Critical behavior of 2,6-dimethylpyridine-water: Measurements of specific heat, dynamic light scattering, and shear viscosity

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(Received 19 January 2006; accepted 27 February 2006; published online 14 April 2006)

The specific heat $C_p$ at constant pressure, the shear viscosity $\eta_s$, and the mutual diffusion coefficient $D$ of the 2,6-dimethylpyridine-water mixture of critical composition have been measured in the homogeneous phase at various temperatures near the lower critical demixing temperature $T_c$. The amplitude of the fluctuation correlation length $\xi_0=(0.198\pm0.004)$ nm has been derived from a combined evaluation of the $\eta_s$ and $D$ data. This value is in reasonable agreement with the one obtained from the amplitude $A^+=(0.26\pm0.01) 1/(g K)$ of the critical term in the specific heat, using the two-scale-factor universality relation. Within the limits of error the relaxation rate $\Gamma$ of order parameter fluctuations follows power law with the theoretical universal exponent and with the amplitude $\Gamma=(25\pm1) \times 10^9$ s$^{-1}$. No indications of interferences of the critical fluctuations with other elementary chemical reactions have been found. A noteworthy result is the agreement of the background viscosity $\eta_b$, resulting from the treatment of $\eta_s$ and $D$ data, with the viscosity $\eta_s(\nu=0)$ extrapolated from high-frequency viscosity data. The latter have been measured in the frequency range of 5–130 MHz using a novel shear impedance spectrometer. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188396]

I. INTRODUCTION

In recent years much interest has been directed towards critical point phenomena. In binary liquids with miscibility gap large concentration fluctuations near the system’s consolute point produce universal phenomena which effectively mask the individual properties of the mixture. Asymptotically close to the critical point several quantities $\chi$ exhibit power-law dependence,

$$\lim_{\epsilon \to -\infty} \chi(\epsilon) = \chi_0 \epsilon^{-\gamma}$$

(1)

upon the reduced temperature

$$\epsilon = |T - T_c|/T_c$$

(2)

when approaching the critical temperature $T_c$. In Eq. (1) $\chi_0$ denotes an amplitude. The exponents $\gamma$ describing these relationships are universal and depend only on the universality class of the relevant order parameter and on the spatial dimensionality of the system. At their critical demixing point, liquid-liquid mixtures belong to the three-dimensional Ising model for which values for the critical exponents have been predicted theoretically.

In addition to the observation that only two critical exponents are linearly independent, a powerful conception is that amplitudes of significant parameters are interrelated. Particularly useful is the relation

$$X = \xi_0^3 A^+/k_B$$

(3)

that combines the amplitude $\xi_0$ of the fluctuation correlation length $\xi$, defined by

$$\lim_{\epsilon \to -0} \xi(\epsilon) = \xi_0 \epsilon^{-\tilde{\nu}}$$

(4)

to the amplitude $A^+$ in the distinct term of the specific heat at constant pressure which, close to $T_c$ in the one-phase regime, may be simply expressed as

$$C_p = \frac{A^+}{\alpha^+} \epsilon^{-\tilde{\nu}} + C_{pb}.$$

(5)

In these relations $k_B$ is Boltzmann’s constant, $C_{pb}$ denotes the background part of the specific heat, and $\tilde{\nu}$ as well as $\alpha$ are universal critical exponents. The value for the exponent of the fluctuation correlation length is $\tilde{\nu}=0.63$; the value for
the specific heat critical exponent is $\alpha = 0.11$.10,11

Simple power-law characteristics hold only close to the critical point where experimental problems, such as arising from temperature fluctuations, impurities, and finite sample sizes, render comparison of measured data with theory difficult.12-14 This is particularly true because the asymptotic critical domain, with universal behavior, has a nonuniversal width. Theoretical models predict corrections to scaling for the crossover region, where the change from Ising to mean-field behavior occurs,15,16 but, as for the asymptotic power laws, do not give criteria for the range of convergence of these corrections.13 A variety of simple liquid-liquid and also liquid-vapor critical systems has been studied to verify the theoretical predictions. These theoretical models are now extended to more complex systems,17-19 including solutions of polymers,20,21 the length of which may compare to the fluctuation correlation length near $T_c$. For this reasons, special attention has been paid to the complex critical system 2,6-DMP-H2O. No uniform picture on the interactions between the local fluctuations in concentration and the stochiometrically defined chemical reactions has been obtained so far. In contrast, a considerable variance in the experimental values of leading amplitudes exist. For the specific heat amplitude values between $A^* = 1.73 \times 10^3$ J/kg K (Ref. 37) and $A^* = (2.0 \pm 0.6) \times 10^3$ J/kg K (Ref. 38) have been reported. The discrepancy in the experimental amplitudes of the fluctuation length is even larger, namely, $L_0 = 0.20$ nm (Ref. 39) as well as $L_0 = 0.27$ nm.40 Combining these data, parameter $X$ in the two-scale-factor universality relation [Eq. (3)] varies in the broad range between 0.0117 and 0.0362.

