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Specific Heat of a Liquid Mixture Near the Consolute Point in the Bulk Phase and in a Porous Medium

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The critical behavior of the specific heat of the mixture 2.6-lutidine + water near the consolute point was investigated in the bulk phase and in a porous medium. The measurements of the bulk specific heat yield a critical exponent $\alpha = 0.111 \pm 0.018$ and a universal amplitude ratio $A^-/A^+ = 1.77$, in good agreement with theoretical predictions. Using previous experimental data for nitroethane + isooctane, we also determined the two-scale-factor ratio $X^+ = 0.271$ between the critical amplitude of the specific heat and of the correlation length in agreement with the results reported for other fluid systems. The specific heat in the porous medium with a pore size of about 100 nm was measured. The behavior of the specific heat differs from that of the bulk specific heat. This may be the result of finite size effects, of a wetting layer in the pores, and of a distortion of the coexistence curve.

KEY WORDS: consolute point; critical phenomena; liquid mixtures; lutidine–water; nitroethane–isooctane; specific heat.

1. INTRODUCTION

The modern theory of critical phenomena manifests universality. First, it predicts universality for the critical exponents of different systems within the same universality class. Second, it predicts universality for ratios of the critical amplitudes below and above the critical temperature. Furthermore, the theory predicts universal relations for the critical amplitudes of different thermodynamic properties. Only two critical amplitudes of the asymptotic power laws are independent, while other amplitudes may be calculated from the universal relations. These predictions are correct for critical phenomena in "infinite" media, where the characteristic size of a system L

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is much larger than the correlation length ξ, and the surface energy F_σ is much less than the bulk energy F_b. Numerous experiments on simple fluids and binary mixtures have confirmed the predictions of the theory. The question arises, How will the singular behavior of thermodynamic properties change in porous media, where the correlation length can become of the same order of magnitude as the characteristic size of a pore and the surface energy can become comparable with the bulk energy?

One can suggest an approximate estimate of the influence of a finite size of a system. The singularities of the thermodynamic properties will be cut off at $\xi \sim L$. The temperature interval of the distortion of the thermodynamic properties is $t \sim (\xi_0/L)^{1/\nu}$, where $t \equiv |T - T_c|/T_c$, the relative difference between the temperature T and the critical temperature T_c, and where ν is the critical exponent in the power law, $\xi = \xi_0 t^{-\nu}$. However, it is difficult to evaluate the influence of the porous surface.

In this paper, we present accurate measurements of the isobaric specific heat c_p of the binary mixture 2,6-lutidine + water near the critical consolute point in the bulk phase and in a porous medium. The data for the bulk specific heat were needed for comparison with the specific-heat data in the porous medium. Moreover, the bulk data for this system have been obtained first, and they have been also used to check various universal relationships.

2. EXPERIMENT

The binary mixture 2,6-lutidine + water (L + W) was chosen for this study. First, a wetting transition in this mixture was observed [1]. Furthermore, the mixture has a lower critical consolute point. Therefore, it was convenient to fill the porous medium with the liquid mixture when it was in the one-phase region.

For the determination of the critical composition of the mixture a visual method was used (Fig. 1). In this method the accuracy of the measurements of the transition temperature is not better than ±0.1 K. However, a detailed study of the coexistence curve was not our intention. A critical composition $x_c = 0.290 \pm 0.005$ wt fraction lutidine and a critical temperature $T_c = (306.8 \pm 0.1)$ K were obtained in agreement with previous data from literature [2]. The specific heat was measured with a high-resolution adiabatic calorimeter. The calorimeter is shown schematically in Fig. 2. The calorimeter cell (1) was surrounded by two copper heat screens (2, 3). The wires leading to the calorimeter cell were placed and glued on the top screens and on two copper blocks (4, 5) to exclude heat supply. The temperatures of the screens and blocks were regulated automatically. The temperatures of the internal screen (2) and block (4) were equal to the

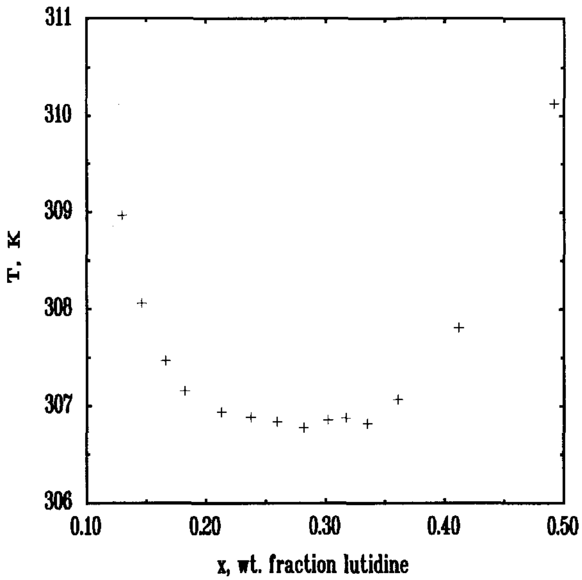

Fig. 1. The coexistence curve of 2,6-lutidine + water.

