*International Journal of Thermophysics, Vol. 9, No. 5, 1988*

# Modeling the Thermodynamic Properties of Sodium Chloride in Steam Through Extended Corresponding States[1]

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Recent precise data on anomalous behavior of apparent molar properties of electrolyte solutions in near-critical steam have raised important questions as to how the thermodynamic properties of these systems should be described. Current Gibbs free energy models fail for highly compressible solutions. Here, a Helmholtz free energy formulation is presented as a first step in modeling compressible dilute aqueous electrolyte solutions. Comparisons are made with the known critical line, coexistence curves, apparent molar volumes, and heat capacities of NaCl in steam, and conclusions presented on improving the model.

**KEY WORDS:** critical line; coexistence curve; Helmholtz free energy; molar heat capacity; molar volume; sodium chloride solution.

## 1. INTRODUCTION

A number of recent experiments reporting large anomalies in enthalpies of dilution [1, 2] and apparent molar heat capacities [3, 4] of dilute high-temperature electrolyte solutions have raised speculation as to the origin of these effects. Once it was realized that the large anomalies reported are common to all dilute mixtures [5] and that the excess Gibbs free energy models traditionally used for describing the properties of aqueous electrolyte solutions [6] are not applicable in highly compressible media [7, 8], the stage was set for alternative approaches. This paper is one such attempt.

In order to justify the use of a century-old model, the law of corresponding states for mixtures [9], for describing a high-temperature

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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0195-928X/88/0900-0649$06.00/0 © 1988 Plenum Publishing Corporation

aqueous electrolyte solution, the following observations are in order: first, an aqueous medium of the density of steam near its critical point has a low dielectric constant [10, 11], so that the ions will tend to pair [12]. At infinite dilution, there is complete ionization, but at any concentration of practical interest the number of charges will be quite low as long as the fluid density is near that of critical steam [13]. Second, effects due to near-criticality prevail over Debye–Hückel effects at low concentrations [7, 8, 14, 15]. Therefore, as a first step, it seems reasonable to ignore the effects of charges and to use a model of proven merit in ordinary fluid mixtures. Third, there is the important issue of classical versus nonclassical critical behavior. Corresponding-states models are classical. They lead to parabolic coexistence curves in pure fluids and fluid mixtures. Pure steam is very well known to be nonclassical: it has a flat, almost cubic coexistence curve [16, 17]. The crossover problem, however, although solved for pure fluids [18], has not been solved for mixtures. Thus our proposed attempt appears doomed. There are several reasons why this conclusion may not hold. First, Pitzer et al. observed that the isothermal coexistence curves of very dilute aqueous NaCl solutions [19] appear to be parabolic [20]. This induced these authors to model the immediate vicinity of the steam critical point by means of a classical expansion [20, 21] similar to that proposed earlier by Chang et al. [5]. Although no satisfactory theory exists for the apparent classical behavior of dilute salt solutions, it seems worthwhile to see how far this idea can be pursued. Second, our applying the corresponding-states model to argon–steam mixtures that display anomalies in their apparent molar heat capacity [22] as striking as those in salt solutions [4] has led to very good results for what is in effect a third derivative (Fig. 1). Although we know that the system argon–steam must be nonclassical, the data are apparently far enough from the critical point that a classical model can be made to work. Third, a "one-fluid" (i.e., no distinction was made between the pseudo- and the real critical line of the mixture) corresponding-states model proposed by Wood and Quint [23] showed good success in describing the 17-MPa liquid–phase ${}^{\phi}C_{\mathrm{p}}$ data [3] for $\mathrm{NaCl/H_2O}$. Finally, once a crossover theory for mixtures becomes available, a classical equation may be required as a starting point [24].

It was suggested by Pitzer [21, 25] that the IAPS 1984 or HGK equation for steam [26] be used as a classical reference equation by omitting the three terms that this equation uses to mimic nonclassical critical behavior. Since mixture corresponding states cannot be combined with a (almost) nonclassical reference equation [27], we decided to use the same ploy. In a parallel effort presented at this conference [25], Pitzer and Tanger performed a Helmholtz free energy expansion in density, composition, and temperature with the unmodified HGK equation as a reference. We compare with their results.