We found it interesting to perform a specific heat at constant pressure, shear viscosity, and dynamic light-scattering study in order to redefine the amplitude parameters. Since there are indications of significant differences in the shear viscosity parameters from different authors31-43 we measured, in addition to the “static” viscosity of the mixture of critical composition, also the high-frequency viscosity $\eta_\nu(\nu)$, using shear impedance spectrometry in the frequency range of 5 MHz $\leq \nu \leq$ 130 MHz. Since, near $T_c$, the critical concentration fluctuations do not contribute to the high-frequency viscosity, $\eta_\nu(\nu)$ can provide the noncritical background part in $\eta$, including information on possibly existing shear viscosity relaxations.34 The accurate knowledge of the specific heat, as well as the amplitude in the fluctuation correlation length and the relaxation rate of concentration fluctuations will also greatly facilitate the evaluation of broadband ultrasonic attenuation spectra of the 2,6-DMP-H2O system in terms of critical and noncritical contributions and will thus allow for a reliable study of correlations between the critical dynamics and elementary chemical reactions.

II. EXPERIMENT

2,6-dimethylpyridine (2,6-DMP, ≥99%) was purchased from Aldrich and was used as delivered by the manufacturer. Water was deionized and additionally bidistilled. The mixture of critical composition [mass fraction of 2,6-DMP: $Y_c =$0.2913 (Ref. 40)] has been prepared by weighing appropriate amounts of the constituents into suitable flasks. The critical temperature, visually determined according to the equal volume criterium, was $T_c = 306.83$ K, which compares to the literature data $T_c = 306.54$,29 306.72,47 306.76,43 306.80,51 306.92,40 307.01,49 307.05,31 307.08,50 307.21,51 and 307.26 K.30 No variations in the critical temperature were noticed during the measurements, indicating that purity changes of the samples along time were negligibly small.

The specific heat measurements were performed using a differential scanning calorimeter (MicroCal Inc., Northampton, Massachusetts; sample volume about 0.5 cm$^3$) without stirring the liquid sample. Measurements were run in an up-scan mode of operation with scan rates 1 and 0.2 K/hour, respectively. The reference cell was filled with deionized, additionally bidistilled, and degassed water. The heat capacity of water used as the reference in the measurements was taken from the literature,52 interpolating the data available at various temperatures by a polynomial. The difference between the values from this polynomial and carefully analyzed data from NIST (http://webbook.nist.gov/chemistry/fluid) was smaller than $6 \times 10^{-4}$.

The (static) shear viscosity $\eta$ of the 2,6-DMP-H2O mixture of critical composition has been measured using Ubbelohde capillary viscosimeters (Schott, Mainz, Germany, length of capillaries smaller than 100 nm) which had been also calibrated against deionized bidistilled and degassed water. The experimental $\eta$ data have been considered in terms of the microscopic theory for nonlinear effects in the shear viscosity near the critical point.53 It was found that the shear rate dependence in the viscosity data was negligibly small as compared to the experimental errors $\Delta \eta(\nu)$. These errors include differences in the data as resulting from the use of different capillaries and also of a falling ball viscosimeter (Haake, Karlsruhe, Germany).
In addition to \( \eta \), the frequency-dependent complex shear viscosity \((i^2=-1)\)
\[
\eta_i(v) = - \eta'_i(v) - i \eta''_i(v)
\]
(8)
of the 2,6-DMP-H\(_2\)O mixture of critical composition has been measured as a function of frequency between 5 and 120 MHz and of temperature near \( T_c \). The complex shear wave impedance
\[
Z_s(v) = (2\pi \rho v \eta(v))^{1/2}
\]
(9)
of the sample has been determined from the resonance frequency and quality factor for shear vibrational modes of AT-cut quartz transducers loaded with the liquid.\(^{54}\) Here \( \rho \) is the density of the sample. Two quartz resonator cells were available, one designed for the frequency range of 5–20 MHz, the other one operated at frequencies between 20 and 120 MHz. The experimental error in the real part \( \eta'_i(v) \) of the viscosity, which is of interest here, was \( \Delta \eta'_i / \eta'_i = 0.1 \) at 5–20 MHz as well as 80–120 MHz and it was \( \Delta \eta'_i / \eta'_i = 0.05 \) at 20–80 MHz.

