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# Critical Locus of Aqueous Solutions of Sodium Chloride

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Experimental data reported in the literature indicate a strong dependence of the critical temperature of aqueous solutions of sodium chloride on salt concentration, especially in the limit of pure water. Critical pressures and densities also show strong dependences on salt concentration. We propose a new set of equations for the critical locus and compare the results with evaluations reported previously by a number of investigators. The new equations yield a better description of the experimental data from the limit of pure water to the highest salt concentration for which data are available (0.3 mass fraction of sodium chloride).

**KEY WORDS:** aqueous salt solutions; critical locus; critical temperatures; ionic fluids; sodium chloride solutions.

## 1. INTRODUCTION

For the vapor–liquid critical locus of solutions of sodium chloride in water, several experimental investigations have been reported [1–10] that are in reasonable mutual agreement. The experimental data have been obtained for concentrations up to 0.3 mass fraction of sodium chloride. These data indicate that the vapor–liquid critical line of aqueous solutions of NaCl is a continuous function of concentration indicating that the system possesses

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a Type I phase diagram in terms of the classification scheme proposed by van Konynenburg and Scott [11, 12].

As noted by a number of investigators [13–15], this result is somewhat of a surprise. The calculations of van Konynenburg and Scott [11] on the basis of the van der Waals equation indicated that a single continuous critical line is present in binary mixtures for which the ratio $T_{c2}/T_{c1}$ of the critical temperatures $T_{c1}$ and $T_{c2}$ of the two components is smaller than about 3. In practice, it turns out that the critical locus of nonelectrolyte mixtures is already interrupted when $T_{c2}/T_{c1}$ becomes larger than 2 [14]. More realistic calculations for aqueous electrolytes have indicated that the critical locus will be interrupted for $T_{c2}/T_{c1} > 3.56$ on the basis of a model with equal molecular and ion sizes considered by Harvey [13]. An extension of that model to unequal sizes by Thiéry et al. [14] showed that the interruption of the critical locus is delayed to somewhat higher values of $T_{c2}/T_{c1}$, if the model ions are made larger than the dipolar hard-sphere "water." Interruption of the critical locus in aqueous salt systems has been observed for the phosphates and hydrogen phosphates of sodium and potassium [16]. For aqueous solutions of NaCl, $T_{c2}/T_{c1}$ is estimated to be about 5, yet no interruption of the critical locus has been observed. As noted by Pitzer in a recent paper [15], "this apparent anomaly merits further research."

In the present paper, we demonstrate that a careful analysis of the most accurate data available for aqueous solutions of NaCl reveals the presence of a dip in the critical locus at low NaCl concentrations, indicating that, while the critical locus remains a continuous function of the concentration, it is actually close to a condition of being interrupted. Taking this effect into account, we then develop a set of equations which accurately represents the critical temperature $T_c$, the critical density $\rho_c$, and the critical pressure $P_c$ of aqueous solutions of NaCl as a function of the NaCl concentration.

## 2. REVIEW OF AVAILABLE DATA AND EQUATIONS

The available experimental data for the critical temperature $T_c$ as a function of the salt concentration are shown in Figs. 1 and 2. Figures 1a and 2a show the data over the entire available concentration range up to a NaCl mass fraction of 0.3; Figs. 1b and 2b show in some detail the available data at low concentrations.

A comprehensive experimental study of the critical temperature at lower salt concentrations was made by Marshall [1]. From Figs. 1b and 2b we note that $T_c$ varies appreciably with the salt concentration. Even