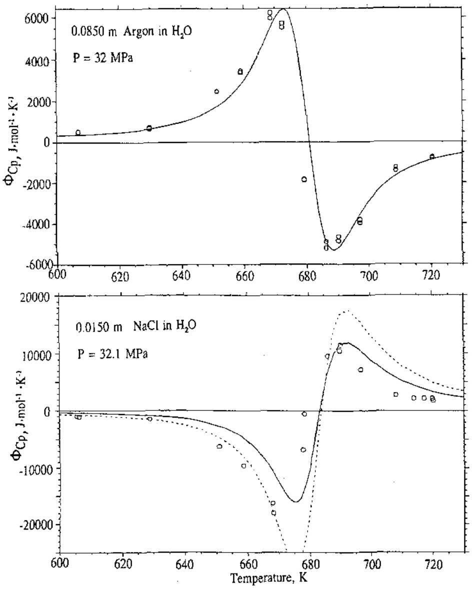

Fig. 1. Apparent molar heat capacities on supercritical isobars. Ar in $H_2O$ at 32 MPa and NaCl in $H_2O$ at 32.1 MPa. (○) Experimental data of Biggerstaff and Wood [22] for argon and of White et al. [4] for NaCl in $H_2O$. Curves represent predicted values from a corresponding states model. For NaCl, the solid line represents results from parameter set I, and the dashed line results from set II.

## 2. PHASE BEHAVIOR

Given the locations of the NaCl–$H_2O$ critical line and solidus [28, 29], it appears unlikely that the solidus will interrupt the critical line. The critical parameters of NaCl have been estimated by Pitzer to be approximately 3900 K in temperature and 25 MPa in pressure [30]. He also surmised that the critical line is uninterrupted. This would be highly unusual, because binary mixture critical lines usually break when the critical temperatures of the components are more than a factor of two apart. There is, however, no experimental evidence available in the region above 1000 K in favor of or against the appearance of other phases.

Since our goal is the description of dilute aqueous solutions, we have not attempted to obtain a continuous critical line. We have also felt at liberty to choose the critical point of NaCl in such a way that the initial behavior of the critical line, which has been repeatedly measured, was well represented. We use the temperatures of Marshall and Jones [13] and the pressures and temperatures of Ölander and Liander [32], supplemented with the less accurate data of Khaibulin [33] and of Sourirajan and Kennedy [34]. Both pressure– and temperature–composition plots of these data display a strong initial curvature (Fig. 2). Pitzer et al. suggested that this is an effect of the nonclassical depression of the critical point of pure steam [20, 21], which would disappear if the three near-critical terms in the HGK equation were omitted. The "classical critical point" so obtained is indicated in Fig. 2. We note that substantial curvature persists.

Bischoff and Rosenbauer recently performed detailed measurements of

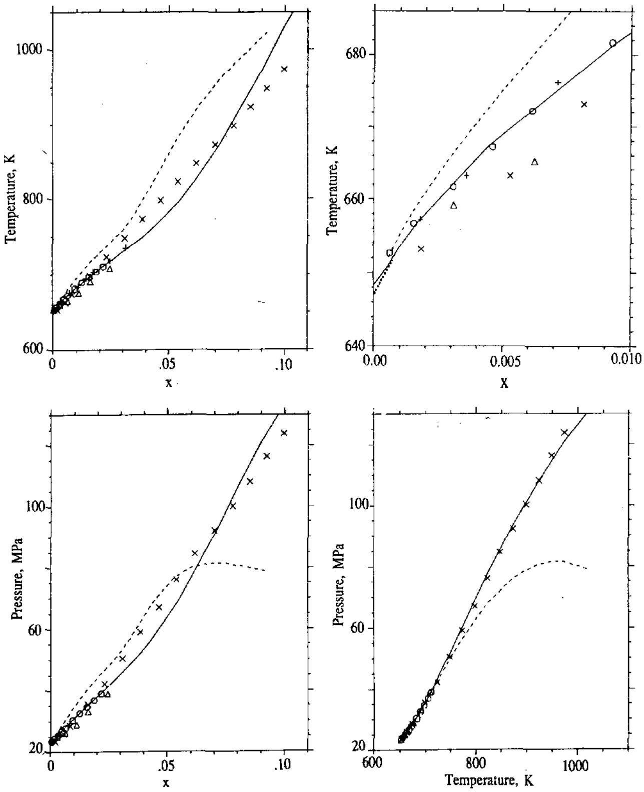

**Fig. 2.** Four aspects of the critical line of NaCl in $H_2O$. The symbols represent the measured points of Ölander and Liander (○) [32], Marshall and Jones (+) [31], Sourirajan and Kennedy (X) [34], and Khaibullin and Borisov (△) [40]. $x$ is the mole fraction of the solute. The solid line represents the predictions of parameter set I, and the dashed line predictions of parameter set II. In the second plot (the enlargement of the low-composition end of the $T$ vs $x$ view), the dotted line is the prediction using the full HGK Helmholtz function as reference.

the isothermal coexistence curves of NaCl–$H_2O$ close to the critical point of steam [19]. Our model is tested by comparison with these data.

