

Freezing Point Depression of Dilute Aqueous Sodium Chloride Solutions

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Freezing point depressions of dilute aqueous sodium chloride solutions have been computed by means of the best osmotic coefficient equations. In the calculations, the equations of Hückel, Hamer and Pitzer were used for the osmotic coefficients. The experimental freezing point data available in the literature for dilute NaCl solutions can in most cases be predicted within experimental error with Hückel's equation, determined in our laboratory for the temperature of 298.15 K. The measured freezing points can also be calculated very accurately with Hamer's equation determined for the same temperature. The freezing point depressions tabulated in this paper for NaCl solutions can be recommended as reference values. These values are very reliable because they agree accurately with the experimental data and have been calculated by means of Hückel's equation, which, in addition, predicts well almost all existing electrochemical data measured in dilute NaCl solutions at 298.15 K.

In our previous paper¹ it was shown that the freezing points of dilute KCl solutions can be predicted within experimental error by using in the calculation the best activity coefficient equations available in the literature. These most accurate equations have been determined from experimental data measured at 298.15 K. Nevertheless, they predict almost all experimental freezing points for KCl solutions up to a molality of 0.1 mol kg⁻¹ within 0.0005 K. In the present paper the work is continued, and cryoscopic results for dilute NaCl solutions are critically studied by means of the best activity coefficient equations for NaCl at 298.15 K. However, all equations in this paper are rewritten using osmotic coefficients instead of activity coefficients, as in the previous paper.¹ For the osmotic coefficients, the equations of Hückel, Hamer and Pitzer are again used. The experimental data employed in this study were collected, as previously, from the literature. Freezing point depressions in dilute NaCl solutions have been measured by Hausrath,² Osaka,³ Jahn,^{4,5} Flügel,⁶ Rivett,⁷ Harkins and Roberts,⁸ Scatchard and Prentiss,⁹ Momicchioli *et al.*,¹⁰ Gibbard and Gossmann¹¹ and Craft and Van Hook.¹²

It is shown in the present work that the experimental freezing point depressions of dilute NaCl solutions can be predicted accurately with the osmotic coefficient equations used in the calculations. In most cases, the measured depressions can be predicted so exactly that the errors are completely random. It thus appears that the most reliable freezing point depression at any dilute molality can be calculated by means of the osmotic coefficient equations presented. Values calculated in this way for NaCl at several rounded molalities are given in Table 1.

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Table 1. Recommended values for the freezing point depressions of NaCl solutions at rounded molalities.

<i>m</i> /mol kg ⁻¹	Δ <i>T</i> _f /K	<i>m</i> /mol kg ⁻¹	Δ <i>T</i> _f /K
0.005	0.0181 ₅	0.055	0.1928
0.01	0.0360	0.06	0.2099
0.015	0.0537	0.065	0.2271
0.02	0.0713	0.07	0.2443
0.025	0.0888	0.075	0.2614
0.03	0.1063	0.08	0.2785
0.035	0.1236	0.085	0.2956
0.04	0.1410	0.09	0.3127
0.045	0.1583	0.095	0.3298
0.05	0.1755	0.10	0.3469

Calculations and results

The relationship given in eqn. (1) can be derived between the freezing point depression (Δ*T*_f) of a solution of a univalent electrolyte and the molality (*m*) of the electro-

$$\Delta T_f = T_f^* - T_f = \frac{2RT_f^*M_1m\varphi}{2RM_1m\varphi + \Delta H_{fus}/T_f^*} + \frac{\Delta C_p \Delta T_f + \Delta C_p(T_f^* - \Delta T_f) \ln [(T_f^* - \Delta T_f)/T_f^*]}{2RM_1m\varphi + \Delta H_{fus}/T_f^*} \quad (1)$$

lyte, where the osmotic coefficient φ is related to the activity coefficient γ_{\pm} by eqn. (2). Moreover, in eqn. (1) T_f^* is

$$\varphi = 1 + \frac{1}{m} \int_0^{\ln \gamma_{\pm}} m \, d \ln \gamma_{\pm} \quad (2)$$

