Registry No. $H_3C(CH_2)_{12}CO_2H$, 544-63-8; $H_3C(CH_2)_{14}CO_2H$, 57-10-3; $H_3C(CH_2)_{16}OH$, 36653-82-4; CO_2, 124-38-9.

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

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The cryoscopic data reported in the literature for aqueous NaCl solutions were systematically recalculated. In these calculations, it was found that most of the measured freezing points up to the molality of 0.45 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 results of the most accurate freezing point measurements found for NaCl solutions in the literature. With these parameter values, accurate estimates of the activity and osmotic coefficients of NaCl solutions at 273 K can be obtained. These values, in addition to the recommended freezing point depressions, have been tabulated at rounded molalities. The standard deviations for the estimated values have been presented graphically and were computed by using the recently developed nonparametric jackknife method.

Introduction

It is well-known that the most reliable activity coefficients of dilute aqueous solutions of alkali-metal halides at different temperatures are obtained from measurements on appropriate concentration cells with transference. In our previous studies (*1*), it has been shown that the existing measured results of the cells of this kind at 298 K can be successfully predicted by 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 molality is less than about 0.1 mol·kg^{-1}. When activities of less dilute alkali-metal-salt solutions are determined, the isopiestic method is most often used. The difficulty in applying this method is that the method needs a reference electrolyte and the activities of the interesting electrolyte alone cannot thus be studied. Another potentially accurate method to study the thermodynamics of less dilute salt solutions is the cryoscopic method. This method was very popular at the beginning of this century, and a number of precise cryoscopic data of different salt solutions have been, therefore, reported in the literature.

In the wide recalculation work carried out by Hamer and Wu (*2*) and by Pitzer and Mayorga (*3*), the activities of uni-univalent electrolytes were determined for aqueous solutions at 298 K. Because of the choice of this temperature, the freezing point data had to be omitted from the calculations. No recent study, as far as we know, has been reported in literature where the existing freezing point results of uni-univalent electrolytes have been collected and critically analyzed. In the present paper, an analysis of this kind is performed for NaCl solutions.

According to our understanding, the generally accepted activities for NaCl solutions at 273 K have not been reported in the literature. The most reliable values so far have been presented by Scatchard and Prentiss (*4*), on the basis of their freezing point determinations, and by Platford (*5*), on the basis of his isopiestic studies. The values of these two origins do not, unfortunately, agree with each other as well as desired. At the molality of 0.1 mol·kg^{-1}, for example, Scatchard and Prentiss presented the value of 0.9337 for the osmotic coefficient and the Platford value is 0.931.

Silvester and Pitzer (*6*) have developed for the activities of NaCl solutions a very general multiparameter equation which covers wide ranges of molalities and temperatures. We tested the validity of this equation at 273 K and used it to predict the measured freezing points of this electrolyte at different molalities (see below). According to our calculations, however, the predictions of this equation are systematically too high above the molality of 0.15 mol·kg^{-1}. At 0.8 mol·kg^{-1}, e.g., the error is about −0.02 K, and this is a value which by far exceeds the experimental precision of the best freezing point determinations presented in the literature (this precision has been probably well below ±0.0005 K).

In the present article, we apply the above-mentioned Hückel equation to the existing freezing point data measured in NaCl solutions and show that even the most accurate experimental cryoscopic results of NaCl solutions can be predicted almost completely up to the molality of 0.45 mol·kg^{-1} by the Hückel equation. In addition, our preliminary calculations with the cryoscopic data reported by Scatchard and his co-workers (*4*, *7*–*10*) show that the activities of all 21 electrolytes considered in those studies can also be correlated to the molalities by a simple equation of the Hückel type. Usually these activities can be predicted within experimental error at least up to the molality of 0.3 mol·kg^{-1}, but in the best cases this equation applies satisfactorily near the molality of 1.5 mol·kg^{-1}. In the previous literature, such simple equations as the Hückel equation are seldom used above the molality of about 0.1 mol·kg^{-1}.