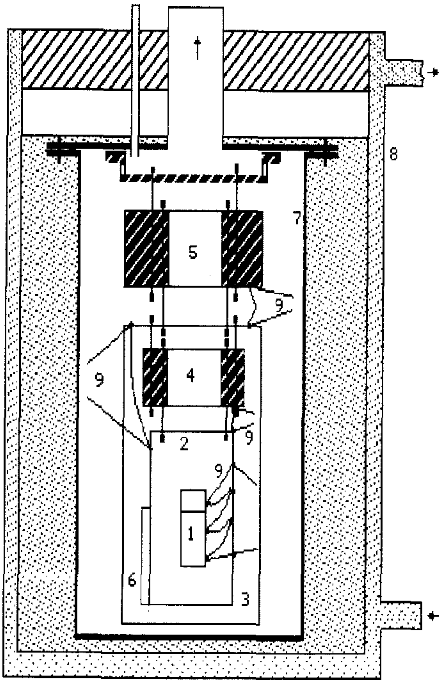

Fig. 2. Schematic diagram of the adiabatic calorimeter.

temperature of the calorimeter cell. The temperatures of the screen (3) and block (5) were 1 to 2° less than that of the cell. The temperature-difference sensors were thermocouples (9) with a sensitivity of about $200\,\mu V \cdot K^{-1}$. This assembly was helf by thin stainless capillaries and located in vacuum (7). The calorimeter cell was suspended from the top of the internal screen by means of thin chromel wires. A water thermostat (8) was used for temperature stabilization. The temperature was measured with a 100-Ω platinum resistance thermometer.

Two calorimeter cells were used. The measurements of the bulk specific heat were made with a cell of about $5\ cm^3$ with a stirring system. The platinum resistance thermometer was located along the axis of the cell. The measurements of the heat capacity in the porous medium were made with a cell with a total volume of about $0.3\ cm^3$. In this case the thermometer (6) was located on the internal screen (see Fig. 2). The heat capacity of the empty cells was about 10 and $0.6\ J \cdot K^{-1}$, respectively.

The porous medium was porous glass with an average characteristic pore size of about 100 nm [3]. The liquid mixture of a certain average composition was impregnated into the porous matrix by capillary forces. The porous matrix was heated at 470 K during 2 hr before being filled with the mixture.

The specific heat was measured with the pulse-heating method. A drift of the calorimeter cell temperature was recorded after each heating and chosen so that thermodynamic equilibrium in the sample could be established. The rate of the drift usually did not exceed $10^{-6}\ K \cdot s^{-1}$. The accuracy of the specific-heat measurements depended on the value of the heating step ΔT and was about 0.03% far away from the critical point ($\Delta T > 0.5$ K) and 0.5–1% in the immediate vicinity ($\Delta T \approx 0.02$ K). The error of measurements was approximately the same for both calorimeter cells.

3. MEASUREMENTS OF THE BULK SPECIFIC HEAT

A few specific-heat measurements were made in the binary mixture 2,6-lutidine + water for the concentration $x = 0.29$ wt fraction lutidine. The results are shown in Fig. 3. The critical temperature $T_c = (306.7939 \pm 0.0002)$ K was measured by the scanning method with constant heating power. The heating rate of the calorimeter cell was $\leqslant 10^{-6}\ K \cdot s^{-1}$.