Accurate heat of dilution (${}^{\phi}L$) measurements have been performed by the Oak Ridge group [1]. Apparent molar heart capacities (${}^{\phi}C_p$) were reported in both sub- and supercritical NaCl–$H_2O$ solutions by Wood and co-workers [3, 4]. We decided to concentrate our efforts on the latter data, with the philosophy that if the "third derivative" ${}^{\phi}C_p$ is fitted, lower-order derivatives such as ${}^{\phi}L$ and ${}^{\phi}V$ should fall into place readily. This philosophy may rightfully be questioned since the apparent volumes and enthalpies are measured more accurately than the heat capacities.

## 3. THE GENERALIZED CORRESPONDING-STATES MODEL

The generalized corresponding-states model used here is based upon the principles set forth by Rowlinson and Watson [35] and Leach et al. [36] and has been successfully used for other mixtures by Ely and Hanley [37] and by Gallager et al. [38]. It makes use of a good representation of the thermodynamic properties of the pure substance which is the main component of the mixture, to be used as the reference in the model. For the mixtures described in this work, water is the principal component, and the (modified) HGK representation [26] is used. All quantities used in this model are in reduced, dimensionless form. The reduction factors are the same as used in the HGK steam representation: the approximate critical parameters for pure $H_2O$ (see Table Ia).

In the following discussion, the subscript 0 refers to properties of the reference fluid (steam), the subscript 1 to properties of the other component of the mixture (the solute), and the subscript $x$ to properties of the two-component mixture with mole-fraction $x$ of the solute (and $1-x$ of the solvent). The superscript c on a quantity refers to its value at the critical point of the mixture, and the bar above a quantity refers to its dimensionless value.

The principle of corresponding states applied to two-component mixtures postulates that, for all $V$ and $T$,

$$\begin{aligned} Z_x(\bar{V}_x, \bar{T}_x) &= Z_0(\bar{V}_0 = \bar{V}_x/h, \bar{T}_0 = \bar{T}_x/f) \\ \bar{A}_x^{\mathrm{cf}}(\bar{V}_x, \bar{T}_x) &= f\bar{A}_0^{\mathrm{cf}}(\bar{V}_0 = \bar{V}_x/h, \bar{T}_0 = \bar{T}_x/f) - R^{**}\bar{T}_x \ln(h) \end{aligned} \tag{1}$$

where $Z$ is the compressibility factor $PV/RT(=\bar{P}\bar{V}/R^{**}\bar{T})$, $\bar{A}^{\mathrm{cf}}$ is the configuration portion of the Helmholtz function, $\bar{A}^{\mathrm{cf}} = \bar{A} - \bar{A}_{\mathrm{pg}}$ ($\bar{A}_{\mathrm{pg}}$ is the perfect gas component of the Helmholtz function), and the quantities $f$ and $h$ introduced here are the critical ratios of the temperatures and volumes defined through

$$f = (\bar{T}_x^{\mathrm{c}}/\bar{T}_0^{\mathrm{c}})\, \Theta(\bar{V}_0, \bar{T}_0, x) \qquad \text{and} \qquad h = (\bar{V}_x^{\mathrm{c}}/V_0^{\mathrm{c}})\, \Phi(\bar{V}_0, \bar{T}_0, x) \tag{2}$$

**Table I.** Parameters Defining the Corresponding-States Model

(a) Primary and derived reduction parameters and physical constants

| | |
|---|---|
| **Primary reduction parameters** | |
| Temperature | $T^* = 647.27$ K |
| Pressure | $P^* = 22.115$ MPa |
| Density | $\rho^* = 1/V^* = 17.639\ \mathrm{mol\ dm^{-1}}$ |
| **Derived reduction parameters** | |
| Energy functions($A$, $G$, $H$, and $U$) | $A^{**} = P^*/\rho^*$ |
| Entropy and heat capacities | $S^{**} = A^{**}/T^*$ |
| **Physical constants** | |
| Gas constant | |
| (Unreduced) | $R = 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}}$ |
| (Reduced) | $R^{**} = R/S^{**} = 4.2923$ |
| Molecular weights | |
| $H_2O$ | $0.0180152\ \mathrm{kg\ mol^{-1}}$ |
| NaCl | $0.05845\ \mathrm{kg\ mol^{-1}}$ |
| Ar | $0.03994\ \mathrm{kg\ mol^{-1}}$ |