Quasielastic light-scattering measurements have been performed to determine the mutual diffusion coefficient
\[
D = \Gamma (q, T)/q^2
\]
(10)
of the mixture of critical composition as a function of temperature \( T \). A self-beating digital photon-correlation spectrometer\(^{55}\) was utilized to determine the decay rate \( \Gamma \) of the autocorrelation function\(^{56}\)
\[
S_\ell(q, T) = \exp[- t \Gamma (q, T)]
\]
(11)
of light scattered from the sample. In these equations
\[
q = (4 \pi \eta \lambda_0) \sin(\theta/2)
\]
(12)
is the amount of the wave vector selected by the scattering geometry. \( \theta (30^\circ C \leq \theta \leq 145^\circ C) \) denotes the scattering angle, \( n \) the refractive index of the sample, and \( \lambda_0 \) the wavelength of the incident light. The refractive index \( n \) has been measured with a refractometer (Zeiss, Obercochem, Germany). The light source was a frequency-doubled Nd:yttrium aluminum garnet (YAG) laser (Coherent, Santa Clara, California) with wavelength of \( \lambda_0=532 \) nm. The digital correlation board for the analysis of scattered light was designed for real-time measurements with characteristic times between 2 \( \times 10^{-7} \) and 3.4 \( \times 10^3 \) s (ALV Laser, Langen, Germany). The error in the diffusion coefficient data is \( \Delta D/D=0.03 \).

In the shear viscosity and light-scattering experiments the temperature of the samples was controlled to within \( \pm 0.02 \) K and measured with an error of less than 0.01 K.

III. RESULTS AND DISCUSSION

In Fig. 1 an original \( \Delta C_p = C_p - C_{p_{ref}} \) scan of the 2,6-DMP-water mixture relative to water is shown at temperatures near \( T_c \). A characteristic increase in \( \Delta C_p \), reflecting the weak heat capacity divergence emerges when \( T \) approaches the critical temperature from the one-phase region. A series of events is visible in the \( \Delta C_p \) data above \( T_c \). This feature is reproducible in new experiments. A similar reproducible behavior has been already found in heat capacity profiles in the two-phase region of the ionic critical system ethylammonium nitrate-n-octanol.\(^{57}\) That system had been also measured on a differential scanning calorimeter without stirring of the sample. We suppose the events in the \( \Delta C_p \)-versus-\( T \) profiles to reflect the formation of nonequilibrium metastable substrates at the 2,6-DMP-H\(_2\)O phase boundary. Obviously, this interesting phenomenon needs further more detailed investigations, in particular, measurements at extremely slow scan rates using adiabatic scanning calorimeters.

In Fig. 2 the specific heat data \( C_p \) in the one-phase region are displayed for the 1 K/h scan rate and, near \( T_c \), also for the smaller scan rate 0.2 K/h. We used a nonlinear least-squares regression algorithm\(^{58}\) to fit the measured data to the relation\(^{10,11}\)
\[
C_p = \frac{A^+}{\alpha} \exp\{-E(1 + D^* \epsilon^3) + E \epsilon + B\},
\]
(13)
which includes correction-to-scaling terms to also apply to the temperature range further from \( T_c \). In Eq. (13) \( D^* \) is the amplitude of the first correction term and \( \Delta \) is the exponent of this (Wegner\(^{15}\)) term. The latter is also a universal constant and predicted to be \( \Delta = 0.51 \pm 0.03 \).\(^{59,60}\) Parameter \( E \) in Eq. (13) is the amplitude of a background term that linearly increases with \( \epsilon \).

FIG. 1. Heat capacity profile at a scan rate 1 K/h of the 2,6-DMP-water mixture of critical composition shown as the difference to the specific heat of water, used as reference.

