Heat capacity behavior in the critical region of the ionic binary mixture ethylammonium nitrate−n-octanol

T. Heimburg,[1] S. Z. Mirzaev,[2] and U. Kaatze[3,*]

[1]*Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg, 37077, Göttingen, Germany*
[2]*Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, Tashkent 700135, Uzbekistan*
[3]*Drittes Physikalisches Institut, Georg-August-Universität, Bürgerstrasse 42-44, 37077 Göttingen, Germany*

At temperatures between 30 °C and 58 °C we have recorded the heat capacity of the ionic ethylammonium nitrate−n-octanol mixture of critical composition and also of the constituents. Different samples of the binary mixture have been measured with its upper critical demixing temperature T_c varying between 41.04 °C and 46.87 °C, depending on small traces of water within the liquid under test. Almost identical heat capacity profiles result if the data are displayed as a function of the temperature distance to the actual T_c value. In the homogeneous phase the critical contribution exhibits power-law behavior with the critical exponent $\alpha = 0.11$ as theoretically predicted for nonionic liquids and in conformity with our understanding of the ionic criticality as being asymptotically Ising like. The noncritical background part of the heat capacity can be related to the heat capacities of the constituents using a simple mixture relation. In the two-phase regime a series of almost perfectly reproducible events is found which may be taken to indicate the existence of nonequilibrium intermediate states in the ethylammonium nitrate−n-octanol system.

PACS number(s): 65.20.+w, 64.70.Md, 83.70.Gp

I. INTRODUCTION

Critical demixing of simple binary liquids has been intensively studied in the past for various reasons [1–4]. Close to the critical point of such systems large local fluctuations in the composition effectively mask the specific molecular interactions. The identity of the liquid systems is largely screened on these conditions by an almost universal behavior. Using molecular liquids, characteristics of universality and scaling have been investigated experimentally and compared to the predictions from theoretical models. Many physical parameters exhibit a simple power-law dependence upon the reduced temperature $t = |T - T_c|/T_c$, where T_c denotes the critical demixing temperature of the particular system under consideration. The critical exponents governing these relationships do not depend upon the molecular properties of the fluid and they are interrelated, so that only two critical exponents are linearly independent [1–4]. Close to T_c the behavior of such systems is determined by their spatial dimensionality and by the universality class of their order parameter only.

In more complex liquids, such as electrolyte solutions, micellar systems, and microemulsions, the interplay between long-range concentration fluctuations and the kinetics of the formation of special molecular structures may cause a considerably more complicated demixing behavior [5–9]. Nonuniversal near-critical demixing properties [10,11] as well as asymptotic universal properties [12,13] have been reported for micellar systems. Conflicting results have been also presented for ionic fluids, suggesting either classical (mean-field) behavior [14,15] or nonclassical (Ising-type) behavior [16–19]. Considerable interest is therefore directed toward

the nature of criticality in ionic systems, particularly since an unusual crossover from Ising-like asymptotic behavior to mean-field behavior has been described [5–8] and has been explained by the simultaneous significance of two crossover parameters, related to two independent characteristic spatial scales of the fluid [20]. Progress in understanding the critical phenomena in ionic fluids requires much more experimental evidence than presently available. We therefore decided to measure the heat capacity C_p of the ionic system ethylammonium nitrate−n-octanol (EAN−n-C$_8$OH) near its upper critical consolute point. It is the aim of this study to determine the critical exponent α of the power law [21]

$$C_p = \frac{A^+}{\alpha} t^{-\alpha} + Et + B, \tag{1}$$

which provides direct access to the universality class defined by the order parameter of the system. To our knowledge no heat capacity measurements near the critical point of an ionic fluid have been published so far. In Eq. (1) A^+, E, and B are coefficients reflecting the specific molecular identity of the mixture. The E term and B represent the background heat capacity at constant pressure, thus describing the system far from T_c in the one-phase region.

The knowledge of C_p as a function of reduced temperature of the ionic critical system is not only of interest for a comparison with theoretical models. It is also of fundamental importance for the discussion of broadband ultrasonic attenuation spectra of the (EAN−n-C$_8$OH) system which are currently under investigation [22]. Ethylammonium nitrate−n-octanol has been used for these first calorimetric and ultrasonic relaxation studies of an ionic critical fluid because the critical demixing temperature of the (EAN−n-C$_8$OH) system (about 41 °C) is easily accessible to measurements.