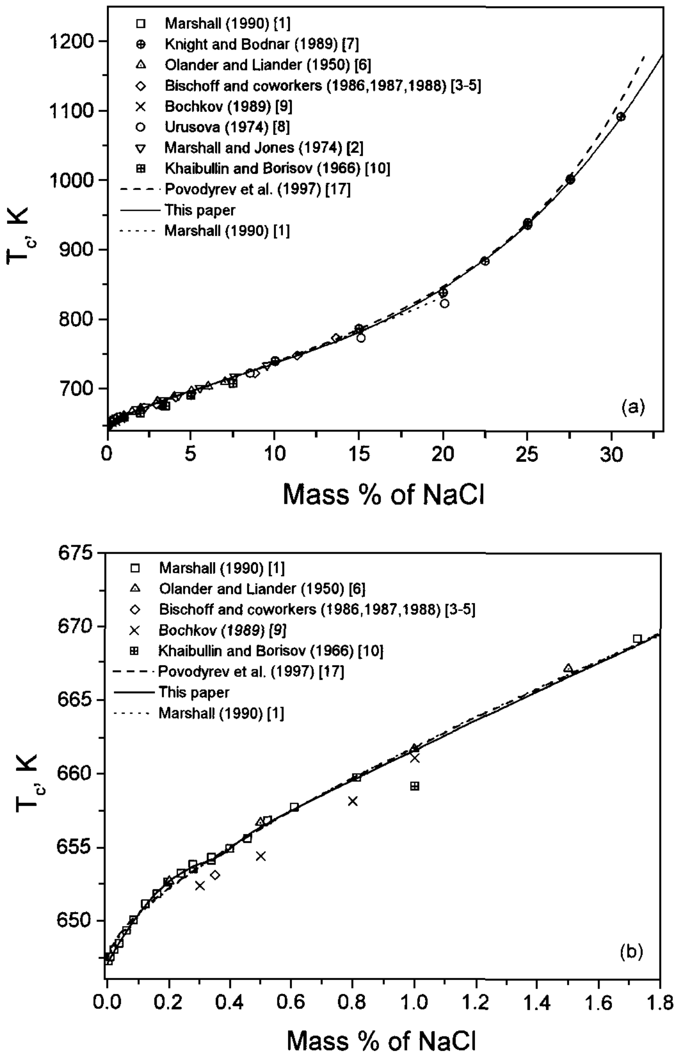

**Fig. 1.** The critical temperature of $H_2O$–NaCl solutions as a function of concentration. The solid curve represents the values calculated with Eq. (1) presented in this report. The dotted and dashed curves represent equations previously proposed by Marshall [1] and Povodyrev et al. [17], respectively. (a) The critical temperature over the entire experimental range of concentrations. (b) The critical temperature at low concentrations of NaCl.

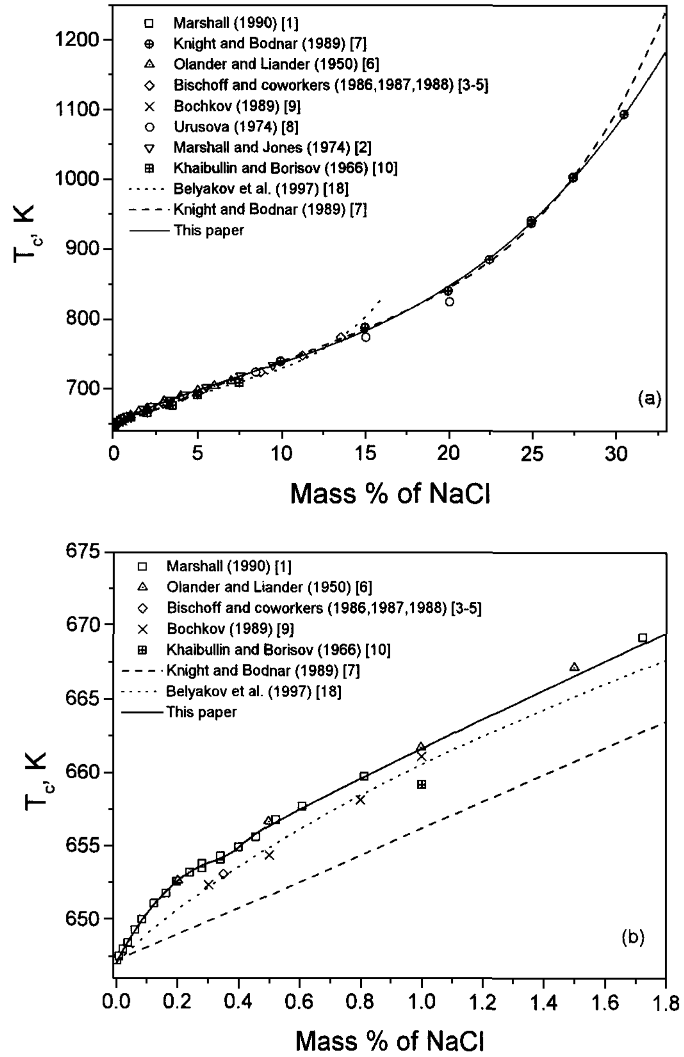

**Fig. 2.** The critical temperature of $H_2O$–NaCl solutions as a function of concentration. The solid curve represents the values calculated with Eq. (1) presented in this report. The dotted and dashed curves represent equations previously proposed by Belyakov et al. [18] and Knight and Bodnar [7], respectively. (a) The critical temperature over the entire experimental range of concentrations. (b) The critical temperature at low concentrations of NaCl.

more importantly, the data of Marshall indicate the presence of a dip in the critical locus in the concentration range between 0.003 and 0.005 mass fractions of NaCl.