(b) Values for the adjustable parameters for NaCl in $H_2O$

| | HGK minus 3 terms | | | |
|---|---|---|---|---|
| | Parameter set I, "good" critical line | Parameter set II, steeper initial slope | HGK | "Real" |
| $T^c(H_2O)$, K | 648.18 | 648.18 | 647.13 | 647.14 |
| $P^c(H_2O)$, MPa | 22.337 | 22.337 | 22.054 | 22.064 |
| $\rho^c(H_2O)$, $\mathrm{mol\ dm^{-3}}$ | 17.87 | 17.87 | 16.48 | 17.87 |
| $T^c$(NaCl), K | 1450 | 1200 | | 3900 [30] |
| $P^c$ (NaCl), MPa | 15 | 8 | | 25 |
| $\Phi_0$ | 3.0 | 6.0 | | |
| $\Theta_v$ | −0.05 | +0.4 | | |
| $\Theta_T$ | +0.30 | −0.4 | | |
| $k$ | 1.00 | 1.00 | | |
| $l$ | 1.25 | 1.40 | | |

The functions $\Theta$ and $\Phi$ (the "shape factors" of Rowlinson et al.) are available to map more accurately chosen properties of the second fluid onto those of the reference fluid. They are unity for simple corresponding states and functions of $T$ and $V$ for generalized corresponding states. In our application, they are assumed to be linear functions of $x$ and simple functions of the other variables:

$$\Theta = (1-x) + x(1 + \Theta_v \bar{V}_0 + \Theta_T \bar{T}_0) \qquad \text{and} \qquad \Phi = (1-x) + x\Phi_0 \tag{3}$$

$\Theta_v$, $\Theta_T$, and $\Phi_0$ are available as adjustable parameters.

The quantities $\bar{T}^c_x$ and $\bar{V}^c_x$ in Eq. (2) are the values of $T$ and $V$ at the composition $x$ on the pseudocritical line, which is defined as the locus where $(\partial P/\partial V)_{Tx}$ and $(\partial^2 P/\partial V^2)_{Tx}$ would be zero if the mixture were constrained to be homogeneous. $\bar{T}^c_x$ and $\bar{V}^c_x$ are defined through "mixing rules" which define the path taken by the pseudocritical line from the critical point of the reference fluid to the critical point of the second fluid. We have used the "van der Waals" mixing rules, which are simpler than most proposed mixing rules and seem to perform just as well. They are

$$\begin{aligned} \bar{T}^c_x &= (1-x)^2\, \bar{T}^c_0 + 2x(1-x)\, l(\bar{T}^c_0 \bar{T}^c_1)^{1/2} + x^2 \bar{T}^c_1 \\ \bar{V}^c_x &= (1-x)^2\, \bar{V}^c_0 + 2x(1-x)\, k[0.5(\bar{V}^c_0)^{1/3} + 0.5(\bar{V}^c_1)^{1/3}]^3 + x^2 \bar{V}^c_1 \end{aligned} \tag{4}$$

These equations contain two more adjustable parameters, $k$ and $l$, available to improve the representation of experimental data.

## 4. THE MODEL PARAMETERS FOR NaCl IN $H_2O$

The values of the $k$ and $l$ required to represent satisfactorily the experimental critical line data are given in Table Ib. The critical line predicted by these parameters is continuous to mole fractions of NaCl of at least 0.15 or 0.20, well beyond the range of the experimental data of interest here.

In a later section, we show that the representation of the liquid-density apparent molar heat capacity data requires a steeper slope of the critical line. Not only does the adjustment of the parameters to achieve a steeper initial slope worsen the representation of the experimental critical-line data, but also, as the slope becomes more steep, the critical line breaks off at lower compositions of NaCl. Table Ib presents a sample set of parameters adjusted for maximum initial steepness, while maintaining the continuity of the critical line at least as far as the experimental data. Note that for both sets of parameters, the critical parameters of NaCl were considered as adjustable, since our purpose is solely to fit the properties at relatively low compositions. In each case, the reference equation was the modified HGK equation for pure water. Table Ib shows the critical parameters for pure $H_20$ as predicted by this modified HGK equation.

