EXPERIMENTAL INVESTIGATION OF THE SINGULARITY OF SPECIFIC HEAT AT THE CRITICAL STRATIFICATION POINT OF A BINARY MIXTURE

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The specific heat $C_{P,X}$ (P is the pressure, X the concentration) near the critical stratification point is measured in a methanol-cyclohexane mixture. It is found that for $5 \times 10^{-3} < \tau < 3 \times 10^{-5}$, where $\tau = (T - T_c)/T_c$ (T_c is the critical temperature), the temperature dependence of the specific heat can be expressed by the formula $C_{P,X} = A\tau^{-\alpha} + B$ where $0 < a^+ \leq 0.2$ ($T > T_c$) and $0 \leq \alpha^- < 0.2$ ($T < T_c$). For $a = 1/8$ one get $A^+ = 4.3$ J/mole-deg, $B^+ = 132$ J/mole-deg ($T > T_c$) and $A^- = 9$ J/mole-deg, $B^- = 133$ J/mole-deg ($T < T_c$). The mean range of the intermolecular forces is evaluated on the basis of the specific heat measurements. Its value (~5 Å) is close to that obtained from light scattering experiments. The effect of water admixture on the nature of the specific heat singularity in this system is investigated.

INTRODUCTION

In an earlier paper[1] we formulated a hypothesis concerning the isomorphism of critical phenomena, meaning that the singularities of physical quantities near transition points of various kinds have the same form if the thermodynamic variables are correctly chosen. This approach makes it possible, in particular, to use such an experimentally convenient object as a binary mixture with a critical liquid-liquid equilibrium point for the study of the general laws of phase transitions[2]. This system has a number of advantages both over matter at the liquid-vapor critical point and, in particular, over solids. The possibility of working with a liquid sample at atmospheric pressure and at room temperatures, with stirring, makes the experimental technique relatively simple.

The isomorphism hypothesis (using the results of similarity theory for an isolated transition point[3]) leads to the following form of the thermodynamic potential near the critical line of a binary mixture:

$$F^*(T, V, \mu) = \tau(\mu)^{2-\alpha} f^* \{v(\mu) / \tau(\mu)^\beta\} + F_0^*(T, V, \mu) \qquad (1)$$

or

$$\Phi(T, X, P) = \tau(P)^{2-\alpha} \varphi \{x(P) / \tau(P)^\beta\} + \Phi_0(T, X, P). \qquad (2)$$

Here X is the molecular concentration of one of the components, V the molar volume, P the pressure, μ the chemical potential of the mixture

$$\mu = \left(\frac{\partial \Phi}{\partial X}\right)_{T,P}, \quad \tau(\mu) = \left|\frac{T - T_c(\mu)}{T_c(\mu)}\right|, \quad v(\mu) = \left|\frac{V - V_c(\mu)}{V_c(\mu)}\right|,$$

$$\tau(P) = \left|\frac{T - T_c(P)}{T_c(P)}\right|, \quad x(P) = |X - X_c(P)|;$$

$f^*\{z(\mu)\}$, $\varphi\{z(P)\}$ functions with known asymptotic forms, $F_0^*(T, V, \mu)$ and $\Phi_0(T, X, P)$ regular functions, and α and β the critical indices of the singular part of the specific heat,

$$\frac{\Delta C_{V,\mu}}{T} = -\frac{\partial^2 F^*}{\partial T^2} \sim \tau(\mu)^{-\alpha}, \quad \frac{\Delta C_{P,X}}{T} = -\frac{\partial^2 \Phi}{\partial T^2} \sim \tau(P)^{-\alpha}$$

and of the coexistence curve

$$v(\mu) \sim \tau(\mu)^\beta, \quad x(P) \sim \tau(P)^\beta.$$

Although expressions (1) and (2) are equivalent for the description of the thermodynamic properties of mixtures near critical points[1], the real experimental conditions in a liquid-liquid system (if the experiment is carried out in the presence of saturated vapor, then the pressure varies little) make it preferable to investigate the form of the potential $\Phi(T, X, P)$. With this in view, we investigated the specific heat $C_{P,X}$ near the critical stratification point of a binary methanol-cyclohexane mixture.