The singular part of the specific heat was not large. For example, in the triethylamine + water mixture [4], which is similar to the one studied here, the singular part of the specific heat is approximately 10 times larger. According to modern theoretical understanding, the behavior of the specific

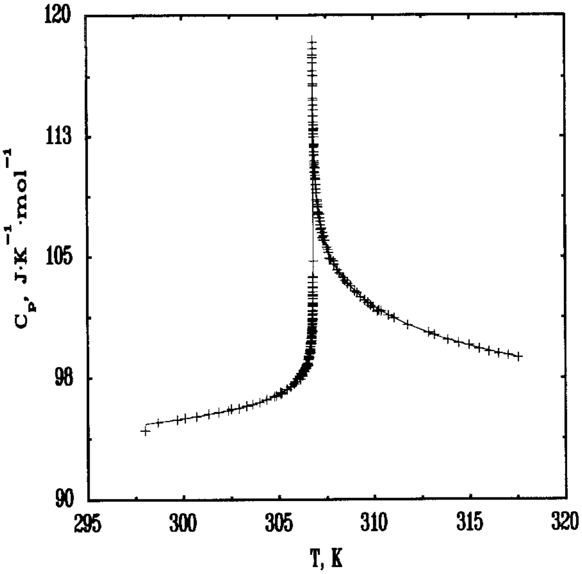

Fig. 3. The bulk specific heat of 2,6-lutidine + water at the critical composition, $x = 0.29$ wt fraction lutidine as a function of temperature. Solid curve represents Eq. (1).

heat near the critical point with the first correction to scaling [5] can be represented as

$$C_p^{\pm} = A_0^{\pm} |t|^{-\alpha} + A_1^{\pm} |t|^{\Delta-\alpha} + A_2^{\pm} + A_3 t + A_4 t^2 \qquad (1)$$

where the superscripts "+" and "−" correspond to the one-phase and two-phase region, respectively. The first term in Eq. (1) represents the dominant contribution to the singularity of the specific heat. The second term represents a correction to the leading power-law singularity. The last three terms in Eq. (1) account for the regular part of the specific heat. A joint fit of Eq. (1) to the specific-heat data above and below T_c has been made. All parameters in Eq. (1) were adjustable except $T_c = 306.7939$ K and the critical exponent Δ, which was fixed at the theoretical value 0.5. The parameter values of the fit with $\chi_v^2 = 1.1$ are given in Table I. It turned out that the values of A_1^+ and A_4 are insignificant. The critical exponent $\alpha = 0.111 \pm 0.018$ is in very good agreement with $\alpha = 0.11$, obtained from the renormalization group calculation [6].

The universal ratio A^-/A^+ between the critical amplitudes of the specific heat can be calculated. The results are presented in Table II. Theoretical estimates for A^-/A^+ have been obtained by several methods [7–9]. They give ratio values from 1.82 to 2.08. All experimental values of

Table I. Values for the Parameters in Eq. (1) Obtained From a Fit to the Data Above and Below T_c at the Critical Composition $x = 0.290$ wt Fraction Lutidine

A_0^+	A_0^-	α	A_1^+	A_1^-	A_2^+	A_2^-	A_3
4.67 ±1.47	8.20 ±2.59	0.111 ±0.018	—	−17.17 ±2.0	88.59 ±0.64	91.10 ±1.0	−8.83 ±1.65

A^-/A^+ coincide with the theoretical ones within 10%. Note that our results are in good agreement with the results for triethylamine + heavy water (TEA + HW) (see Table II), where the critical amplitudes of the specific heat approximately are 10 times larger.

A universal relation between the critical amplitude, A_0^+, of the specific heat and of the bare correlation length, ξ_0^+, follows from the hypothesis of a two-scale-factor universality [10]. It states that the singular part of the free energy per unit volume in a region of volume ξ^d is a universal number, where $d = 3$ is the dimensionality of space. If the specific heat per mole is represented by the first term in Eq. (1), then for the one-phase region the hypothesis yields a universal relation in the form

$$X^+ = \left(\frac{A_0^+ \alpha\rho}{M k_B}\right)^{1/3} \xi_0^+ \tag{2}$$

where ρ is density, M is molar mass, and k_B is Boltzmann's constant.

Table II. Universal Amplitude Relations

Fluids	α	A^-/A^+	ξ_0 (nm)	X^+
L + W[a]	0.111	1.77	(0.23)	
TEA + W[b]	0.107	1.75	0.108	0.267
N–I[c]	0.105	2.04	0.24	0.271
Average Value				0.271[d]
Theory				
RG		1.82–2.08[e]		0.270[g]
Series		1.96[f]		0.253[h]

Note. Values in parentheses indicate that the parameters were calculated.
[a] This work.
[b] Ref. 4.
[c] Ref. 11.
[d] Ref. 13.
[e] Refs. 7 and 8.
[f] Ref. 9.
[g] Ref. 8.
[h] Refs. 8, 14, and 15.