## 5. FITS TO THE CRITICAL-LINE DATA

The critical lines predicted by two sets of parameters given in Table Ib are shown, along with the experimental measurements, in Fig. 2. Figure 2 describes three aspects of the initia part of the critical line—temperature $T$ vs $x$, pressure $P$ vs $x$, and pressure $P$ vs temperature $T$—as well as an enlargement of the very low-composition end of the $T$ vs $x$ to show in detail the behavior of the predicted and experimental critical lines in the limit of small $x$. In each case, the "good" critical line is indicated by the solid line, and the critical line with the steeper initial slope by the dashed line. The representation of the Marshall and Jones and of the Ölander and Liander data is good but the experimental point at the lowest composition of Ölander and Liander might be indicating a need for more curvature for mole fractions less than 0.001 than can be obtained through the use of a corresponding-states model. The experimental data for higher compositions indicate a nearly straight critical line, intersecting the pure $H_2O$ axis at about 652 K, several degrees above the real critical point and above that of the modified HGK equation. The dotted critical line in the detailed plot follows if the original HGK equation is used. It can be seen that the effects of the three critical-region terms have completely disappeared for mole fractions greater than 0.001.

## 6. PREDICTION OF OTHER PROPERTIES OF THE MIXTURE

Since our model is now a complete Helmholtz function, calculations of all desirable equilibrium thermophysical properties are possible, and predictions of several properties for which experimental data exist have been made as a test of the model. Let us look first at the isothermal coexistence data of Bischoff et al. [19]: Fig. 3 shows the experimental measurements and the predicted values of pressure and composition for two of the isotherms measured—one, at 373°C, just below the critical temperature of pure steam, and one, at 380°C, a few degrees above. They are plotted with logarithmic composition scales because the composition varies over several orders of magnitude. Note that the qualitative features of this data are well reproduced, including the unusual "beak" in the immediately subcritical isotherms, which was theoretically predicted by van der Waals. This feature is exaggerated because of the logarithmic scale, [41].

As a test of the model in the single-phase region, we compare the

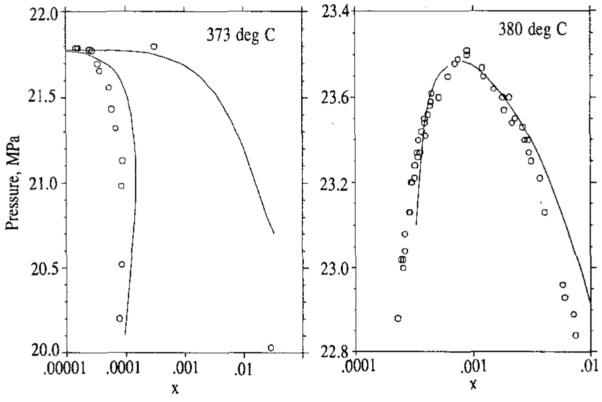

**Fig. 3.** Pressure vs composition plots for the liquid–vapor coexistence curves for two isotherms, one just below the critical point of pure $H_2O$ showing the "beak" and one a few degrees above. The experimental data of Bischoff et al. [19] and the predicted values of parameter set I are shown.

predicted apparent molar heat capacities with the measurements of Wood and co-workers [3, 22] in Figs. 1 and 4. On the supercritical isobar at 32 MPa [22], these measurements show large negative values in the liquid-like region and large positive values in the vapor-like region. Our model was able to predict qualitatively this behavior, although the predicted values appear to be shifted to more positive values by 100 to 200 J mol$^{-1}$ K$^{-1}$ and the crossover from negative to positive values on the supercritical isobar is shifted to higher temperatures by a few degrees

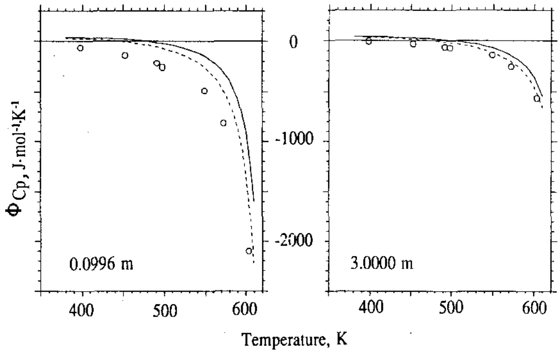

**Fig. 4.** Apparent molar heat capacities of NaCl in $H_2O$ in the liquid for two compositions. (○) Experimental data of Smith-Magowan and Wood [3]. Solid and dashed lines represent predicted values as in Figs. 1 and 2.