There is very little material relative to the behavior of the specific heat $C_{P,X}$ near the critical stratification point of a binary mixture. Whereas the specific heat C_V near the critical point of the pure substance has recently been the subject of dozens of studies, the specific heat $C_{P,X}$ has not, insofar as we know, been investigated since 1960, and the reduction[4] of older experimental data[5] does not lead to sufficiently definite conclusions. The results of our investigation confirm the consequence of the isomorphism hypothesis concerning the presence of a singularity of the specific heat near the critical point of a binary mixture, in the form of $\Delta C_{P,X}/T \sim \tau(P)^{-\alpha}$ ($0 < \alpha \leq 0.2$ at $T > T_c$; $0 \leq \alpha < 0.2$ at $T < T_c$), although important questions concerning the equality of the values of α at $T > T_c$ and $T < T_c$, and also the equality of the critical indices in the pure substance and in mixtures still remain open.

EXPERIMENTAL PART

According to data by various authors, the values of

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[1] Like other second-order phase transitions, the critical points of binary mixtures lie on a certain line in T–P(T–μ) space. Among real systems, only the liquid-vapor critical point of a pure substance is isolated.

the critical stratification temperature of the methanol-cyclohexane system (at saturated-vapor pressure) range from 318.30 322.36°K, and the critical compositions range from 28 to 30 wt.% of methanol ~50 mol.%)[6-11]. Such differences in the values of the critical temperature are apparently connected with the strong sensitivity of the properties of this mixture to the presence of traces of water (an admixture of ~0.03% water changes the transition temperature in this system by ~1°).

We have already reported[12] preliminary results of an investigation of the specific heat $C_{P,X}$ in a methanol-cyclohexane mixture with methanol concentration 28.4 wt.%. The temperature of the maximum specific heat T_{max} turned out to be 319.25°K. The degree to which the character of the obtained singularity is distorted by the possible deviation of the mixture composition from critical or by the presence of impurities remained unclear.

In this paper we present the results of an experimental study of the specific heat $C_{P,X}$ in mixtures with methanol concentrations 28.3 and 29 wt.%, and also with water contents 0.2 and 0.35 wt.% (the initial system with 29 wt.% of methanol).

The measurements were performed in a copper calorimeter of 77 cm³ volume (the heat capacity of the calorimeter was ~10% of the heat capacity of the sample) with two adiabatic screens and with automatic maintenance of the regime. Unlike in[12], where one of the screens was isothermal, in the subsequent investigation the heat exchange between the calorimeter and the ambient medium was minimized with the aid of two screens. Such an improvement of the procedure has made it possible to decrease the random error to 0.3–0.5% at a calorimeter step width 0.005–0.01°, and to 0.1% at a larger width (far from the critical point).

The calorimeter was filled in a hermetic box in an atmosphere of dry nitrogen. The liquids were introduced through a fitting with the aid of a syringe. The accuracy with which the necessary mixture concentration was set was several hundredths of 1%. Since the measurements were performed in the presence of saturated vapor (a gas volume equal to 0.1–0.2 of the total volume remained in the calorimeter) the measured quantity (C_{sat}) does not equal, strictly speaking, the specific heat at constant pressure, but is connected with it by the relation

$$C_{\text{sat}} - C_{P,x} \approx -T\left(\frac{\partial V}{\partial T}\right)_{P,x}\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} \tag{3}$$

At T ≈ 320°K the value of $C_{P,X} - C_{sat}$ amounts in our case to ~0.1 J/deg, which lies within the limits of experimental error. The close densities of the mixture components ($\Delta\rho \approx 0.014$ g/cm³ at 20°C) gave grounds for hoping that the influence of the gravitational effect would not be appreciable. To decrease the gradients of the density, concentration, and temperature, the liquid was stirred with an automatic magnetic mixer during the measurement time. It turned out that at a stirring frequency of 1–4 times per minute the temperature variation became linear already after 3–5 minutes, and the results were independent of the frequency. However, as shown by our analysis of the experimental data, it is not excluded that at $\tau < 10^{-4}$ the gradients inside the sample did not succeed in becoming equalized during the time of plotting the temperature variation (50–200 min).