──────────
*Electronic address: uka@physik3.gwdg.de

II. EXPERIMENT

Ethylammonium nitrate was supplied by H. Weingärtner, Ruhr-Universität Bochum, Germany. The salt had been carefully dried when delivered. Immediately before sample preparation it was desiccated again by keeping it at 65 °C for three days under vacuum in a drying cabinet. The nonionic constituent n-octanol was purchased from Fluka (Neu-Ulm, Germany) and was used as specified by the manufacturer ($\geq$99.5%). Mixtures of critical composition ($x_c = 0.766$, where x is the mole fraction of EAN [23]) where prepared under dry nitrogen by weighing appropriate amounts of the constituents into suitable flasks. All subsequent manipulations of the samples were also performed under dry nitrogen in order to avoid any water uptake. The dry samples were carefully stirred at 70 °C (29 K above T_c) to essentially reach thermal equilibrium and were injected into the preheated calorimeter cell afterwards. All calorimetric experiments were performed on a differential scanning calorimeter (MicroCal Inc., Northhampton, MA, USA; sample volume about 0.5 cm^3) without stirring the sample. Measurements were run in a downscan mode of operation with the minimum achievable downscan rate 1.05 K per hour. The reference cell was filled with pure n-octanol in the EAN$-n$-C$_8$OH and the EAN measurements. To be able to calculate absolute heat capacity values we also recorded C_p traces of n-octanol against n-octanol, of EAN against n-octanol, and also of n-octanol against deionized, additionally bidistilled and degassed water. The absolute heat capacity of water used as a reference was taken from the literature [24]. Within the temperature range under consideration (30 °C to 58 °C) it can be represented by the polynomial

$$\frac{C_p}{\text{J cm}^{-3}\text{K}^{-1}} = 4.2097 - 2.415 \times 10^{-3}\,\text{K}^{-1}\theta$$
$$+ 4.466 \times 10^{-5}\,\text{K}^{-2}\theta^2 - 7.650 \times 10^{-7}\,\text{K}^{-3}\theta^3$$
$$+ 4.143 \times 10^{-9}\,\text{K}^{-4}\theta^4, \qquad (2)$$

where $\theta = T - 273.15$ K.

III. RESULTS AND DISCUSSION

In Fig. 1 one original C_p scan of an EAN$-n$-C$_8$OH mixture of critical composition is displayed along with another one of a sample, the critical temperature of which was 5.83 K higher than that of the first sample, indicating a slightly higher residual water content. The curve for the second sample has been shifted for this difference in T_c in order to show that the structure of the C_p-versus-T profiles remains almost unaltered if mixtures of critical composition with different critical temperature (41 °C$\leq T_c \leq$47 °C) are measured. The rather high variations in T_c indicate the well-known high sensitivity of the critical temperature of ionic binary mixtures against small traces of impurity [19].

Both curves shown in Fig. 1 exhibit the characteristic increase in the heat capacity when approaching the actual critical temperature T_c from the one-phase region ($T > T_c$). In addition, a series of subsequent events is visible below T_c. This series at $T < T_c$ was reproducible in new experiments with identical sample preparation but different critical tem-
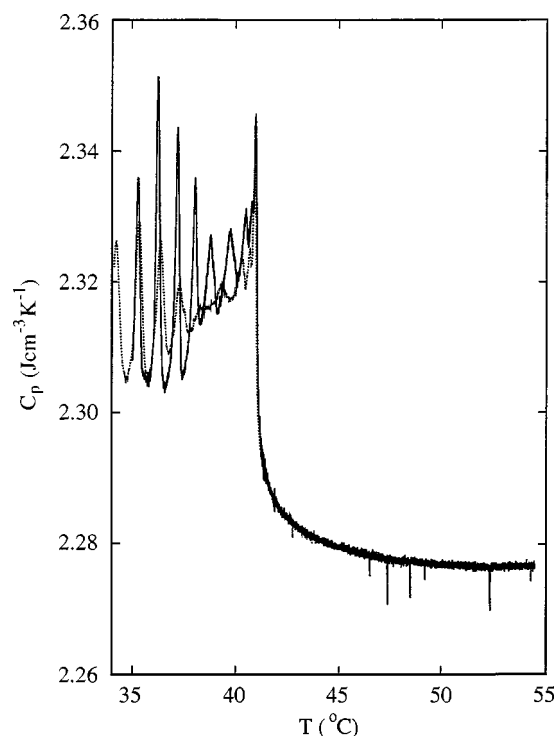