An important question to be addressed is whether the dip observed in the critical locus exceeds the experimental error. In Ref. 1, the critical point was determined from the observed disappearance of separate liquid and vapor phases with increasing temperature (the meniscus between liquid and vapor flattens out and disappears at the center of the tube as the surface tension reaches zero) and from the appearance of separate liquid and vapor phases with decreasing temperature (an instantaneous cloud-like condensation appears throughout the tube with the previously transparent supercritical fluid). As documented in Ref. 1, the reproducibility of the experimental temperatures was ±0.1 to 0.2°C, with the better precision at lower concentrations and with an overall experimental accuracy estimated to be within 0.2 to 0.5°C [1]. Using the same apparatus, Marshall and Simonson [19] obtained the critical temperatures of mixtures of $H_2O$ and $D_2O$ with the same reproducibility of ±0.1°C in approximately the same range of temperatures; a recent analysis of the critical locus of mixtures of $H_2O$ and $D_2O$ has confirmed that the critical temperatures determined by Marshall and Simonson indeed have a precision of about ±0.1°C [20]. From the experimental critical temperatures obtained by Marshall for the aqueous salt solutions, one can estimate that the dip has a value of 0.4–0.5°C relative to a smooth curve connecting the low concentration (less than 0.003 mass fraction) and the high concentration (larger than 0.005 mass fraction) regions. Hence, the size of the dip is well beyond the experimental precision, and we have concluded that the observed structure is not an artifact.

Although evaluations of the critical temperatures of NaCl solutions reported previously by Marshall [1] and Povodyrev et al. [17] are in good agreement, both exhibit small systematic deviations from the experimental data in the dilute-solution region as the observed dip in the critical line was ignored. For a description of the critical temperature as a function of the composition, Marshall adopted an implicit function based on an ionization chemical model [1]. The function that was proposed by Marshall contained six parameters. Two of these were adjustable, and the other four were taken from independent experiments of the ionization constant [21, 22]. The equation is capable of representing the experimental data reasonably well up to $\approx 0.15$ mass fraction ($\approx 4\ \mathrm{mol \cdot kg^{-1}}$) of sodium chloride. The two adjustable parameters were obtained from experimental data up to only 0.015 mass fraction but provided a good representation of data to 10 times that concentration, lending strong support for the ionization model.

Povodyrev et al. [17] have reported a crossover model for the phase-equilibrium properties of aqueous solutions of sodium chloride near the critical locus. The equation for the critical-temperature curve adopted in the crossover model has only three adjustable parameters and covers all experimental data up to ≈0.3 mass fraction of sodium chloride. A disadvantage of this equation is that the calculated curve for the critical temperature (as well as for the critical pressure and the critical density) exhibits an infinite slope in the pure-water limit. The experimentally observed dip in the critical temperature is not described by either the equation of Marshall [1] or the equation of Povodyrev et al. [17], as shown in Fig. 1b. In the region of concentrations up to ≈0.15 mass fraction of sodium chloride, the two equations [1, 17] are in excellent agreement.

The equation for the critical pressure as a function of temperature, proposed by Povodyrev et al. [17], has four adjustable parameters. To calculate the critical pressure as a function of concentration, one then needs to employ the equation for the dependence of the critical temperature on concentration. Hence, the critical pressure versus concentration curve, thus obtained [17], inherits disadvantages implied by the equation adopted for the critical temperature as a function of concentration, i.e., it also exhibits an infinite slope at the pure-water limit.

In an earlier publication, Knight and Bodnar [7] presented equations to describe their own experimental data for the critical temperature, pressure, and density. The experimental data obtained by Knight and Bodnar [7] for concentrations exceeding 0.032 mass fraction of NaCl are in reasonable agreement with other experimental investigations. The dilute region was not investigated by these authors. The equations of Knight and Bodnar [7] for the critical temperature and pressure, while well representing the experimental data at high concentrations, show systematic deviations from the experimental data in the dilute region as can be seen in Fig. 2. The equation for the critical density as a function of concentration proposed by Knight and Bodnar [7] has three adjustable parameters (the fourth parameter is the critical density of pure water), which is one parameter less than in the equation for the critical density proposed by Povodyrev et al. [17]. Both equations for the critical density fit the experimental data of Knight and Bodnar [7], with no significant differences. Marshall [23] applied a chemical-ionization-electrostriction treatment based on his previous investigations of the ionization constant [21, 22] and of the critical temperature of aqueous NaCl solutions [1]. The equation obtained by Marshall for the critical density [23] reproduces the critical densities reported by Knight and Bodnar [7] with approximately the same accuracy as the equation in Ref. 7 at concentrations up to 0.2 mass fraction of NaCl, but it is relatively complicated because it has to be solved by iteration.

Belyakov et al. [18] developed a crossover model to describe the phase behavior of dilute aqueous ionic solutions. Their set of equations for the critical locus was obtained from fits to the experimental data for the critical locus jointly with phase-equilibrium data. A description of the phase-equilibrium data is complicated by the ionic nature of the system, especially in the dilute region. Although the authors used a large number of adjustable parameters for each critical property (nine parameters), the range of validity of their equations does not exceed $\approx 0.13$ mass fraction of NaCl. Since the accuracy of the equations for the critical temperature, density, and pressure was affected by the accuracy of their crossover model for representing the phase-equilibrium data, the resulting equations do not yield an optimal representation of available experimental data for the critical locus as can be seen in Fig. 2.