MEASUREMENT RESULTS AND DISCUSSION

The results of our measurements of specific heat are shown in Fig. 1. We call attention immediately to the strong dependence of the transition temperature on the content of the water admixture ($T_c^{-1}dT_c/dX \approx 10$). Apparently the difference between the transition temperatures determined from the maximum of the specific heat, in the case of mixtures of the investigated compositions (28.3% methanol–319.302°K, 28.4%–319.250°K[12], 29%–319.302°K) is due mainly to the intake of small amounts of water (~0.001%) during the course of filling the calorimeter. We have therefore processed the results of the measurements in each sample with respect to its "own" transition temperature.

Figure 2 shows the temperature dependence of $C_{P,X}/T$ for two samples (28.3 and 29% methanol) in a semilogarithmic scale, the coordinates of the center of the calorimeter step being chosen in the same scale. In accordance with (2), a singularity of the type $\tau(P)^{-\alpha}$ should be sought for the quantity $\partial^2\Phi/\partial T^2 = -C_{P,X}/T$. The factor $1/T$ becomes significant (at our accuracy) in the analysis of the dependence of $\partial^2\Phi/\partial T^2$ on τ already at $\tau \gtrsim 10^{-2}$–10^{-3}. As seen from Fig. 2, the character of the singularity of $C_{P,X}/T$ is the same

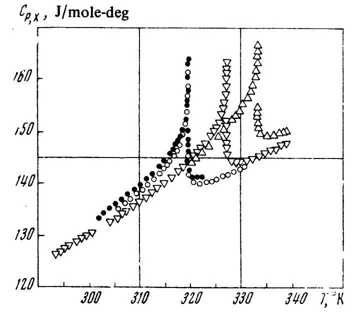

FIG. 1. Dependence of the specific heat $C_{P,X}$ on the temperature in the methanol–cyclohexane system: ●–28.3 wt.% methanol, ○–29 wt. % methanol, ▽–29. wt.% methanol plus 0.2% water, △–29 wt.% methanol plus 0.35% water. (Only some of the experimental points are shown.)

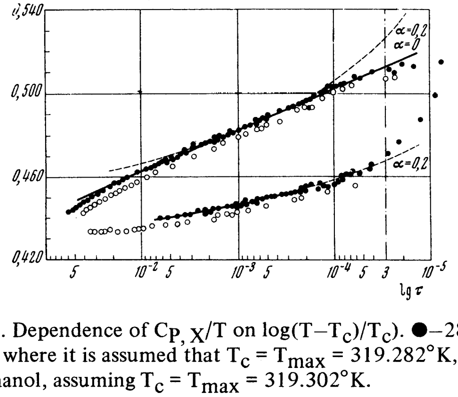

FIG. 2. Dependence of $C_{P,X}/T$ on $\log(T-T_c)/T_c$). ●–28.3 wt.% methanol, where it is assumed that $T_c = T_{max} = 319.282$°K, ○–29 wt.% methanol, assuming $T_c = T_{max} = 319.302$°K.

in both cases, in addition to an insignificant difference in the regular parts[2]. An uncertainty of $\lesssim 1\%$ in the determination of the critical composition apparently does not influence the character of the singularity of the specific heat in this system. This also makes it possible to neglect the change of the critical composition upon addition of an impurity (0.2 and 0.35% water). Unlike the results of[12], we have observed here with the aid of the thermograms only one selected point that coincides with the maximum of the specific heat (accurate to $\sim 10^{-3}$ deg). The character of the $C_{P,X}(T)$ dependence remained the same, i.e., the region of the maximum slope of this dependence ("jump" smeared out over 0.01°) lies above the temperature of the maximum of the specific heat. Let us stop to discuss the results of (more detailed) measurements of $C_{P,X}$ in the sample containing 28.3% methanol.

