Critical Locus of Aqueous Solutions of Sodium Chloride Revisited

D. A. Fuentevilla · J. V. Sengers · M. A. Anisimov

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Abstract There exists a formulation for the critical locus of aqueous solution of NaCl recommended by the International Association for the Properties of Water and Steam. In this article, we present slightly modified equations for the critical parameters of H2O + NaCl that incorporate a non-analytic concentration dependence predicted by theory.

Keywords Aqueous salt solutions · Critical parameters · Critical phenomena · Ionic fluids · Sodium chloride solutions

1 Introduction

The thermodynamics of high-temperature aqueous solutions, especially of aqueous salt solutions, has important industrial, geochemical, and biological applications. Examples include the use of supercritical water as a solvent [1–3] and supercritical aqueous solutions that are encountered in geochemical problems [4].

This article is concerned with the concentration dependence of the critical temperature, density, and pressure of an aqueous salt solution, namely, that of sodium chloride in water. Equations for the critical temperature $T_c$, the critical pressure $P_c$, and the critical density $\rho_c$ have previously been developed by Marshall [5], Kiselev et al. [6], Belyakov et al. [7], and Povodyrev et al. [8,9]. Because of the practical importance of an accurate knowledge of these critical parameters, the most recent representative set of equations obtained by Povodyrev et al. [9] has been adopted by the International Association for the Properties of Water and Steam (IAPWS) as a
Guideline on the Critical Locus of Aqueous Solutions of Sodium Chloride [10]. However, since this IAPWS Guideline was developed, two new theoretical developments have occurred, motivating us to reconsider the formulation of the critical parameters of aqueous sodium chloride solutions.

First, just as for molecular fluid mixtures, the critical temperature, pressure, and density were assumed by Povodyrev et al. [9] to be analytic functions of the concentration. However, Kim and Fisher [11] have subsequently shown that a classical theory for a solvent + ion mixture combined with a Debye–Hückel theory for the ionic interactions yields a non-analytic dependence of $T_c$, $P_c$, and $\rho_c$ on the concentration in salt solutions. They also presented evidence for such a non-analytic concentration dependence based on the experimental data of Marshall [5] for the critical temperature of sodium chloride solutions.

Second, there is considerable evidence that molecular, as well as ionic fluids, belong to the critical universality class of Ising-like systems [12,13]. For Ising-like systems, the critical behavior is characterized by two independent scaling fields, $h_1$ and $h_2$, and one dependent scaling field, $h_3$, which are analytic functions of the physical fields. Originally it was thought that for fluid mixtures with $N$ thermodynamic degrees of freedom, the two independent scaling fields should be analytic functions of the $N$ independent physical fields [14,15]. However, more recently, Fisher and co-workers [16–18] have pointed out that for a proper description of critical phase transitions in fluids, all three Ising scaling fields should be taken as analytic functions of all $N + 1$ physical fields, thus also including the dependent physical field. This improved principle of scaling behavior is now referred to as complete scaling. And indeed, complete scaling has turned out to give a proper account of the observed asymmetric critical phase behavior in fluids [19–23]. In this article, we shall show that complete scaling implies an analytic relationship between the critical pressure and the critical temperature, even though $P_c$ and $T_c$ individually exhibit a non-analytic dependence on the concentration as predicted by Kim and Fisher [11].

The purpose of this article is to present a slightly modified formulation for the critical locus of aqueous sodium chloride solutions, but one which is fully consistent with these new theoretical developments. We shall proceed as follows. In Sect. 2, we briefly review the available experimental information for the critical parameters of aqueous sodium chloride solutions. In Sect. 3, we discuss the theoretical predictions for the concentration dependence of the critical parameters of salt solutions and for the relationship between the critical pressure and the critical temperature. In Sect. 4, we then develop a set of equations for the critical parameters of aqueous solutions of sodium chloride consistent with these theoretical predictions. We also discuss the corresponding value of the Krichevskii parameter for the $\text{H}_2\text{O} + \text{NaCl}$ solution. Our results are summarized in Sect. 5.

2 Experimental Data

A comprehensive review of the available experimental data for the critical parameters of aqueous sodium chloride solutions has been presented by Povodyrev et al. [9]. To the best our knowledge, no new experimental data have been published since 1999.