Equations and Estimation of the Hückel Parameters

The Hückel equation for the activity coefficient ($\gamma_{\pm}$) of a uni-univalent electrolyte can be written in the form presented by Pan (*11*):

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

From eq 1, the following equation can be derived for the osmotic coefficient φ:

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

In eqs 1 and 2, m is the molality of the solution, M_1 is the molar mass of water (=0.018 015 kg·mol^{-1}), and α and β are the Debye–Hückel constants (on the molality scale at 273 K their values are, according to Archer and Wang (*12*), 1.1293 (kg/mol)$^{1/2}$ and 3.245 (kg/mol)$^{1/2}$ nm^{-1}, respectively). In these equations, moreover, the two parameters depending on the electrolyte are the ion-size parameter a^{*} and the hydration number h. On the other hand, the Pitzer equation (*6*) for the osmotic coefficient of a uni-univalent electrolyte has the form

$$\varphi = 1 - \frac{A_{\varphi} m^{1/2}}{1 + b m^{1/2}} + (\beta^0 + \beta^1 e^{-\alpha_P m^{1/2}})(m/m^0) + C^{\varphi}(m/m^0)^2 \qquad (3)$$

In this equation m^0 = 1 mol·kg^{-1}, b = 1.2 (kg/mol)$^{1/2}$, α_P = 2.0 (kg/mol)$^{1/2}$, and, at 273 K, A_{φ} = 0.377 (kg/mol)$^{1/2}$. According to Silvester and Pitzer (*6*), the electrolyte parameters β^0, β^1, and C^{φ} depend on the temperature by equations containing altogether 12 parameters. With the values tabulated in that paper for these parameters, the following values can be calculated for β^0, β^1, and C^{φ} at 273 K: 0.0532, 0.2496 and 0.0044, respectively. Another recent application of the Pitzer equation has been presented by Thurmond and Brass (*13*) in their calorimetric study concerning supercooled NaCl solutions. These workers present for the parameters β^0, β^1, and C^{φ} such equations which contain entirely 15 parameters. The following values can be obtained from these equations at 273 K: β^0 = 0.0442, β^1 = 0.1893, and C^{φ} = 0.0061.

When osmotic coefficient φ is used, the following relationship can be thermodynamically derived between the freezing point depression (ΔT_f) and the molality of the solution:

$$\Delta T_f = T_f^{*} - T_f = \frac{2RT_f^{*} M_1 m \varphi}{2RM_1 m \varphi + \Delta H_{fus}/T_f^{*}} + \frac{\Delta C_p \Delta T_f + \Delta C_p (T_f^{*} - \Delta T_f) \ln [(T_f^{*} - \Delta T_f)/T_f^{*}]}{2RM_1 m \varphi + \Delta H_{fus}/T_f^{*}} \qquad (4)$$

where T_f^{*} is the freezing point of pure water (i.e. 273.15 K) and T_f that of the solution, ΔH_{fus} is the molar enthalpy of fusion of water at T_f^{*} (=6009.5 J·mol^{-1}; see Osborne (*14*)), ΔC_p is the difference between the molar heat capacities of water as liquid and as solid at 101.325 kPa and at T_f^{*} (this difference is 37.87 J·K^{-1}·mol^{-1}; see Osborne (*14*) and Osborne et al. (*15*)), and R is the gas constant (=8.3145 J·K^{-1}·mol^{-1}). We verified that within the limited temperature range used in the freezing point experiments, ΔC_p can be regarded as constant since the influence of the temperature corrections of ΔC_p on the ΔT_f values is insignificant.

The advantage of eq 4 in freezing point data analysis is that it allows the direct comparison of the predicted values to the observed experimental values. If osmotic coefficients or some other derived values were used to compare the fit results with the experimental data, as often is done, there is always a danger that some relevant information is lost. A minor disadvantage of the form of eq 4 is that ΔT_f is also on the right-hand side and some iterative calculations are, therefore, needed when the equation is used to estimate this quantity.