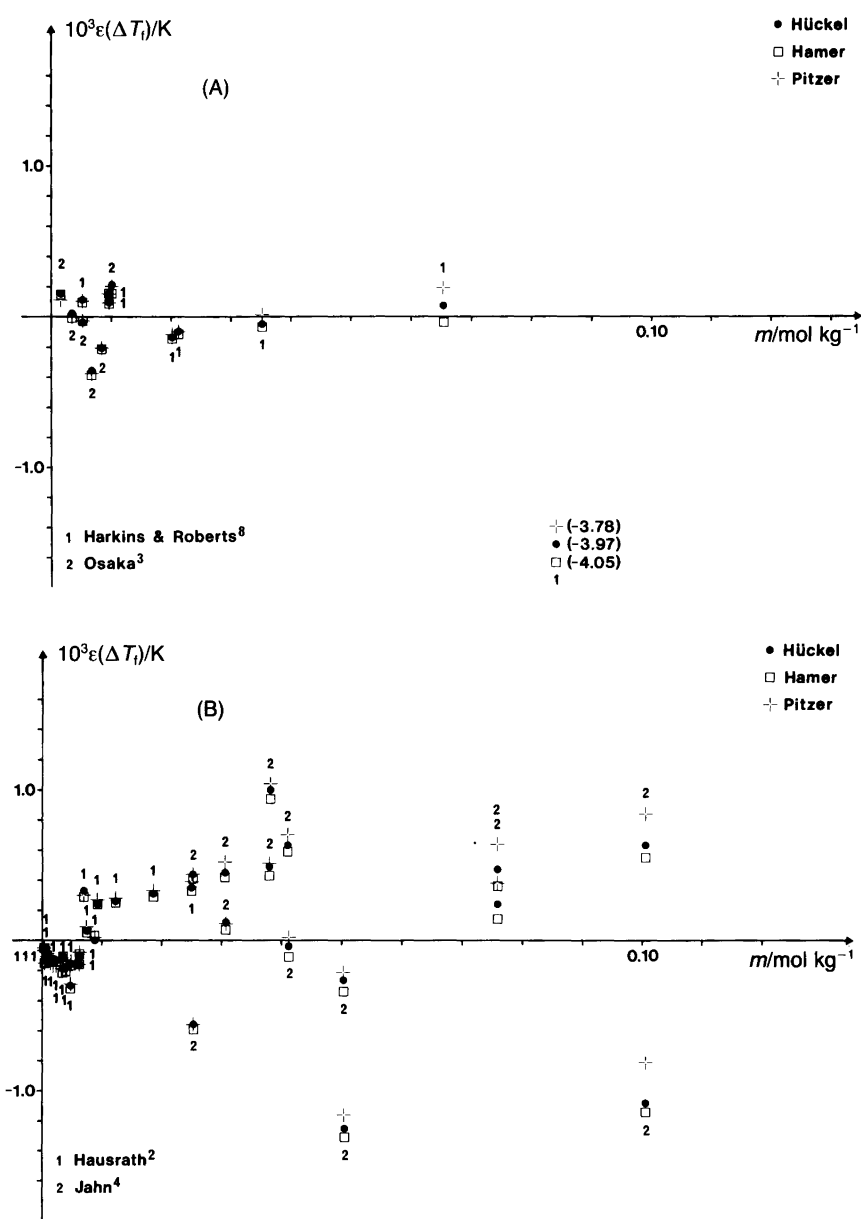


Fig. 1. Differences between the measured and predicted freezing point depressions as a function of molality in the sets containing dilute NaCl solutions. The errors for the different osmotic coefficient equations are denoted by the symbols shown in the graphs. Each graph contains the results of the measured sets noted in the graphs. In the first graph a point in the set of Harkins and Roberts⁸ is outside the ranges of the scale of $\varepsilon(\Delta T_f)$; the errors on that point are denoted numerically using the same scale as on the $\varepsilon(\Delta T_f)$ -axis.

the freezing point of pure water (i.e. 273.15 K), T_f that of the solution, ΔH_{fus} is the molar enthalpy of fusion of water at T_f^* (6008 J mol⁻¹), ΔC_p is the difference between the molar heat capacities of liquid and solid water at 101.3 kPa (this difference is 38.07 J K⁻¹ mol⁻¹ and is assumed to be independent of the temperature), M_1 is the molar mass of water (= 0.018015 kg mol⁻¹) and R is the gas constant (= 8.31451 J K⁻¹ mol⁻¹).