This paper presents a set of equations that represents the critical locus of aqueous solutions of sodium chloride over the *entire* experimental range of concentrations with a minimum of adjustable parameters.

## 3. DESCRIPTION OF THE CRITICAL LOCUS

Although the experimental values for the critical temperatures obtained by Marshall [1] for low concentrations of sodium chloride yield a very strong concentration dependence, we do not expect the limiting slope (in the pure-water limit) to be infinite. However, to obtain a uniform function for reproducing the experimental critical temperatures by a single equation reasonably well over the entire range of concentrations (up to 0.3 mass fraction of NaCl), in Ref. 17 we were forced to assume a singular cusp-like behavior of the critical curve in the pure-water limit. Another option, which we adopt in the present work, is to use two functions, one for low and the other for high concentrations, and then provide a smooth crossover transformation between them. To represent the experimental data for the critical temperature over the entire range of concentrations (up to 0.3 mass fraction of NaCl), we propose the following single equation:

$$T_c = \frac{f_1}{2}\{\tanh[w_1(w_2 - w)] + 1\} + \frac{f_2}{2}\{\tanh[w_1(w - w_2)] + 1\} \quad (1)$$

with

$$f_1 = T_c^{H_2O} + T_1 w + T_2 w^2$$

$$f_2 = T_3 + T_4 w + T_5 w^2 + T_6 w^3$$

where $T_c^{H_2O}$ indicates the critical temperature of pure $H_2O$ and $w$ represents the sodium chloride concentration as mass percentage of sodium chloride. This equation contains eight adjustable coefficients, given in Table I. Note that $w_1$ and $w_2$ are dimensionless, while the coefficients $T_i$ ($i = 1,..., 6$) have the dimension of temperature. To determine the values of these coefficients, we fit Eq. (1) to experimental data obtained by Marshall [1], Marshall and Jones [2], Bischoff and co-workers [3–5], Ölander and Liander [6], and Knight and Bodnar [7]. The critical-temperature curve calculated from Eq. (1) together with curves calculated from the equations proposed in Refs. 1, 7, 17, and 18 and the experimental data are shown in Figs. 1 and 2.

In Fig. 3, we show the deviations of the experimental data obtained by Marshall [1], which cover the dilute-solution range up to 1 mass% of NaCl, from the values calculated with Eq. (1). In the same figure we also show the deviations of the values calculated with the equations previously reported by Marshall [1] and Povodyrev et al. [17]. It is evident that

**Table I.** Parameters in Eqs. (1)–(3) for the Critical Locus of NaCl-$H_2O$ Solutions up to 0.3 Mass Fraction of NaCl[a]

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Critical temperature $T_c$ (K)

$T_c^{H_2O} = 647.096$
$T_1 = 38.688$
$T_2 = -53.982$
$T_3 = 651.093$
$T_4 = 10.900$
$T_5 = -0.39821$
$T_6 = 0.016880$
$w_1 = 17.034$
$w_2 = 0.37587$

Critical pressure $P_c$ (MPa)

$P_c^{H_2O} = 22.064$
$P_1 = 0.20176$
$P_2 = 1.1393 \times 10^{-3}$
$P_3 = -5.5960 \times 10^{-6}$
$P_4 = 8.0521 \times 10^{-9}$

Critical density $\rho_c$ (kg · m$^{-3}$)

$\rho_c^{H_2O} = 322.0$
$R_1 = 66.868$
$R_2 = 13.668$
$R_3 = -6.3107 \times 10^{-4}$

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[a] The values of the critical parameters of pure water are taken from Ref. 25.

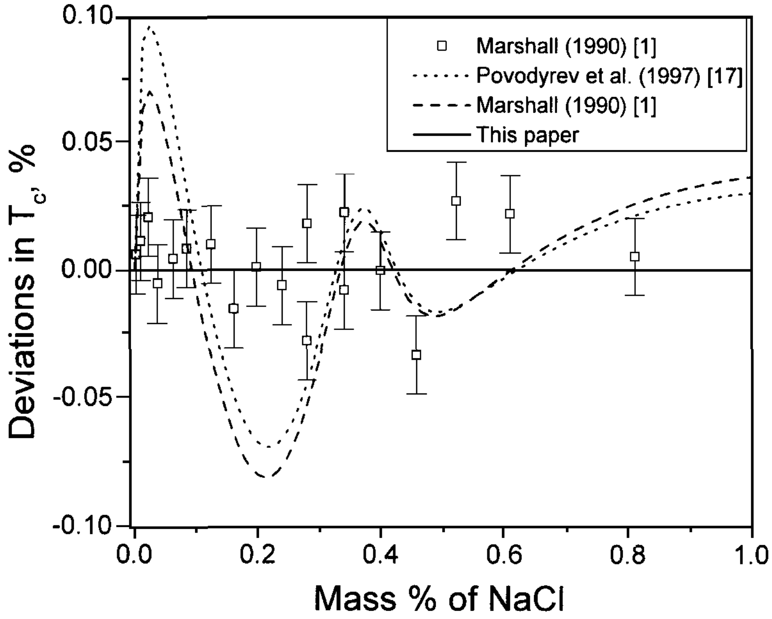

**Fig. 3.** Percentage deviations of the critical temperatures reported by Marshall [1] (squares), of the values calculated with the equation earlier proposed by Marshall [1] (dashed curve), and of the values calculated with the equation earlier proposed by Povodyrev et al. [17] (dotted line) from the values calculated with Eq. (1) presented in this paper.