FIG. 1. Heat capacity profiles for two EAN$-n$-C$_8$OH mixtures of critical composition. Full curve, $T_c = 314.188$ K; dashed curve, $T_c = 320.018$ K. In order to comply with the different critical temperatures the latter curve has been shifted by 5.83 K.

perature. A similar reproducible behavior had been already reported by Voronel (quoted in Ref. [2]). We assume that these events correspond to the formation of intermediate states, possibly related to a formation of nonequilibrium metastable substates of the ethylammonium nitrate$-n$-octanol phase boundary. This striking phenomenon, however, is only mentioned here. It needs to be carefully investigated, preferably by the use of further experimental approaches, including an adiabatic scanning calorimeter with extremely slow scanning rates. Well below the critical point both subliquids of the mixture are phase separated. In a consecutive upscan no heat capacity anomalies have been observed. The phase separation was not reversible on the time scale of the calorimeter.

In Fig. 2 the heat capacity data in the one-phase region are displayed versus temperature for the sample with the smallest upper critical demixing temperature. A weak heat capacity anomaly clearly emerges so that Eq. (1) has been fitted to the measured spectra. A nonlinear least-squares regression algorithm [25] has been used for this purpose. In first runs of the fitting procedure a value close to the theoretical prediction $\alpha = 0.11$ [26] for nonionic liquids has been found for the critical exponent. In order to enhance the significance in the values of the other parameters of Eq. (1) we therefore repeated the regression analysis keeping α fixed at the theoretical value. The results from this final run are presented in Table I.

The suitability of Eq. (1) to represent the measured heat capacity data of the EAN$-n$-C$_8$OH system is illustrated by Fig. 3 where the relative deviations $[C_p(T) - C_p^{\text{calc}}(T)]/C_p(T)$ are shown as a function of reduced temperature t. Just at a very few temperatures these deviations slightly exceed 0.1%.
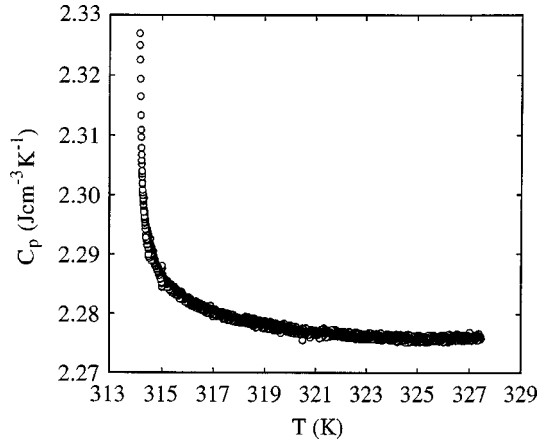
FIG. 2. Heat capacity of the EAN–n-C_8OH mixture of critical composition with $T_c = 314.188$ K (Fig. 1) displayed versus temperature in the homogeneous phase.

Here $C_p(T)$ again denotes the measured data whereas $C_p^{calc}(T)$ represents those calculated according to Eq. (1), with the parameter values from Table I. Another indication for the appropriate description of the ionic system by Eq. (1) is given by Fig. 4. The plot of $\log(C_p^{crit})$ versus $\log(t)$ with $C_p^{crit} = C_p - Et - B$ displays a straight line with slope $-\alpha$ as predicted by Eq. (1). The scatter in the C_p^{crit} data reflects the fact that, within our range of measurements, C_p^{crit} is smaller than 49 mJ cm^{-3} K^{-3} and thus smaller than $0.021 C_p(T)$. Introducing a first correction-to-scaling term in Eq. (1) thus using [21]

$$C_p = \frac{A^+}{\alpha} t^{-\alpha} (1 + D^+ t^\Delta) + Et + B \qquad (3)$$

does not noticeably improve the description of the measured heat capacities. The parameters A^+, E, and B are only insufficiently defined if the correction term ($D^+ \neq 0$) is used (Table I). In addition, as shown by Fig. 5, the theoretical description of the measured heat capacity values changes within the limits of experimental error only.

For an evaluation of the background contribution to the heat capacity of the mixture of critical composition let us first inspect the heat capacities of the constituents. At

TABLE I. Parameters of Eqs. (1) and (3) for the ethylammonium nitrate–n-octanol mixture of critical composition. Data refer to the sample with the lowest upper critical demixing temperature T_c (=41.038 °C). The critical exponents and T_c have been fixed at the theoretical values. Errors are one standard deviation estimates as provided by the regression analysis.