Experimental freezing points are compared in this paper with the ΔT_f values obtained from eqn. (1) by iterative calculations using the osmotic coefficient equations mentioned above. From the activity coefficient equations of Hückel, Hamer and Pitzer for uni-univalent electrolytes, eqns. (3)–(5) can be derived for the osmotic coefficient. In eqn. (5) f^{ϕ} is given by eqn. (6) and B^{ϕ} is given by eqn. (7).

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

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

$$\varphi = 1 + f^{\phi} + B^{\phi}(m/m^{\circ}) + C^{\phi}(m/m^{\circ})^2 \quad (5)$$

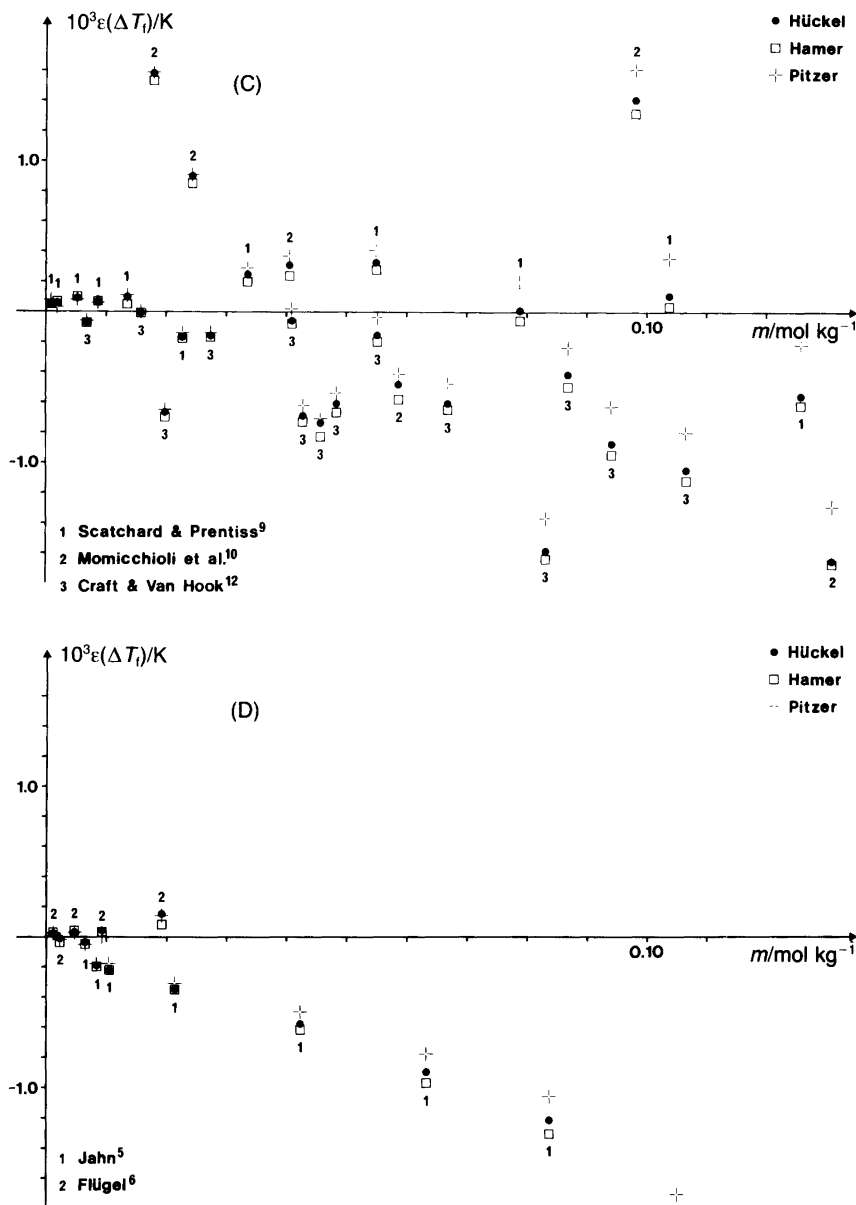


Fig. 1 (contd).