FIG. 2. Heat capacity of the 2,6-DMP-water mixture of critical composition (scan rates: \( \bigcirc \), 1 K/h; \( \bigtriangleup \), 0.2 K/h) in the homogeneous phase displayed vs temperature difference to the critical temperature. In the inset the residuals \( (C_p - C_{p_{ref}})/C_p \) are plotted vs reduced temperature for the 1 K/h scan.
The values for the parameters of Eq. (13) as resulting from the 1 K/h scan of the 2,6-DMP/H2O mixture of critical composition are presented in Table I. Data from four fits are given along with the results from the literature and also from a fit of the data to the simple heat capacity relation (5). The first line of the table shows the best fit in our judgment. Since $E$ seems to play a minor role in Eq. (13), this parameter has been omitted in the second fit. Only small changes in the other parameters were observed. In particular, the amplitude of the critical term in Eq. (13) changed only insignificantly from $A^*=0.26$ J/(g K) to $A^*=0.27$ J/(g K). Variations in the parameter values are strong, however, if $D^*$ is fixed at zero (fit 3). The results of the regression analysis become very uncertain if the critical exponent $\alpha$ is not fixed at its theoretical value (fit 4), even though the theoretical value is obtained from the fitting procedure. Alternatively, the heat capacity data have been fitted only on the region of validity of simple scaling using Eq. (5). Again the exponent $\alpha$ from the regression analysis is rather uncertain if treated as an unknown parameter.

The critical amplitude from the literature38 [$A^*=(0.20\pm0.06)$ J/(g K)] agrees with our fit [$A^*=(0.26\pm0.005)$ J/(g K)] within the limits of the rather large errors of the former. Also in agreement is the amplitude $A^*=(0.25\pm0.002)$ J/(g K) as resulting from our 0.2 K/h scan of the heat capacity. Due to a compensation by a negative $E$ the literature value $B=(3.73\pm0.02)$ J/(g K) for the background term38 is noticeably larger than the $B$ values from our data (Table I).

It may be concluded that Eq. (13) contains too many unknown parameters to allow for a clear-cut description of the 2,6-DMP/H2O heat capacity profiles. We thus also used Eq. (5) to represent the $C_p$ data just by a sum of a critical term, following power-law behavior with $\alpha$ fixed at 0.11, and a background term, independent of temperature. This simple relation yields $A^*=(0.23\pm0.01)$ J/(g K), in fair agreement with the best fits from our 1 and 0.2 K/h scans, from which $A^*=(0.26\pm0.01)$ J/(g K) results as a mean.

The fluctuation correlation length $\xi$ can be derived from the mutual diffusion coefficient $D$ and the (static) shear viscosity $\eta$, which, close to the critical point, are related to one another according to the Stokes-Einstein-Kawasaki-Ferrell relation61–64

$$D = \frac{k_BT}{6\pi\eta_x\xi^2} \tag{14}$$

Since measurements include the transition region to the hydrodynamic regime, crossover corrections have to be considered, resulting in the more complex representation65,66

$$D = \bar{D} \left[ R\Omega_L(x)(1+b^2x^2)q^2 + \frac{3\pi\eta_y}{16\eta_x} \frac{1+x^2}{x} \left( \frac{1}{q_c} - \frac{1}{q_D} \right) \right] \tag{15}$$

of the diffusion coefficient. Here $\bar{D}$ denotes the diffusion coefficient as following from Eq. (14), $R=1.03$, $b=0.55$, and $x=\xi q$ with $q$ according to Eq. (12). $\Omega_L(x)$ is the Kawasaki function,67

$$\Omega_L(x) = \frac{3}{4x} \left[ 1 + x^2 + \left( x^3 - \frac{1}{x} \right) \arctan x \right], \tag{16}$$

and $\bar{q}=[q_c^{-1}+(2q_D)^{-1}]^{-1}$, where $q_c$ and $q_D$ are cut-off wave numbers. In Eq. (15) $\eta_y$ is the background part in the shear viscosity, assumed to be given by65,66,68

$$\eta_y(\epsilon) = \eta_h(\epsilon) \exp (Z_c^\epsilon H), \tag{17}$$

with the critical exponent $Z_c=0.065$ (Refs. 69 and 70) of the viscosity and with the crossover function $H=H(\xi, q_D, q_c)$ also depending on parameters $\xi$, $q_D$, and $q_c$. The background contribution

$$\eta_h(\epsilon) = A_{\eta} \exp (B_{\eta}/(T-T_\eta)) \tag{18}$$

is governed by parameters $A_{\eta}$, $B_{\eta}$, and $T_\eta$ that are characteristic of the system under consideration.