Using our previous experimental data in nitroethane + isooctane [11] (N–I) we have checked the ratio X^+. The values A_0^+ and ξ_0^+ were determined with the critical exponent value fixed at $\alpha = 0.11$ and $\nu = 0.63$. The result is presented in Table II. The value $X^+ = 0.271$ agrees with the average experimental value [12, 13] and is close to the theoretical one. We could not check Eq. (2) for 2,6-lutidine + water, because the experimental value ξ_0^+ was not available. However, using the average experimental values X^+ we have calculated ξ_0^+ for 2,6-lutidine + water (see Table II). The practical benefit of the universal relation is evident. On the base of specific heat data only, the correlation length can be predicted with an accuracy of 10% (as accurate as the universal relation has been verified).

4. MEASUREMENTS OF THE SPECIFIC HEAT IN A POROUS MEDIUM

The result of the measurements of the specific heat in a porous medium at the composition $x = 0.290$ wt fraction lutidine are presented in Fig. 4. The data for the bulk specific heat are also presented for comparison. The character of the behavior of the specific heat in a porous medium has a few peculiarities: (1) the anomaly of the specific heat near

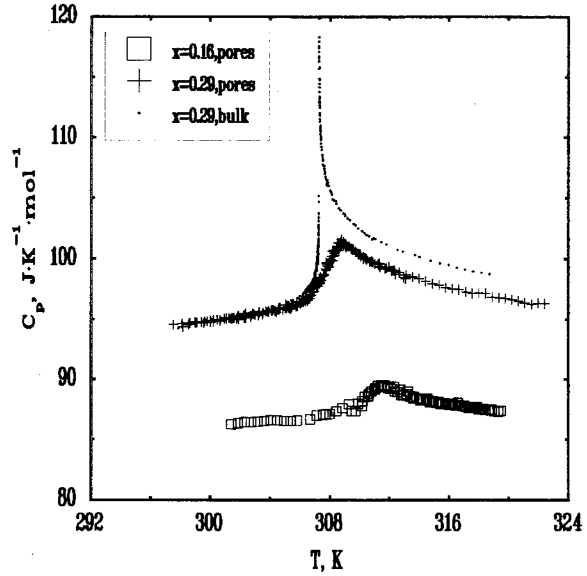

Fig. 4. The specific heat of 2,6-lutidine + water in a porous medium at $x = 0.29$ and at $x = 0.16$ and also the bulk specific heat at $x = 0.29$ as functions of temperature.

the transition temperature is suppressed; (2) the transition temperature in a porous medium is shifted toward higher temperatures; and (3) the specific heat in a porous medium is less than the bulk specific heat.

These differences could not be explained only by a finite size of the system. The temperature region of the anomalous distortion of the specific heat in the porous medium with the average characteristic size of a pore $L \approx 100$ nm, $\xi_0 = 0.23$ nm, and $\nu = 0.63$ is $t \sim (\xi_0/L)^{1/\nu} = 5.7 \times 10^{-5}$. That is very close to the critical temperature, $T - T_c < 0.02$ K; as seen from Fig. 4 the actual region is much wider.

There are a few other reasons which could qualitatively explain the behavior of the specific heat in a porous medium. They are the existence of a wetting layer in the pores and distortion of the coexistence curve.

A wall layer with thickness $l \sim \xi$ distorts the composition in pores. As a result, a concentration gradient appears and the effective transition temperature increases. Therefore, the specific heat in a porous medium at $T < T_c$ will be less than the bulk specific heat at the same temperature. The correlation length increases when the critical temperature is approached and the influence of the wall layer also increases. For the temperatures above the transition, we have observed large relaxation times for the establishment of thermal equilibrium (about 10 hr). Hence, the measurements of the specific heat in that region do not correspond to equilibrium, and therefore their values are lower than those of the bulk specific heat. Moreover, the porous medium distorts the coexistence curve and the composition $x = 0.290$ wt fraction lutidine is no longer the critical composition.

The data for the specific heat in the porous medium at the composition $x = 0.16$ wt fraction lutidine are also shown in Fig. 4. The difference between the transition temperatures for $x = 0.290$ and $x = 0.16$ wt fraction lutidine is about 2.3 K. It is seen from the coexistence curve (Fig. 1) that the difference between the transition temperatures for these concentrations is about 0.9 K. It indicates that the critical composition in the porous medium has been shifted to a higher value.

It is clear that more measurements of the coexistence curve in porous media are necessary. We also intend to study the behavior of the specific heat in porous media with various pores sizes.

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