Whereas for the heterogeneous region (upper curves of Fig. 2) the logarithmic dependence of $T^{-1}C_{P,X}(\tau)$ is a good approximation (although a careful analysis of the region $10^{-4} < \tau < 10^{-3}$ shows that the dependence is possibly stronger than logarithmic here), for the homogeneous region one must certainly look for a power law $T^{-1}C_{P,X} \sim \tau^{-\alpha}$ (where $\alpha > 0$), and if we exclude the smearing region $\tau < 3 \times 10^{-5}$, the upper limit for the critical index α is 0.2. A change of T_c by 0.008° (see Fig. 3), corresponding to a reduction of the results relative to the "jump" of the specific heat[12] leads to the same values of the critical index α above and below T_c, with the $T^{-1}C_{P,X}(\tau)$ dependence definitely stronger than logarithmic. If it is assumed that such systems satisfy the conclusion of similarity theory[3], namely that the critical indices are equal above and below the transition point, then the choice of $T_c = 319.290°K$ should be regarded as more correct. The disparity between this temperature and the temperature of the maximum specific heat (319.382°K) can be attributed to the presence of slowly diffusing inhomogeneities in the system, which lead to a smearing of the "jump" of the specific heat by 0.01°. The choice of T_c is limited to values between the maximum point of $C_{P,X}$ and the point of the maximum slope of the curve $C_{P,X}(T)$. We would be unable to shift T_c in the opposite direction without sacrificing many reliable points on the curve at $T < T_c$.

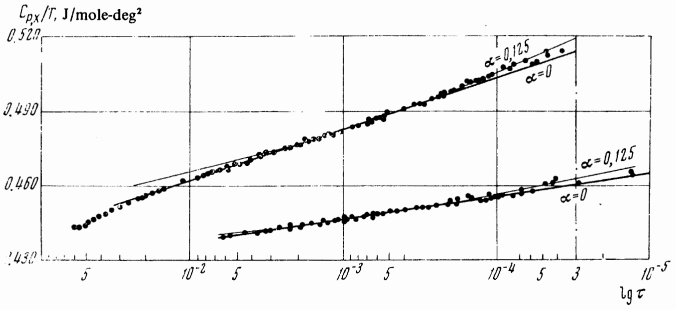

FIG. 3. Dependence of $T^{-1}C_{P,X}$ on log $((T-T_C)/T_C)$, where T_C = 319.290°K (28.3 wt.% methanol).

A similar smearing was observed by Edwards et al.[13] in an investigation of the specific heat near the critical point of xenon. In their succeeding paper[14], the authors used a planar calorimeter 1 mm high, and this led to elimination of the smearing and to identical values of α above and below T_c. Although in our case the usual gravitational effect is small (owing to the proximity of the densities of the components), there apparently exists another reason leading to noticeable inhomogeneities at $\tau < 10^{-4}$. Experimental results[15,16] show that in a system that stratifies into two liquid phases in the presence of a vapor phase, concentration and density inhomogeneities can appear near the liquid-vapor interface, and that this effect is much stronger at $T > T_c$. It is shown in[16] that this phenomenon is connected with the temperature gradients (a gradient of $\sim 10^{-3}$ deg/cm led to noticeable concentration inhomogeneities). It is quite possible for slowly-equalizing temperature gradients to appear also inside our sample. Thus, by varying the values of T_c inside the smearing region $\tau \lesssim (2-3) \times 10^{-5}$, it is possible to obtain equal exponents α $(\alpha^- = \alpha^+)$ (with $0 < \alpha < 0.2$ always) above and below the transition point, but it is not excluded, of course, that the correct values of α^+ and α^- are different from each other. The results do not exclude the possible equality of the values of α in mixtures and in the pure substance, where the latest experiments[14,17] yield $\alpha = 0.12-0.14$, and in the three-dimensional model of a lattice gas, where, according to the results of a computer calculation, $\alpha \approx 0.125$[18]. If, for example, we approximate our results near the critical point by the formula