Kelvin. Figure 4 shows similar plots for two compositions in the liquid, and the remarks concerning the liquid-like region of the supercritical isobar apply here as well. Wood and Quint [23] and Pitzer and Tanger [25], in their analysis of the experimental data, assumed a negligible contribution from the ideal-gas heat capacity of NaCl, and we have done the same. Any positive value of $C_p^0$ for NaCl shifts the predicted curve upward.

The effect of the initial slope of the critical line on the prediction of the apparent molar heat capacity is indicated by the dashed curve in Figs. 1 and 4, calculated by means of the parameters in the third column in Table Ib, which correspond to the steep critical line in Fig. 2, as discussed in the previous section. Note that although the critical line is now unacceptably far from the experimental values, this choice does indeed give noticeably more negative values of the apparent heat capacities in the liquid and liquid-like regions.

## 7. COMPARISON WITH OTHER MODELS

The simple corresponding-states model of Wood and Quint [23] that assumed identity between the pseudo- and the real critical lines gave almost perfect agreement with the heart capacities on the 17-MPa isobar. Our model, however, insists on a very large difference in slope of the pseudocritical line and the critical line, so that the subcritical heat capacities can be fitted only by increasing the slope of the crtical line. We have not seen the Wood and Quint model applied to the 32-MPa data. Since it has the unphysical feature of strong divergence of the mixture compressibility and heat capacity at the critical line, difficulties must be expected near this line.

At this conference, Pitzer and Tanger [25] presented an effort parallel to ours: they created a Helmholtz free energy for the aqueous NaCl solution by using the unmodified HGK equation, evaluated at the density of the water in the solution, as a reference, and adding low-order polynomials in density, temperature, and composition. With 10 adjustable parameters, they obtained a fit to the 32-MPa ${}^{\phi}C_p$ data of a quality comparable to ours. They did not attempt to fit the 17-MPa ${}^{\phi}C_p$ isobar. They explored the two-phase region to a much greater extent than we did and have an excellent representation for the data from 250 to 450°C. Although they do do not explicitly show their fit to the critical line, it appears that they experienced similar problems with the initial curvature and have reached conclusions similar to ours about unresolved issues (next section).

## 8. DISCUSSION

We have constructed a classical Helmholtz function for the system NaCl–$H_2O$ as a first step in formulating thermodynamic properties of compressible dilute aqueous solutions. We have ignored all effects of charges and of nonclassical critical fluctuations. With six adjustable parameters, and the modified HGK equation as a reference, we have obtained qualitative to semiquantitative agreement with the data on the critical line, coexistence curves, and apparent molar heat capacity. This demonstrates that the major anomalies seen in this system are those common to all dilute near-critical mixtures.

The dominance of critical over charge effects [8, 14, 15] will first break down on the high-density, high-dielectric side, where NaCl will be dissociated. On redoing the problem, one would want to emphasize the initial, relatively low-density part of the critical line and the low-density part of the supercritical ${}^{\phi}C_{\mathrm{p}}$ isobar. The classical Helmholtz free energy so obtained would then have to be modified to incorporate dissociation. The way we have dealt with the issue of classical versus nonclassical critical behavior in this system is clearly unsatisfactory. It is known that nonclassical effects in pure steam may become manifest as much as 30°C from the critical point [18]. They cannot be eliminated by omitting the three near-critical terms in the HGK equation. Even if the NaCl solution would behave classically, for which there is no theoretical justification, there must exist a crossover region as the NaCl mole fraction increases. We believe that the initial behavior of the critical line of this system is a complex interplay of crossover effects in the mixture and changing degree of dissociation and that the current theoretical status is not yet capable of dealing with these combined problems.

Finally, it may be objected that we have ignored one of the most curious aspects of the phase diagram of NaCl–$H_2O$, the presumably continuous critical line, and by ignoring this may have left out essential parts of the science. Our goal, however, has been the more modest one of constructing a Helmholtz free energy model capable of describing the effects of solvent compressibility in dilute solutions. Our corresponding-states model does not claim to incorporating all the science of the problem. We are, however, confident that it provides a base for incorporating at least the infinite-dilution effects of charges in a way that is free of the problems posed by excess Gibbs free energy models applied to high-temperature electrolyte solutions.

## ACKNOWLEDGMENTS

This work was supported by the Office of Standard Reference Data, National Bureau of Standards. We had many inspiring discussions with Professor R. H. Wood. Both he and Professor K. S. Pitzer sent us prepublication manuscripts. G. Morrison, K. S. Pitzer, and D. G. Archer provided constructive criticisms.

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