experimental results based on amalgam cells by Smith,[23] and by Harned and Cook,[5] can be predicted up to a molality of 0.3 mol kg^{-1} within 0.2 mV

Table 2. Activity and osmotic coefficients of KCl solutions.

$m/m°$	$\gamma_\pm$ (273 K)[a]	$\gamma_\pm$ (S&P)[b]	$\gamma_\pm$ (H&C)[c]	$\gamma_\pm$ (298 K)[d]	φ (273 K)[a]	φ (298 K)[d]
0.005	0.9291	0.9296	0.929	0.9266	0.9765	0.9756
0.01	0.9042	0.9049	0.904	0.9010	0.9683	0.9673
0.02	0.8725	0.8736		0.8687	0.9580	0.9570
0.05	0.8194	0.8209	0.819	0.8157	0.9412	0.9407
0.10	0.7712	0.7725	0.768	0.7691	0.9264	0.9275
0.20	0.7175	0.7194	0.717		0.9106	
0.30	0.6841	0.6867	0.683		0.9012	
0.5	0.642[e]	0.645	0.642			
0.7	0.614[e]	0.618	0.613			
1.0	0.585[e]	0.589	0.588			

[a]This study. [b]Ref. 4. [c]Ref. 5. [d]Ref. 24. [e]Calculated by eqn. (1) with $a^* = 0.368$ nm and $h = 0.42$. $m° = 1$ mol kg^{-1}.

by means of the Hückel equation with the parameter values of $a^* = 0.390$ nm and $h = -0.32$. The second Hückel equation determined above explains within 0.4 mV the measured results of these sets up to a molality of 1.0 mol kg^{-1}. Apparently, the experimental data of the two electrochemical data sets support these Hückel equations.

According to Figs. 2 and 4, the Hückel equation with $a^* = 0.390$ nm and $h = -0.32$ for KCl solutions seems to be as reliable as the corresponding Hückel equation for NaCl solutions obtained in the previous study.[6] Very accurate ΔT_f values can therefore be calculated by eqn. (3) for any molality of KCl up to 0.3 mol kg^{-1}, provided that the osmotic coefficient is first estimated by eqn. (2) with these parameter values. The ΔT_f values calculated in this way at several rounded molalities are given in Table 1. Jack-knife standard deviations of the predicted freezing points were also estimated (see Appendix) and are presented in Fig. 5A. For dilute solutions the values in Table 1 agree within 0.0002 K with the recommended values in the previous paper[15] for dilute KCl solutions. Above a molality of 0.3 mol kg^{-1} the Hückel equation with $a^* = 0.368$ nm and $h = 0.42$ predicts the experimental data satisfactorily, as shown in Fig. 3. Table 1 therefore also contains the ΔT_f values calculated by means of this Hückel equation for the less dilute solutions.

Table 2 gives the activity and osmotic coefficients of KCl solutions calculated by eqns. (1) and (2) with the parameter values of $a^* = 0.390$ nm and $h = -0.32$. Table 2 also includes the original activity coefficients reported by Scatchard and Prentiss,[4] the activity coefficients of Harned and Cook[5] based on their measurements on an amalgam cell at 273 K, and the activity and osmotic coefficients at 298 K presented in Ref. 24. According to Table 2, the new activity coefficients obtained in this study agree well with the values of Harned and Cook.[5] The activity coefficients presented by Scatchard and Prentiss[4] are, however, not close to the new values. The same discrepancy was also observed in the case of NaCl solutions.[6] The osmotic coefficients presented in this table for dilute KCl solutions at 273 and 298 K agree satisfactorily with each other. The jack-knife standard deviations for the estimated activity and

osmotic coefficients are shown graphically in Figs. 5B and C (see Appendix).

Appendix: estimation of standard deviation by the jack-knife method

The jack-knife method is a nonparametric method which can be used to estimate the standard deviation of any statistics calculated from experimental data. The method is described, e.g., by Efron and Gong[11] and is outlined below:

Let $\theta = \theta (x_1, x_2, ..., x_N)$ be an estimator of any statistics evaluated from a set of N measurements, $x_1, x_2, ..., x_N$. The standard deviation of θ is then obtained as follows. First N estimates, $\hat{\theta}_1, \hat{\theta}_2, ..., \hat{\theta}_N$, of θ are calculated from the data set by deleting each of the N observations once, and only once, from the data set. The mean of these estimates obtained from the deleted sets is $\bar{\theta}$, and $\bar{\theta} = \Sigma_i \hat{\theta}_i/N$. The jack-knife estimate for the standard deviation of the statistics θ will be given by eqn. (A1)

$$\sigma(\theta) = \left(\frac{N-1}{N} \sum_{i=1}^{N} (\hat{\theta}_i - \bar{\theta})^2 \right)^{\frac{1}{2}} \tag{A1}$$

In our application the data set consists of the freezing points due to Scatchard and Prentiss[4] for which the molality is less than 0.3 mol kg^{-1}. N is therefore 15. 15 estimates of a^* and h were first calculated, according to the method described above and in the text, and the values of $\sigma(a^*)$ and $\sigma(h)$ were then estimated from these estimates by eqn. (A1). For predicted freezing-point depressions, activity coefficients and osmotic coefficients the 15 estimates of a^* and h were used in the evaluation of the jack-knife standard deviations.

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