$$C_{P,X} = A^{\pm}\tau^{-0,125} + B^{\pm}, \tag{4}$$

then $A^+ = 4.3$, $B^+ = 132$ $(T > T_c)$, $A^- = 9$, and $B^- = 133$ $(T < T_c)$ (all in J/mole-deg). We call attention to the fact that B^+ and B^- turned out to be practically identical, while the coefficients $A^{\pm}$ were different and smaller by almost one order of magnitude than the corresponding coefficients in the $C_V(\tau)$ dependence for the pure substance[14,17]. Owing to the smallness of the coefficients $A^{\pm}$, the singular part at $\tau = 10^{-4}$ amounts to 17% of the entire specific heat $C_{P,X}$ for $T < T_c$ and only 9% for $T > T_c$, which led, in the main, to the relatively low accuracy in the determination of α. A quantity more universal than $A^{\pm}$ is apparently the ratio A^-/A^+. In our case its value is approximately 2, which is close to $A^-/A^+ = 1.88$ in carbon dioxide[14] (for $\alpha = 0.125$) and $A^-/A^+ = 1.9-1.96$ in argon[17] (for $\alpha = 0.12-0.14$).

Fixman[19], taking into account in the expansion of the thermodynamic potential the term proportional to the square of the gradient of the concentration fluctuation[2], obtained a singular increment to the specific heat $C_{P,X}$ near the critical mixing point in the form[3]

$$\frac{\Delta C_{P,X}}{k} = V\frac{6^{3/2}}{16\pi}\mathscr{L}\left\{T\frac{\partial}{\partial T}\left(\frac{1}{\mathscr{L}}\right)^2\right\}^2, \tag{5}$$

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[2] The results of the measurements of $C_{P,X}$ in a sample containing 28.4% methanol are analogous to those presented here if the results are referred to the maximum of the specific heat [12]. In the main, the points fall (with a somewhat larger scatter) on the curve of the sample containing 28.3% methanol.

[3] Near the critical point of the pure substance, a singular increment similar to (4) can also be obtained for the specific heat C_V [20].

where $\mathscr{L}$ is the correlation radius and k is Boltzmann's constant. The calculation in[20] was carried out in the self-consistent-field approximation (with allowance for the fluctuations after Ornstein and Zernike)[2], where $\mathscr{L} \sim \tau^{-1/2}$ and $\partial\mathscr{L}^{-2}/\partial T = \text{const}$, and therefore in accordance with[19] we have $\Delta C_{P,X} \sim \tau^{-1/2}$. However, as noted in[21], formula (5) satisfies the similarity-theory relation

$$\alpha = 2 - d\nu, \tag{6}$$

where d = 3 (the dimensionality of the space) and ν is the critical index of the correlation radius ($\mathscr{L} \sim \tau^{-\nu}$). If now we assume in accordance with the results of the experiment on scattering of light in the methanol--cyclohexane system[11] that

$$\mathscr{L} = l\tau^{-5/8}, \qquad \frac{\partial}{\partial T}(\mathscr{L}^{-2}) = \frac{1}{T_c}\frac{5}{4}l^{-2}\tau^{1/4},$$

then

$$\frac{\Delta C_{P,X}}{k} = V\frac{6^{3/2}}{16\pi}\frac{25}{16}l^{-3}\tau^{-1/8}. \tag{7}$$

Here l is the characteristic microscopic dimension in the system, close in order of magnitude to the average effective radius of the intermolecular forces. From our data on the specific heat we obtain for the single-phase region l = 5.1 Å. This result practically coincides with the value l = 5.5 Å obtained in[11], since the accuracy with which l is determined in either case can hardly exceed ±0.5 Å. This agreement seems somewhat surprising, since the result of[19] were obtained for a crude model of the solution, but we call attention to the fact that the final formula of that reference (see (5)) does not contain the characteristics of the concrete model.

In any case, such an approach explains the difference between the coefficients of the singular parts of the specific heat for different systems. It is seen from (7) that the larger the ratio of the average distance between the centers of the particles to the effective radius of the intermolecular forces ($\Delta C \sim (a/l)^3$, where $a \sim V^{1/3}$), the stronger is the singularity. We note that the same parameter determines, in accordance with[22], the fluctuation corrections to the quantities determined by the self-consistent-field method. In this case $a/l < 1$. In our case $a/l \approx 1$ and there is apparently no region where the self-consistent field is applicable. At the same time, the agreement between the coefficients is apparently due to the fact that in the three-dimensional case the correlation function differs little from the Ornstein-Zernike function in spite of the absence of a region where the self-consistent field is applicable[3].