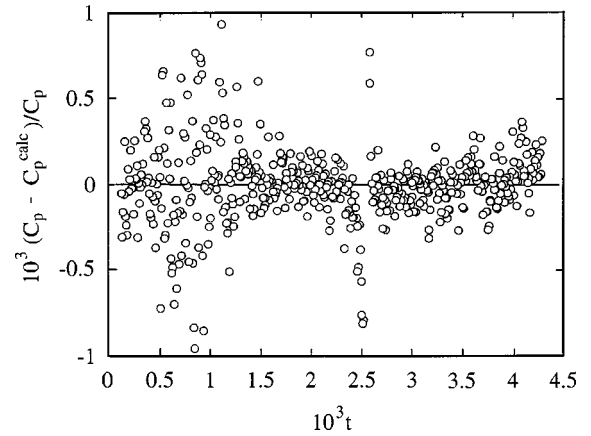|	Eq. (1)	Eq. (3)
α		0.11
A^+/α (10^{-2} J/cm^3 K^{-1})	2.02 ± 0.08	1.76 ± 0.77
A^+ (10^{-3} J cm^{-3} K^{-1})	2.22 ± 0.09	1.94 ± 1.09
E (J cm^{-3} K^{-1})	$-(0.9 \pm 0.14)$	$-(0.9 \pm 0.9)$
B (J cm^{-3} K^{-1})	2.248 ± 0.002	2.254 ± 0.024
T_c (K)		314.188
D^+		0.5 ± 0.5

FIG. 3. Residuals $(C_p - C_p^{calc})/C_p$ displayed versus reduced temperature for the C_p data shown in Fig. 2.

30 °C $\leq T \leq$ 60 °C the heat capacities $C_p(0) = C_p(x=0)$ and $C_p(1) = C_p(x=1)$ for n-octanol and EAN, respectively, can be represented by the following polynomials:

$$\frac{C_p(0)}{\text{J cm}^{-3} \text{K}^{-1}} = 1.9339 - 3.409 \times 10^{-3} \text{ K}^{-1} \theta$$

$$+ 2.950 \times 10^{-4} \text{ K}^{-2} \theta^2$$

$$- 4.502 \times 10^{-6} \text{ K}^{-3} \theta^3 + 2.476 \times 10^{-8} \text{ K}^{-4} \theta^4, \qquad (4)$$

$$\frac{C_p(1)}{\text{J cm}^{-3} \text{K}^{-1}} = 2.4415 - 8.603 \times 10^{-3} \text{ K}^{-1} \theta$$

$$+ 3.224 \times 10^{-4} \text{ K}^{-2} \theta^2$$

$$- 5.200 \times 10^{-6} \text{ K}^{-3} \theta^3 + 3.058 \times 10^{-8} \text{ K}^{-4} \theta^4. \qquad (5)$$

From Eq. (3) follows $C_p(0) = 1.956$ J/(cm^3 K) at $T = 298.15$ K whereas Vesely et $al.$ found $C_p = 304.0$ J/(mol K) independent of temperature at 298 K $\leq T$
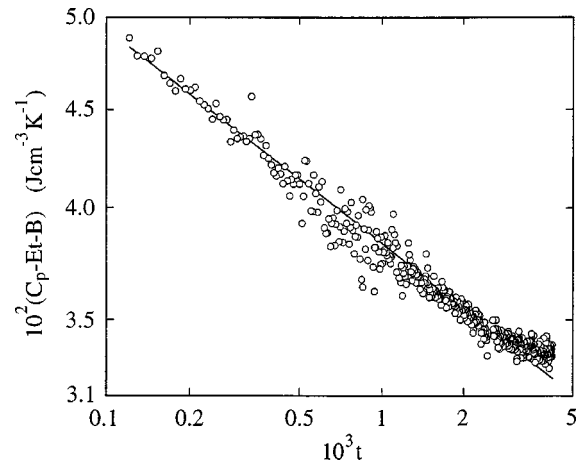