To estimate the Hückel parameters a^{*} and h in eqs 1 and 2 from the experimental data, the sum of squared prediction errors (S) was minimized as follows. Systematically varied values were given for a^{*} and h, and the predictions of the ΔT_f values were estimated from eq 4 (by using eq 2 for φ) with these parameter values for each experimental molality. For each pair of the values of a^{*} and h, the sum of squared prediction errors was calculated from

$$S = \sum_{i=1}^{N} \epsilon_i(\Delta T_f)^2 \qquad (5)$$

where N is the number of the experimental points and where $\epsilon(\Delta T_f)$ is defined by

$$\epsilon(\Delta T_f) = \Delta T_f(\text{observed}) - \Delta T_f(\text{predicted}) \qquad (6)$$

The residual standard deviation of the fit is s_0, and

$$s_0 = [S/(N - 2)]^{1/2} \qquad (7)$$

To find the exact values of a^{*} and h, which minimize S, a nonlinear function minimizer (fmins) available in PC-MATLAB (*16*) was used. To estimate the precision of a^{*} and h, the jackknifing technique (see Appendix or ref 17) was used.

Results and Discussion

For dilute NaCl solutions, as well as for the solutions of some other electrolytes, there are in the literature several very precisely measured freezing point sets. We based our estimates of a^{*} and h in the Hückel equation on the freezing point data of Scatchard and Prentiss (*4*), because these workers have succeeded to carry out their ΔT_f measurement up to the molality of 1.2 mol·kg^{-1} nearly with the precision comparable to that of the best dilute sets. The ΔT_f values of the other published NaCl sets were used in our present calculations to verify the validity of the resulting values of a^{*} and h. By using error plots and the jackknifing technique, we came to a conclusion that the Hückel equation is able to explain the experimental points of Scatchard and Prentiss (*4*) up to the molality of 0.45 mol·kg^{-1} without any lack of fit. The obtained parameter values with the corresponding jackknife standard deviation in parentheses are a^{*} = 0.430 nm (0.0028 nm) and h = 1.19 (0.064). With these values, a deep minimum of S in eq 5, 3.1 × 10^{-7} K^2, is obtained corresponding to the value of 1.4 × 10^{-4} K for s_0 in eq 7.

The prediction errors, $\epsilon(\Delta T_f)$ in eq 6, obtained by using our Hückel equation were calculated for all experimental data sets found in the literature. For the dilute sets (i.e. where all molalities are less than about 0.1 mol·kg^{-1}), we have published the prediction errors based on the most accurate osmotic coefficient equations at 298 K (see ref 18). The predictions of these equations agree well (i.e. within ±0.0002 K) in dilute solutions with the predictions of our new Hückel equation, and therefore we did not include the results of these dilute sets in the present paper. The results of the calculations with the less dilute sets are shown as error plots in the two graphs of Figure 1. The only data set in which the measured ΔT_f values do not agree with he predicted values within experimental error is the one of Craft and Van Hook (*21*). The discrepancy is, however, also in this case so small that a systematic error of only -0.0008 K in their ΔT_f measurements could explain it. Because the estimation of freezing points from eq 4 requires iterative calculations, we report in Table I the recommended ΔT_f values at several rounded molalities. The jackknife standard deviation estimates for these values are presented in graph A of Figure 2.

Table II gives the activity and osmotic coefficients of NaCl solutions calculated from eqs 1 and 2, respectively, with the parameter values a^{*} = 0.430 nm and h = 1.19. The re-