Eq. (1) yields a significantly better description of the experimental data in this range than the equations of Marshall [1] and Povodyrev et al. [17]. Equation (1) represents the experimental data of Marshall [1] with a standard deviation $\sigma = 0.017\%$, which agrees with the estimated experimental precision of $\pm 0.1$ K. Figure 4 shows how the dip in the critical temperature curve calculated from Eq. (1) is produced by a "crossover" between two functions, $f_1$ and $f_2$, which represent the behavior of the experimental data in different ranges.

Equation (1) represents the experimental critical temperatures in the entire range of concentrations up to a NaCl mass fraction of 30% with a standard deviation $\sigma = 0.3\%$; for comparison, we note that the equations previously proposed by Marshall [1] and Povodyrev et al. [17] represent the same experimental data with a standard deviation $\sigma = 0.4\%$.

The critical pressure $P_c$ and the critical density $\rho_c$ have been investigated experimentally less extensively at low concentrations than has the critical temperature. There are no experimental data for the critical

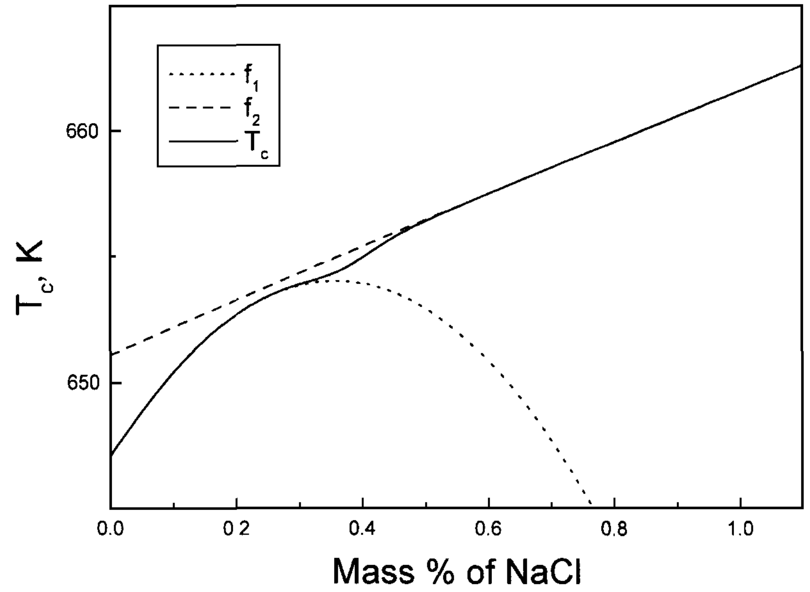

**Fig. 4.** Illustration of how the dip in the critical-temperature curve is calculated from Eq. (1) by a "crossover" between two functions, $f_1$ and $f_2$, which represent the behavior of the experimental data in different concentration ranges.

density and pressure in the concentration region close to the critical point of pure water, where the critical-temperature line has an appreciable curvature. We have expressed the equation for the critical pressure in terms of $\Delta T = T_c - T_c^{H_2O}$, which is the difference between the critical temperature $T_c$ of the solution and the critical temperature $T_c^{H_2O}$ of pure water:

$$P_c = P_c^{H_2O} + P_1 \Delta T + P_2(\Delta T)^2 + P_3(\Delta T)^3 + P_4(\Delta T)^4 \tag{2}$$

Equation (2) assumes that the critical pressure is an analytical function of the critical temperature. This assumption may not be true in the concentration range (0.003 to 0.004 mass fraction) where the dip in the critical temperature is observed. Thus, we use four adjustable parameters $P_i$ ($i = 1, ..., 4$) to represent the critical pressure. The coefficients in Eq. (2) for the critical pressure were obtained from a fit of Eq. (2) to the experimental data obtained by Knight and Bodnar [7], Bischoff and co-workers [3–5], Urusova [8], and Ölander and Liander [6]. The critical-pressure curve as a function of the critical temperature is shown in Fig. 5. The critical-pressure curve as a function of concentration calculated with Eqs. (1) and (2), together with curves calculated from the equations proposed in Refs. 7, 17, and 18 and the experimental data, are shown in Fig. 6. The standard