We proceed to discuss the results of an investigation of the influence of the water admixtures on the character of the singularities of the specific heat in the methanol-cyclohexane system. As seen from Fig. 4, the influence of water admixtures becomes clearly pronounced in the heterogeneous region (the specific heat increases more slowly), whereas the homogeneous branch remains unchanged within the limits of the measurement errors. In[1] we obtained formulas that make it possible to estimate the influence of the impurities on the character of the singularities of different physical quantities at the critical point. In accord with[1] in a ternary mixture (for example methane-cyclohexane-water), a singularity similar to the singularity of $C_{P,X}$ in a binary mixture is possessed by the specific heat measured at a constant chemical potential μ^* of the third component (impurity):

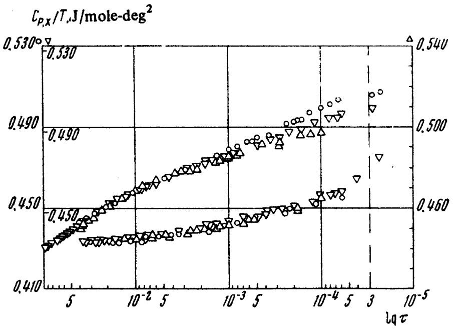

FIG. 4. Dependence of $T^{-1}C_{P,X}$ onllog $((T-T_C)/T_C)$ for samples with different water contents (the regular parts are made to coincide at $\tau = 10^{-2}$). ○–29 wt.% methanol (T_C = 319.302°K), ▽–29 wt.% methanol + 0.2% water (T_C = 326.892°K), △–29 wt.% methanol + 0.35% water (T_C = 332.982°K).

$$\Delta C_{P,X,\mu^*} \sim \tau(P, \mu^*)^{-\alpha}, \tag{8}$$

where $\mu^* = (\partial\Phi/\partial X^*)_{T,P,X}$ and X^* is the impurity concentration. The specific heat measured in the experiment (when the concentrations of all the components of the solution are constant) in a sufficiently close vicinity of the critical point should take instead of (4) the form

$$C_{P,X,X^*} = A^*\{\tau(P, X^*)\}^{\alpha/(1-\alpha)} + B^*. \tag{9}$$

According to[1] (see also[23]), renormalization of the critical exponent ($-\alpha \to \alpha/(1-\alpha)$) is effected in the "cone"[4)]

$$\tau^{\alpha} \lessgtr \left\{\frac{A}{R}\left(\frac{1}{T}\frac{dT_c}{dX^*}\right)^2 X^*\right\} \equiv \zeta. \tag{10}$$

We present the solutions of the equation $\tau = \zeta^{1/\alpha}$ ($\alpha = 1/8$) for different values of water admixtures in the methanol-cyclohexane system:

	X^*	$3\cdot10^{-4}$	$2\cdot10^{-3}$	$3{,}5\cdot10^{-3}$
τ	$T < T_c$:	10^{-11}	10^{-4}	10^{-2}
	$T > T_c$:	10^{-14}	10^{-7}	10^{-5}

Owing to the smallness of α, there exists a broad intermediate region (extending over several order in τ) where the exponent in the temperature dependence of the specific heat is variable[1,23]. Therefore the possible presence of ~0.03% water in the original mixture (if this explains the increase of the value of T_c in our mixture by 1° over the lowest values might affect the points of the $C_{P,X}(\tau)$ dependence closest to T_c in the heterogeneous region ($\tau \approx 10^{-5}$).

At $X^* = 4 \times 10^{-3}$ the critical index is apparently renormalized mainly for $\tau < 10^{-3}$ (at $T < T_c$). In the homogeneous region at our measurement accuracy, it

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[4)] The inequality (10) was obtained for a dilute solution near the critical point of a single-component liquid. This inequality is apparently valid, at least qualitatively, also for an estimate of the influence of a third-component admixture.

is impossible to observe the renormalization, all the more since at $\tau < 10^{-4}$ the main contribution to the distortion of the singularity is apparently made here by the presence of the inhomogeneities referred to above.

In conclusion we take the opportunity to thank Professor M. E. Fisher for a preprint of[23].

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