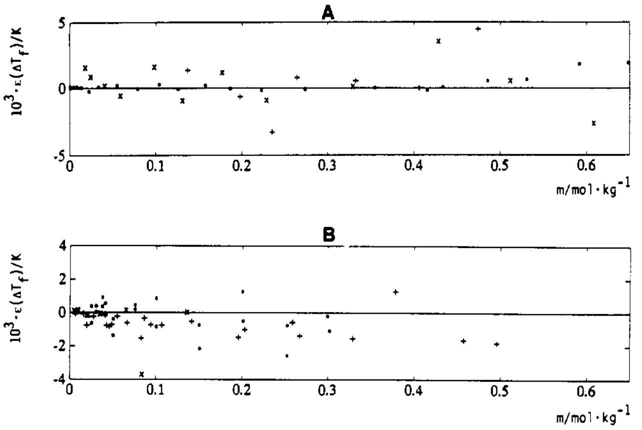

Figure 1. The differences $\varepsilon(\Delta T_f)$ between experimental freezing point depressions and those predicted by using the Hückel equation with $a^* = 0.430$ nm and $h = 1.19$. The sets of different investigators are indicated as follows: (✱) Scatchard and Prentiss (*4*) (A) and Jahn (*22*) (B); (×) Momicchioli et al. (*19*) (A) and Harkins and Roberts (*23*) (B); (+) Gibbard and Gossman (*20*) (A) and Craft and Van Hook (*21*) (B).

Table I. Recommended Freezing Point Depressions of NaCl Solutions at Rounded Molalities

m/(mol·kg^{-1})	ΔT_f/K	m/(mol·kg^{-1})	ΔT_f/K
0.01	0.0360	0.24	0.8192
0.02	0.0714	0.25	0.8528
0.03	0.1063	0.26	0.8864
0.04	0.1411	0.27	0.9200
0.05	0.1756	0.28	0.9535
0.06	0.2101	0.29	0.9871
0.07	0.2443	0.30	1.0206
0.08	0.2785	0.31	1.0542
0.09	0.3126	0.32	1.0877
0.10	0.3467	0.33	1.1212
0.11	0.3807	0.34	1.1547
0.12	0.4146	0.35	1.1883
0.13	0.4485	0.36	1.2218
0.14	0.4823	0.37	1.2553
0.15	0.5161	0.38	1.2888
0.16	0.5499	0.39	1.3223
0.17	0.5836	0.40	1.3558
0.18	0.6173	0.41	1.3893
0.19	0.6510	0.42	1.4228
0.20	0.6847	0.43	1.4563
0.21	0.7183	0.44	1.4898
0.22	0.7520	0.45	1.5233
0.23	0.7856		

spective jackknife standard deviation estimates for the predicted values are given in graphs B and C of Figure 2. Table II contains for comparison the original activity coefficients reported by Scatchard and Prentiss (*4*), the activity and osmotic coefficients at 298 K reported in ref 1 (these values were based on the measurements of Brown and MacInnes (*24*) on concentration cells with transference), and the Platford osmotic coefficients based on isopiestic determination at 273 K (*5*). Our new osmotic coefficients in Table II agree fairly well with those of Platford, but our activity coefficients are smaller than the values of Scatchard and Prentiss. This discrepancy is probably due to the fact that Scatchard and Prentiss had to treat their data in a complicated way with nowadays unnecessary approximations (*25*). Our osmotic coefficients at 273 K in dilute solutions also agree well with those estimated from the electrochemical data at 298 K. This result was expected because the osmotic coefficients at 298 K are able to predict successfully the freezing points of dilute solutions (see above).