$$f^{\psi} = -A_{\psi} \frac{m^{1/2}}{1 + b m^{1/2}} \quad (6)$$

$$B^{\varphi} = \beta^{\circ} + \beta^1 \exp(-\alpha_p m^{1/2}) \quad (7)$$

Eqn. (3) has been derived from Hückel's equation and has the form presented by Pan.¹³ Eqn. (4) has been presented by Hamer and Wu¹⁴ and eqn. (5) by Pitzer.¹⁵ The general parameters in these equations have the following values at 298.15 K: $\alpha = 1.1762 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $\beta = 3.287 \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ nm}^{-1}$, $A = 0.5108 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $m^{\circ} = 1 \text{ mol kg}^{-1}$, $A_{\psi} = 0.392 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $\alpha_p = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$. From the results of an earlier paper¹⁶ of our laboratory, the following values can be obtained for the parameters of eqn. (3) in the case of NaCl: $a^* = 0.42 \text{ nm}$ and

$h = 3.16$. Hamer and Wu¹⁴ have suggested the following values for the parameters of eqn. (4) in NaCl solutions: $B^* = 1.4495 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $\beta_H = 0.020442$, $C = 0.0057927$ and $D = -0.00028860$. Pitzer and Mayorga¹⁷ have tabulated the following values for NaCl in Pitzer's equation [eqn. (5)]: $\beta^{\circ} = 0.0765$, $\beta^1 = 0.2664$ and $C^{\varphi} = 0.00127$.

The results of the comparison of the theoretical freezing point depressions of NaCl solutions with the experimental values are given in the six graphs of Figs. 1 and 2. The theoretical depressions were calculated, as explained above, from eqn. (1) by means of eqn. (3), (4) or (5). In both figures, the differences between the experimental and theoretical values are presented as a function of the molality. This difference (or error) is defined by eqn. (8). The