FIG. 4. The critical contribution $C_p^{crit} = C_p - Et - B$ to the heat capacity data shown in Fig. 2 bilogarithmically plotted versus the reduced temperature. The full curve with slope -0.11 represents the power-law behavior predicted by Eq. (1).
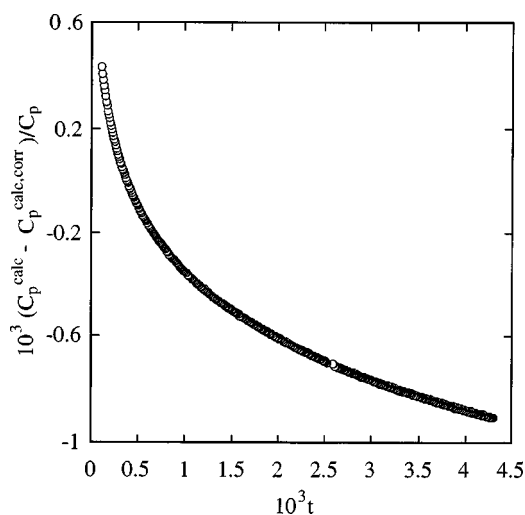
FIG. 5. Relative difference $(C_p^{calc} - C_p^{calc,corr})/C_p$ between the calculated heat capacities when simply using Eq. (1) (C_p^{calc}) on the one hand or when introducing an additional correction-to-scaling term [Eq. (3), $C_p^{calc,corr}$]. The parameter values as resulted from the fit of the theoretical models to the measured C_p data (Table I) have been used here.

$\leqslant 318$ K [27] for n-octanol. From this latter value follows $C_p(0) = 1.913$ J/(cm^3 K) which is only slightly smaller than our value. Equation (4) yields $C_p(1) = 2.358$ J/(cm^3 K) at 298.15 K which compares with $C_p(1) = 2.299$ J/(cm^3 K) as derived from flow calorimeter measurements of ethylammonium nitrate by Allen et $al.$ [28]. The heat capacity $C_p = 2.255$ J/(cm^3 K) of the mixture at $T = T_c + 9$ K almost agrees with the value $C_p^{mix} = 2.29$ J/(cm^3 K) which results from the simple mixture relation.

$$C_p^{mix} = x_c C_p(x=1) + (1-x_c)C_p(x=0) \qquad (6)$$

if $C_p(0) = 2.091$ J/(cm^3 K) and $C_p(1) = 2.353$ J/(cm^3 K) from Eqs. (4) and (5), respectively, is used for the constituents at 323 K. The small negative value $E = -(0.9 \pm 0.14)$ J/(cm^3 K) corresponds with $E = -0.86$ J/(cm^3 K) as recently found for the critical system aniline-cyclohexane utilizing an adiabatic calorimeter [21]. Hence there is nothing unexpected in the noncritical background contribution to the heat capacity of the mixture of critical composition.

Let us finally estimate the amplitude ξ_0 of the correlation length $\xi = \xi_0 t^{-\nu}$ of the local fluctuations in the EAN–n-C$_8$OH composition. According to the two-scale-factor universality conception [29]

$$\xi_0 = 0.27(k_B/A^+)^{1/3}, \qquad (7)$$

where k_B denotes Boltzmann's constant. Using the amplitude factor A^+ of the critical contribution to the heat capacity (Table I) $\xi_0 = (0.50 \pm 0.04)$ nm follows, in nice agreement with $\xi_0 = 0.47$ nm [18] and $\xi_0 = 0.49$ nm [30] as determined by light scattering experiments. The nice agreement with data from other experiments of the values obtained for the noncritical background contribution to the heat capacity and for the amplitude of the fluctuation correlation length, when using the amplitude of the critical contribution to the heat capacity, may be taken to indicate a sufficiently small scanrate in the differential scanning calorimeter measurements.

IV. CONCLUSIONS

In the one-phase region of the ionic binary ethylammonium nitrate–n-octanol mixture of critical composition the heat capacity can be well represented by a critical contribution and two background terms, in correspondence with nonionic systems. The noncritical background part can be calculated from the heat capacities of the constituents using a simple mixture relation. The critical exponent is consistent with the theoretical value $\alpha = 0.11$. It is also in conformity with our current understanding of the ionic criticality as being asymptotic Ising like for short chain solvents. The study of the coexistence curves of tetra-n-butylammonium picrate in alkyl alcohols showed small but systematic deviations from asymptotic Ising behavior with decreasing dielectric permittivity of the solvent [31]. In order to study the crossover from Ising-like toward mean-field behavior in the critical contribution of the heat capacity, a systematic investigation of ionic alcohol solutions as a function of solute chain length is in progress. The amplitude factor A^+ of the critical contribution, along with the two-scale-factor university ratio $X = 0.27$, yields the amplitude of the fluctuation correlation length $\xi_0 = 0.5$ nm, consistent with $\xi_0 = 0.47$ nm and $\xi_0 = 0.49$ nm as resulted from light scattering experiments. Hence with respect to the heat capacity in the homogeneous phase the ionic EAN–n-C$_8$OH systems behaves like a nonionic binary mixture. A series of heat capacity events in the two-phase region of the unstirred sample indicates the formation of intermediate states.