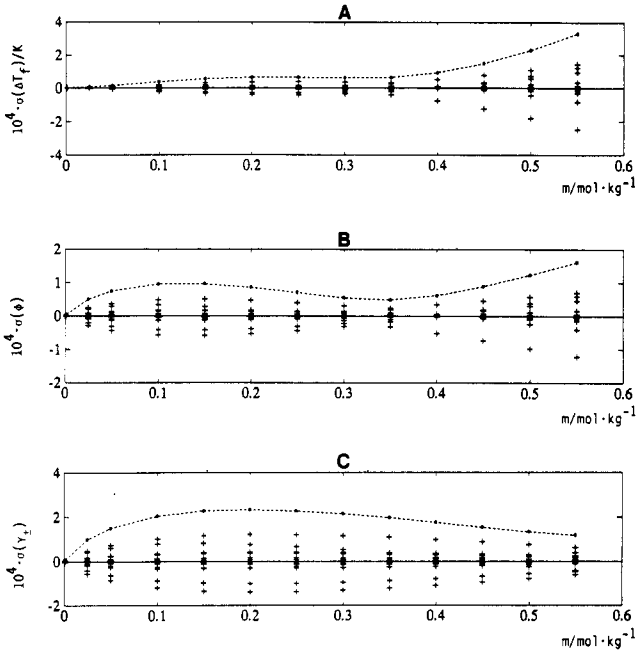

Figure 2. Jackknife standard deviation estimates of the freezing point depressions $\sigma(\Delta T_f)$ (A), osmotic coefficients $\sigma(\varphi)$ (B), and activity coefficients $\sigma(\gamma_\pm)$ (C), calculated by using the Hückel equation with $a^* = 0.430$ nm and $h = 1.19$: (+) $\theta_i - \theta$ in Appendix; (–•–) $\sigma(\theta)$ in the equation of Appendix.

The Hückel equation presented above shows no lack of fit up to the molality of 0.45 mol·kg^{-1}. We also tested another Hückel equation which was obtained from the points of more concentrated solutions by the method described above. If the Scatchard and Prentiss data points up to the molality of 0.81 mol·kg^{-1} were included in the fit, our method gave slightly different parameter values: $a^* = 0.415$ nm and $h = 1.52$. The value of s_0 in eq 7 in this case is 0.000 27 K. Despite the fact that this fit is also a very good fit, the pattern of the residuals cannot in this case be regarded as random, so this Hückel equation is not able to explain the data within experimental error.

We also compared the freezing point predictions of our Hückel equations with those obtained by using the osmotic coefficients estimated from the Pitzer equation (eq 3). The prediction errors calculated with the different models (i.e. with the two Hückel equations and two Pitzer equations presented above) from the Scatchard and Prentiss data up to the molality of 1.0 mol·kg^{-1} are presented in Figure 3. All predictions agree

Table II. Activity and Osmotic Coefficients of NaCl Solutions

m/m^0	$\gamma_\pm$(273K)[a]	$\gamma_\pm$(298K)[b]	$\gamma_\pm$(SP)[c]	φ(273K)[a]	φ(298K)[b]	φ(Pl)[d]
0.005	0.9299	0.9274	0.9320	0.9769	0.9761	
0.01	0.9057	0.9025	0.9087	0.9691	0.9681	
0.02	0.8752	0.8714	0.8796	0.9595	0.9584	
0.05	0.8252	0.821	0.8310	0.9445	0.9437	
0.1	0.7811	0.778	0.7872	0.9322	0.9326	0.931
0.2	0.7337		0.7398	0.9208		0.923
0.3	0.7057		0.7119	0.9151		0.917
0.4	0.6861		0.6925	0.9119		0.913
0.45	0.6782			0.9108		

[a] This study. [b] Our laboratory (*1*). [c] Scatchard and Prentiss (SP) (*4*). [d] Platford (Pl) (*5*).

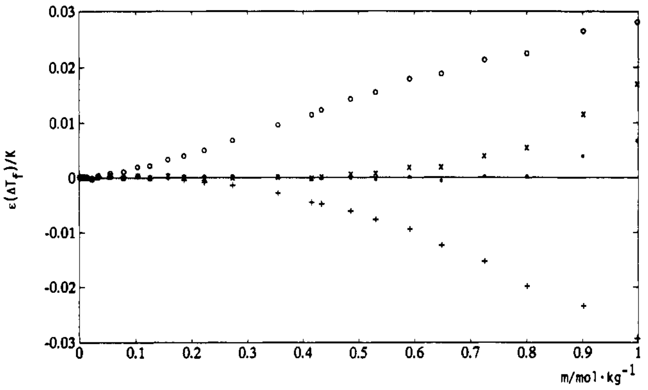

Figure 3. The differences $\epsilon(\Delta T_f)$ between experimental freezing point depressions of Scatchard and Prentiss (*4*) and those predicted by the different osmotic coefficient models: (✱) Hückel equation with parameters a^* and h estimated from the set where $m < 0.81$ mol·kg^{-1}, $a^* = 0.415$ nm, and $h = 1.52$; (×) Hückel equation with parameters a^* and h estimated from the set where $m < 0.45$ mol·kg^{-1}, $a^* = 0.430$ nm, and $h = 1.19$; (+) Pitzer equation with the parameter values of Silvester and Pitzer (*6*); (○) Pitzer equation with the parameter values of Thurmond and Brass (*13*).