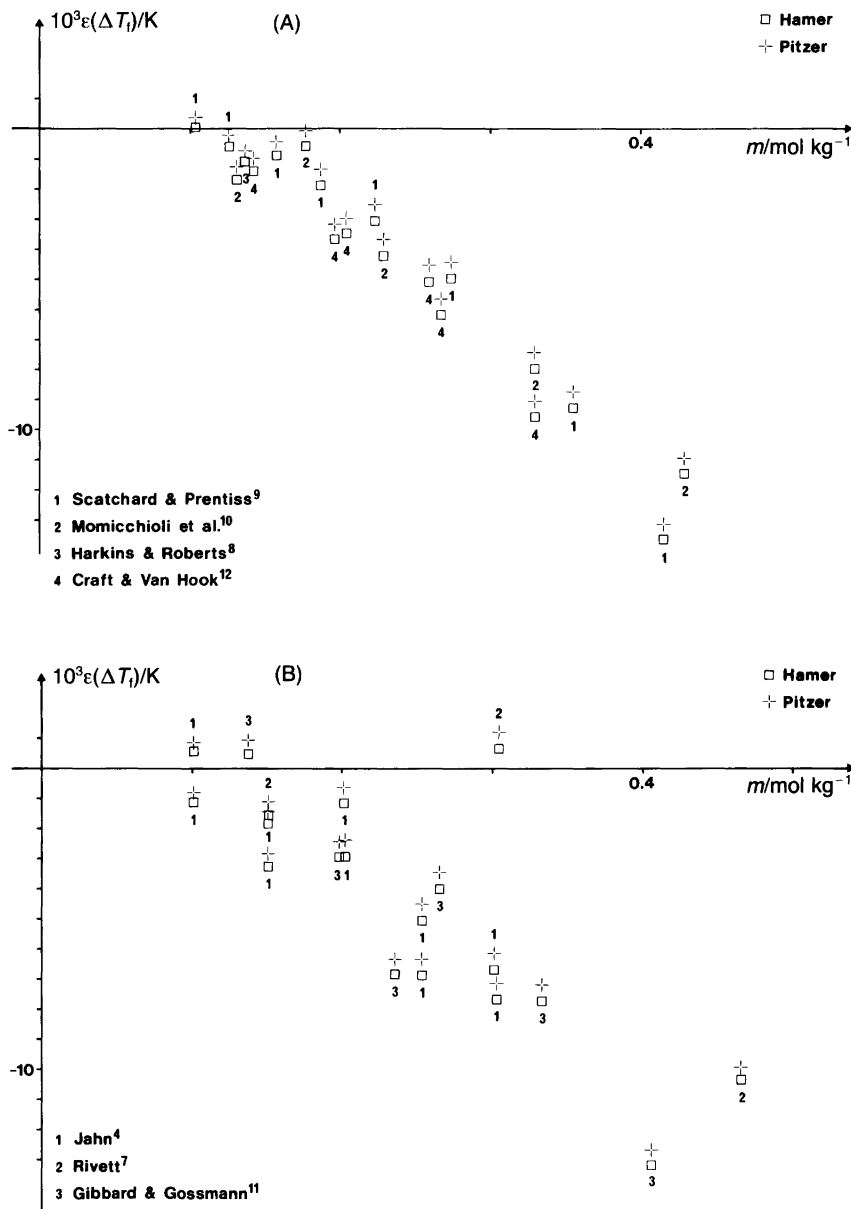


Fig. 2. Differences between the measured and predicted freezing point depressions as a function of molality in the sets containing less dilute NaCl solutions. For the symbols see the caption to Fig. 1.

$$\epsilon(\Delta T_f) = \Delta T_f(\text{observed}) - \Delta T_f(\text{predicted}) \quad (8)$$

results obtained for dilute NaCl solutions are included in Fig. 1. In the graphs of the figure, the errors of the predicted values of the different osmotic coefficient models are noted by different symbols. The results for the more concentrated NaCl solutions are shown in Fig. 2. The results obtained by means of Hückel's equation are not included in this figure because it is usually not of interest to use so simple an equation at molalities higher than about 0.1 mol kg⁻¹ (Ref. 16).

Discussion

According to Fig. 1, the freezing points of dilute NaCl solutions can be accurately predicted by means of the best osmotic coefficient equations used in this paper. Most of the experimental ΔT_f values of the figure can be predicted within 0.0005 K. The exceptions are an outlier in the set of points of Harkins and Roberts,⁸ three points at the highest concentrations in Jahn's more recent set⁵ (also the corresponding KCl set seems to be unreliable, see Ref. 1), and some points in the less precise sets of Jahn,⁴ Momicchioli *et al.*¹⁰ and Craft and Van Hook.¹² In the last-mentioned set, the measured values also appear to be systematically too small by about 0.0006 K. Above the molality of 0.05 mol kg⁻¹, the Pitzer equation predicts smaller values for ΔT_f than the other two equations. The experimental data can,

however, be predicted slightly better with either Hamer's or Hückel's equation. The results for the less dilute NaCl solution in Fig. 2 show that neither Pitzer's nor Hamer's equation at 298.15 K can be used when accurate freezing points at molalities stronger than 0.1 mol kg^{-1} are needed.

Owing to the large amount of experimental evidence presented in Fig. 1, the osmotic coefficient equations used in this paper can be successfully applied to predict the freezing points of dilute NaCl solutions. With these equations, very accurate estimates of the real freezing points can, therefore, be obtained at any dilute molality. The very accurate estimates of this kind are presented at rounded molalities in Table 1. The values of this table have been computed from eqn. (1) by means of Hückel's equation [eqn. (3)]. The freezing point depressions of Table 1, as well as the corresponding values for KCl solutions presented in an earlier paper¹ on this subject, can be highly recommended as reference values. They can, for example, be used for the exact calibration of thermocouples at temperatures near 273 K.¹⁸ The values in Table 1 were based above on the activity coefficient equation, which predicts, in addition to the experimental ΔT_f -values, a considerable number of electrochemical data measured at 298.15 K.¹⁶ According to the present paper and our previous paper,¹ it is theoretically interesting to remark that freezing point measurements in dilute NaCl or KCl solutions probably provide no information on the thermodynamics of the solutions that cannot be obtained by high-precision electrochemical measurements made at 298.15 K.

Attempts have recently been made to generate a general equation which can be used to predict the properties of salt solutions covering wide ranges of molalities and temperatures. For NaCl solutions a set of such equations has been presented by Silvester and Pitzer.¹⁹ These equations have been based on the ion interaction theory of Pitzer, and therefore the equation for the osmotic coefficient has the same form as in eqn. (5). According to Silvester and Pitzer, the electrolyte parameters β^0 , β^1 and C^ϕ in that equation

depend on the temperature through equations containing altogether twelve parameters. The freezing point depressions at rounded molalities of dilute NaCl solutions were also calculated with Pitzer's equation [eqn. (5)] at 273 K by using the parameter values estimated from the equations of Silvester and Pitzer.¹⁹ The predicted ΔT_f -values of these calculations agree within 0.0002 K with the values recommended in Table 1. Therefore, this multiparameter version of Pitzer's equation also applies well to the existing freezing point data for dilute NaCl solutions.

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