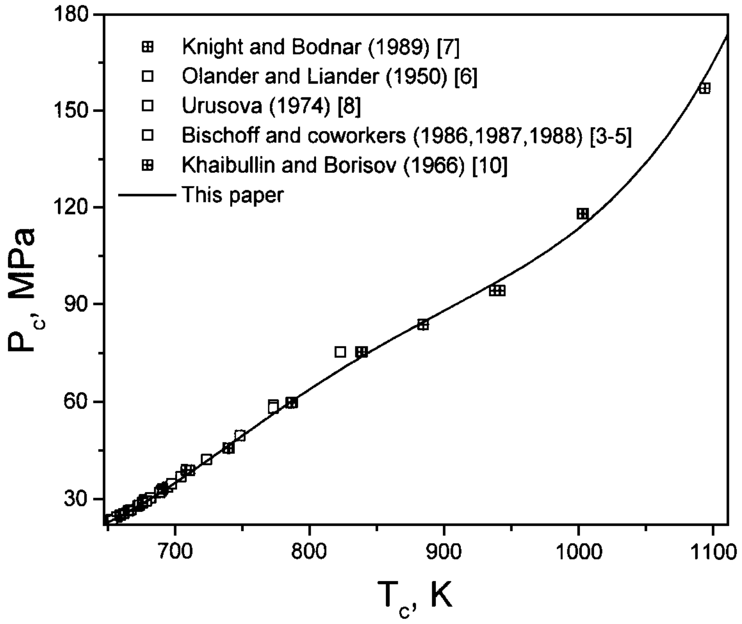

**Fig. 5.** The critical pressure of $H_2O$–NaCl solutions as a function of temperature. The solid curve represents the values calculated with Eq. (2) presented in this paper.

deviation of the fit with Eq. (2) to the experimental critical pressure data is 1.7%. Deviations of the experimental data [3–7] and of the two equations reported in the literature [7, 18] from Eq. (2) for the critical pressure are shown in Fig. 7.

For a description of the experimental data for the critical density $\rho_c$, we adopt the following equation:

$$\rho_c = \rho_c^{H_2O} + R_1 \psi + R_2 \psi^2 + R_3 \psi^3 w^2 \tag{3}$$

where, after Knight and Bodnar [7], $\psi = \ln(w+1)$. To determine the coefficients in Eq. (3) for the critical density, we fit the equation to the experimental data obtained by Knight and Bodnar [7] and Bochkov [9] and to data compiled by Bischoff [24]. The critical-density curve calculated with Eq. (3), together with the curves calculated with the equations proposed in Refs. 7, 17, and 18 and the experimental data, are shown in Fig. 8. The standard deviation of the fit with Eq. (3) is 1.5%. The equations for the critical density earlier proposed by Knight and Bodnar [7] and Povodyrev et al. [17] yield standard deviations of 1.7 and 1.8%, respectively. The

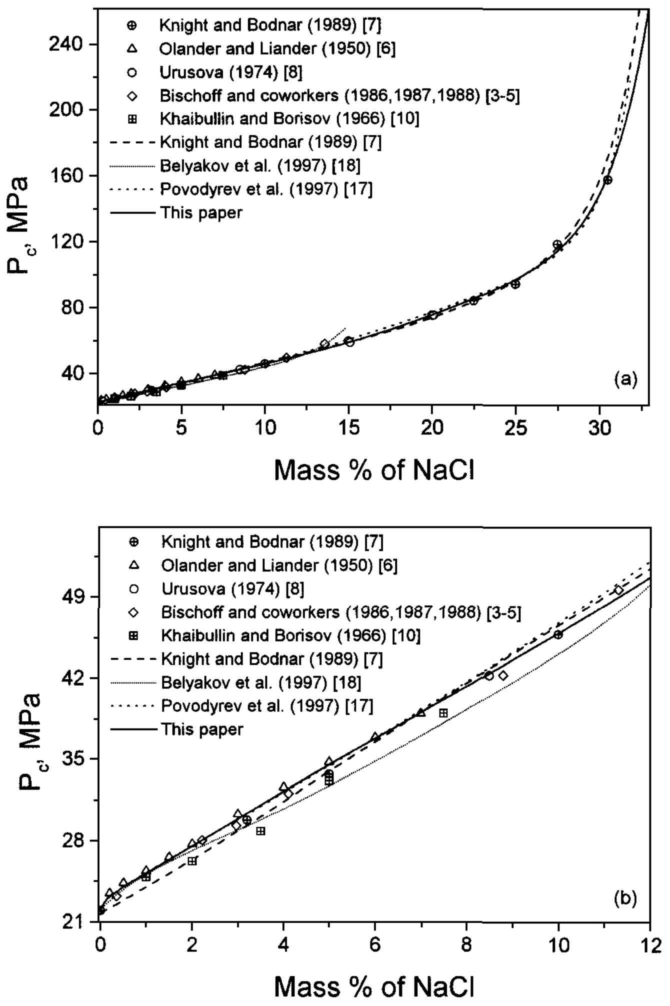

**Fig. 6.** The critical pressure of $H_2O$–NaCl solutions as a function of concentration. The solid curve represents the values calculated with Eq. (2) presented in this paper. The dotted, short-dotted, and dashed curves represent equations previously proposed by Povodyrev et al. [17], Belyakov et al. [18], and Knight and Bodnar [7], respectively. (a) The critical pressure over the entire experimental range of concentrations. (b) The critical pressure at low concentrations of NaCl.