with the experimental data up to the molality of 0.05 mol·kg^{-1}. Above this molality the Pitzer equation with the parameter values of Thurmond and Brass (*13*) gives too low ΔT_f values, and above 0.15 mol·kg^{-1} the other Pitzer equation gives too high ΔT_f values. It is also clear according to this figure that the Hückel equation recommended by us for molalities less than 0.45 mol·kg^{-1} should not be used above this value. The alternative Hückel equation, though it shows some systematic residual pattern (not very obvious at the scale of this figure), can be used quite safely up to 0.8 mol·kg^{-1}, if not extremely high accuracy is needed (below these limits, the errors are probably not larger than ±0.0006 K).

Glossary

a^*	ion-size parameter in Hückel equation, m
A_φ	Debye–Hückel constant in Pitzer equation, at 273.15 K, 0.377 (kg/mol)$^{1/2}$
b	constant in Pitzer equation, 1.2 (kg/mol)$^{1/2}$
C^φ	third parameter in Pitzer equation
ΔC_p	difference between the molar heat capacities of water as liquid and as solid at 101.325 kPa and at 273.15 K, 37.87 J·K^{-1}·mol^{-1}
h	hydration number parameter in the Hückel equation
ΔH_{fus}	molar enthalpy of fusion of water at 273.15 K, 6009.5 J·mol^{-1}
m	molality of solute, mol·kg^{-1}
m^0	constant, 1 mol·kg^{-1}
M_1	molar mass of water, 0.018 015 kg·mol^{-1}
N	number of points
R	molar gas constants, 8.3145 J·K^{-1}·mol^{-1}
s_0	residual standard deviation of the fit in eq 7, K
S	sum of squared prediction errors in eq 5, K^2
T_f	freezing point of solution, K
T_f^*	freezing point of pure water, 273.15 K
ΔT_f	freezing point depression of solution ($=T_f^* - T_f$), K

Greek Letters

α	Debye–Hückel constant in the Hückel equation, at 273.15 K, 1.1293 (kg/mol)$^{1/2}$
α_P	constant in the Pitzer equation, 2.0 (kg/mol)$^{1/2}$
β	Debye–Hückel constant in the Hückel equation, at 273.15 K, 3.245 (kg/mol)$^{1/2}$·nm^{-1}
β^0	first parameter in the Pitzer equation
β^1	second parameter in the Pitzer equation
$\gamma_\pm$	mean activity coefficient of the solute
$\epsilon(\Delta T_f)$	prediction error of freezing point depression defined by eq 6, K
φ	osmotic coefficient
θ	statistic to be estimated in the Appendix
$\hat{\theta}_1, \hat{\theta}_2, ...$	jackknife estimates of θ (Appendix)
$\bar{\theta}$	mean value of jackknife estimates of θ (Appendix)
$\sigma(\theta)$	standard deviation of jackknife estimates of θ (Appendix)

Appendix: Estimation of Standard Deviation by Jackknife Method

Jackknife 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 (*17*) and is outlined below.

Let $\theta = \hat{\theta}(x_1, x_2, ..., x_N)$ 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 data sets is $\bar{\theta}$ and $\bar{\theta} = \sum\hat{\theta}_i/N$. Now the jackknife estimate for the standard deviation of the statistics θ is

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

In our application, the data set consists of such freezing points of Scatchard and Prentiss (*4*) where the molality is less than 0.45 mol·kg^{-1} and N is therefore 18. We first calculated, according to the method described above and in the text, 18 estimates of a^* and h and then from the above-mentioned equation the estimates of $\sigma(a^*)$ and $\sigma(h)$. For the predicted freezing point depressions, osmotic coefficients, and activity coefficients, the 18 estimates of a^* and h were used in the evaluation of the jackknife standard deviations.

Registry No. NaCl, 7647-14-5.

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