[1] J. V. Sengers and J. M. H. Levelt Sengers, Annu. Rev. Phys. Chem. **37**, 189 (1986).

[2] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gorden and Breach, Philadephia, 1991).

[3] L. M. Brown, *Renormaliziation* (Springer, Berlin, 1993).

[4] M. E. Fisher, Rev. Mod. Phys. **70**, 653 (1998).

[5] K. S. Pitzer, Acc. Chem. Res. **22**, 333 (1990).

[6] J. M. H. Levelt Sengers and J. A. Given, Mol. Phys. **80**, 899 (1993).

[7] M. E. Fisher, J. Stat. Phys. **75**, 1 (1994).

[8] H. Weingärtner, M. Kleemeier, S. Wiegand, and W. Schröer, J. Stat. Phys. **78**, 169 (1995).

[9] T. Telgmann and U. Kaatze, J. Phys. Chem. **104**, 1085 (2000).

[10] V. Degiorgio, R. Piazza, M. Corti, and C. Minero, J. Chem.

Phys. **82**, 1025 (1985).

[11] M. Corti and V. Degiorgio, Phys. Rev. Lett. **55**, 2005 (1985).

[12] G. Dietler and D. S. Cannell, Phys. Rev. Lett. **60**, 1852 (1988).

[13] K. Hamano, N. Kuwahara, I. Mitsushima, K. Kubota, and T. Kamura, J. Chem. Phys. **94**, 2172 (1991).

[14] H. G. Glasbrenner and H. Weingärtner, J. Phys. Chem. **93**, 3378 (1989).

[15] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. M. H. Levelt Sengers, J. Chem. Phys. **97**, 8692 (1992).

[16] H. Weingärtner, S. Wiegand, and W. Schröer, J. Chem. Phys. **96**, 848 (1992).

[17] H. Weingärtner, T. Merkel, S. Käshammer, W. Schröer, and S. Wiegand, Ber. Bunsenges. Phys. Chem. **97**, 970 (1993).

[18] W. Schröer, S. Wiegand, and H. Weingärtner, Ber. Bunsenges. Phys. Chem. **97**, 975 (1993).

[19] S. Wiegand, J. M. H. Levelt Sengers, K. J. Zang, M. E. Briggs, and R. W. Gammon, J. Chem. Phys. **106**, 2777 (1997).

[20] M. A. Anisimov, A. A. Povodyrev, V. D. Kulikov, and J. V. Sengers, Phys. Rev. Lett. **75**, 3146 (1995); **76**, 4095 (1996).

[21] P. F. Rebillot and D. T. Jacobs, J. Chem. Phys. **109**, 4009 (1998).

[22] U. Kaatze and S. Z. Mirzaev, J. Phys. Chem. (to be published).

[23] A. Oleinikova and M. Bonetti, J. Chem. Phys. **104**, 3111 (1996).

[24] D. R. Linde and H. P. R. Frederikse, *Handbook of Chemistry and Physics*, 77th ed. (CRC Press, Boca Raton, FL, 1996).

[25] D. W. Marquardt, J. Soc. Ind. Appl. Math. **2**, 2 (1963).

[26] A. J. Liu and M. E. Fisher, Physica A **156**, 35 (1989).

[27] F. Vesely, P. Barcal, M. Zabransky, and V. Svoboda, Collect. Czech. Chem. Commun. **54**, 602 (1989).

[28] M. Allen, D. F. Evans, R. Lumry, J. Solution Chem. **14**, 549 (1985).

[29] E. A. Clerke, J. V. Sengers, R. A. Ferrell, and J. K. Bhattacharjee, Phys. Rev. A **27**, 2140 (1983).

[30] M. Bonetti, C. Bagnuls, and C. Bervillier, J. Chem. Phys. **107**, 550 (1997).

[31] M. Kleemeier, S. Wiegand, W. Schröer, and H. Weingärtner, J. Chem. Phys. **110**, 3085 (1999).