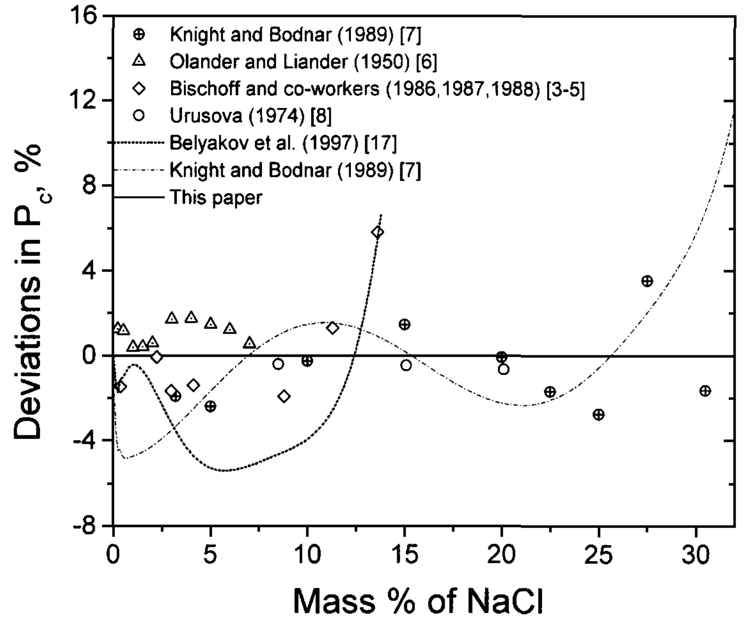

**Fig. 7.** Percentage deviations of the experimental critical pressures [3–8], of the values calculated with the equation reported by Belyakov et al. [18] (short-dotted line), and of the values calculated with the equation earlier reported by Knight and Bodnar [7] (dotted–dashed line) from the values calculated with Eq. (2) presented in this paper.

equation for the critical density proposed in Ref. 18 does not yield a reasonable description of the experimental data [7, 24]. It describes the experimental data reported by Khaibullin and Borisov [10] somewhat better; however, these data are not in agreement with the data reported in Refs. 7 and 24. Deviations of the experimental data and of the equation of Knight and Bodnar [7] from Eq. (3) for the critical density are shown in Fig. 9. It is difficult to distinguish between the quality of the representation provided by Eq. (3) and the equation in Ref. 7. However, a slight improvement in the representation of the experimental data by the equation proposed in the present paper can be observed.

The values of the coefficients in Eqs. (1)–(3) obtained from the fits to the experimental data are presented in Table I.

## 4. DISCUSSION

We have obtained a set of equations for the vapor–liquid critical locus of aqueous solutions of sodium chloride. The equations do not have a

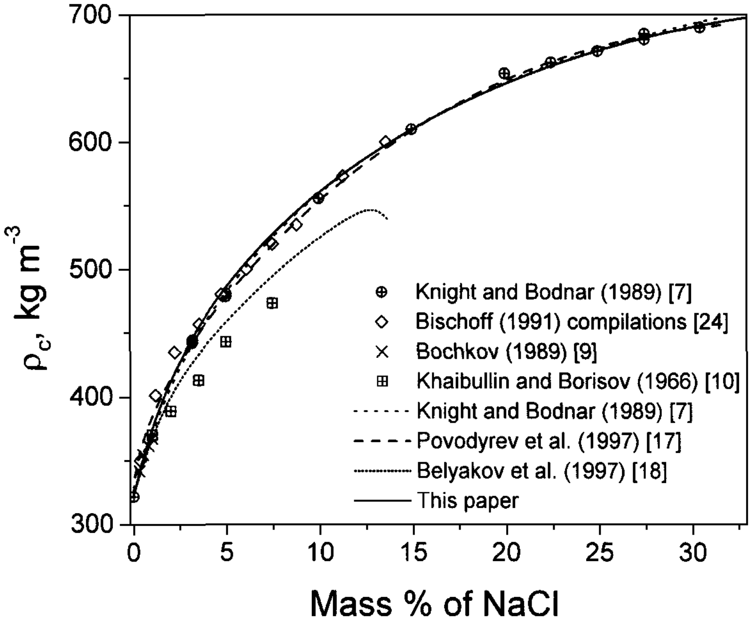

**Fig. 8.** The critical density of $H_2O$–NaCl solutions as a function of concentration. The solid curve represents the values calculated with Eq. (3). The dotted curve represents the equation earlier proposed by Knight and Bodnar [7], the dashed curve represents the equation earlier proposed by Povodyrev et al. [17], and the short-dotted curve represents the equation of Belyakov et al. [18].

singular behavior at infinite dilution and yield a consistent description of the existing experimental data. The equation for the critical temperature incorporates a crossover function to account for an apparent dip in the critical line observed experimentally in the range of 0.003 to 0.005 mass fraction of NaCl. The presence of this dip strongly affects the description of the critical locus over a wider range of concentrations, and this is the main reason the critical locus cannot be represented by a simple polynomial form.

Unlike previous attempts to represent the critical locus of aqueous solutions of NaCl, in this report we have incorporated the irregular behavior of the critical-temperature locus at concentrations between 0.003 and 0.005 mass fraction of NaCl. In doing so, we were motivated by the following considerations. First, the dip in the critical-temperature curve is clearly revealed by the experimental data that have a precision of about $\pm 0.1^\circ$C. Moreover, the observed critical-temperature curve has a non-interrupted shape corresponding to a Type I phase diagram, but whose

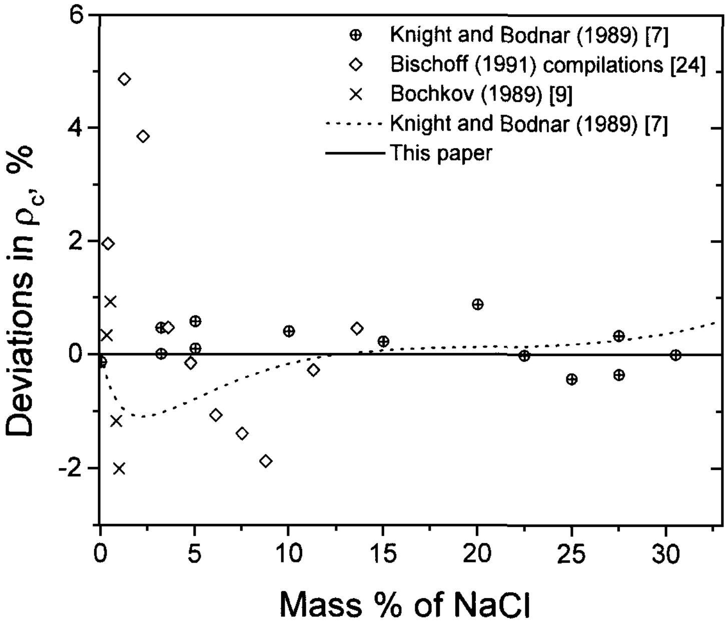

Fig. 9. Percentage deviations of the experimental critical densities [7, 9, 24] and the values calculated with the equation of Knight and Bodnar [7] (dashed curve) from the values calculated with Eq. (3) presented in this paper.

properties are close to those of a system with a Type V phase diagram with an interrupted critical locus [11]. Two factors have been suggested for producing a steep slope of the critical temperature versus concentration: ionization of the electrolyte approaching infinity at the limit of pure water [1, 26] and the shift of the critical temperature caused by fluctuations, the effect of which becomes more pronounced with dilution [17, 27]. However, we note that, regardless of its physical origin, the very steep slope of the critical temperature physically means that the system is close to a virtual instability. Thus, the conditions of the system may be close to the development of an interruption of the critical line and the possible emergence of three-phase coexistence [12]. In this connection, it is interesting to note that the model proposed by Harvey [13] indicates that a possible interruption of the critical locus would occur at a salt mass fraction of about 0.003 (0.002 ion mole fraction), which is a low salt concentration indeed. To explore this feature in more detail, additional experimental studies of aqueous electrolyte solutions are desirable.

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## NOMENCLATURE

| | |
|---|---|
| $P_c$ | Critical pressure (MPa) |
| $P_c^{H_2O}$ | Critical pressure of pure water (MPa) |
| $P_i$ $(i = 1,..., 4)$ | Parameters in Eq. (2) $(\mathrm{MPa \cdot K^{-i}})$ |
| $R_i$ $(i = 1,..., 3)$ | Parameters in Eq. (3) $(\mathrm{kg \cdot m^{-3}})$ |
| $T_c$ | Critical temperature (K) |
| $T_c^{H_2O}$ | Critical temperature of pure water (K) |
| $T_i$ $(i = 1,..., 6)$ | Parameters in Eq. (1) (K) |
| $w$ | Sodium chloride concentration as mass percentage of sodium chloride |
| $w_1$, $w_2$ | Dimensionless parameters in Eq. (1) |
| $\rho_c$ | Critical density $(\mathrm{kg \cdot m^{-3}})$ |
| $\rho_c^{H_2O}$ | Critical density of pure water $(\mathrm{kg \cdot m^{-3}})$ |

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