The fluctuation correlation length $\xi$ is implicitly contained in the relations for the diffusion coefficient and the shear viscosity. Hence it has been obtained from a combined regression analysis of the $\eta$ and $D$ data. In this analysis power-law behavior of the correlation length [Eq. (4)] was assumed to also hold in the crossover region

$$\xi(\epsilon) = \xi_0 e^{-\beta}. \tag{19}$$

The shear viscosity data as measured with capillary viscometers are displayed as a function of temperature in Fig. 3. Also given are results from the literature.61–64 Two sets of literature data31,43 fit to our $\eta_i$ values, the $\eta_i$ values of the third set43 are somewhat larger than the other ones. This is

<table>
<thead>
<tr>
<th>Fit</th>
<th>$B$ or $C_{p,b}$</th>
<th>$E$</th>
<th>$A^*$</th>
<th>$D^*$</th>
<th>$\alpha$</th>
<th>$T_\eta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.46±0.01</td>
<td>0.10±0.05</td>
<td>0.26±0.005</td>
<td>1.0±0.06</td>
<td>0.11</td>
<td>306.959±0.004</td>
</tr>
<tr>
<td>2</td>
<td>3.43±0.01</td>
<td>0.27±0.002</td>
<td>1.1±0.01</td>
<td>0.11</td>
<td>306.959±0.003</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.59±0.02</td>
<td>0.20±0.001</td>
<td>0</td>
<td>0.11</td>
<td>306.959±0.003</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.3±0.5</td>
<td>0.3±0.3</td>
<td>1±0.1</td>
<td>0.11±0.02</td>
<td>307±1</td>
<td></td>
</tr>
<tr>
<td>Ref. 33</td>
<td>3.73±0.02</td>
<td>-0.37±0.13</td>
<td>0.20±0.06</td>
<td>0</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td>Eq. (5)</td>
<td>3.58±0.01</td>
<td>⋯</td>
<td>0.23±0.01</td>
<td>⋯</td>
<td>0.11</td>
<td>306.963±0.001</td>
</tr>
</tbody>
</table>
also true if the viscosities are plotted versus $T-T_c$ (inset of Fig. 3) in order to account for the differences in the critical temperature of the different samples.

In Fig. 4 the shear viscosity data from our capillary viscosimeter measurements are shown along with the graph of the viscosity function [Eq. (17)] using the parameter values as found from the regression analysis of the $\eta_i$ and $D$ data: $A_s=(0.14\pm0.03)\times10^{-6}$ Pa s, $B_s=(2916\pm300)$ K, $T_c=0.2$ K, $q_s=10^{11}$ m$^{-1}$, $q_D=10^9$ m$^{-1}$, and $\xi_0=(0.198\pm0.004)$ nm. Also indicated in Fig. 4 is the background part $\eta_i$ of the shear viscosity, which nicely agrees with the $\eta_i(t)\approx1$ values as derived from the high-frequency shear viscosity measurements. At $T$ close to $T_c$, $\eta_i(n)$ data are shown as a function of frequency $n$ in the inset of Fig. 4. The real part of the shear viscosity displays a dispersion, in conformity with a nonvanishing imaginary part within the frequency range of measurements. Within the limited measuring range this behavior can be well described by a Debye-type relaxation function with discrete relaxation time $\tau_\eta$.

$$\eta_i(n) = \eta_i(\infty) + [\eta_i(0) - \eta_i(\infty)]/[1 + i2\pi n \tau_\eta].$$

The finding that the $\eta_i(0)$ values, extrapolated from high frequencies, where the critical fluctuations are expected to not contribute to the viscosity, agree with the background part from Eq. (17) confirms the evaluation of the $\eta_i$ and $D$ data.

Along with the graph of Eq. (15) the diffusion coefficients of the 2,6-DMP/H$_2$O mixture of critical composition are plotted in the inset of Fig. 5, indicating consistency of the data treatment. Illustrated by this figure is the fact that the diffusion coefficient does not follow simple power law if the crossover region is included. Within the limits of errors in the measurement of the temperatures the relaxation rate $\Gamma$ of order parameter fluctuations (Fig. 5) follows power law,

$$\Gamma = \Gamma_0 e^{Z_0\bar{p}},$$

with the theoretical universal exponent $Z_0\bar{p}=1.93$ and the amplitude $\Gamma_0=(25\pm1)\times10^9$ s$^{-1}$. According to the dynamic scaling hypothesis the relaxation rate has been derived as

$$\Gamma = 2D/\xi^2$$

from the diffusion coefficient and fluctuation correlation length data.

Using the two-scale-factor universality relation [Eq. (3)] the amplitude of the critical contribution to the heat capacity $A^h=(0.26\pm0.01)$ J/(g K) yields $\xi_0=(0.21\pm0.01)$ nm if the theoretical value $X=1.966\times10^{-2}$ from renormalization group theory is used. This $\xi_0$ value agrees reasonably with the amplitude $\xi_0=(0.198\pm0.004)$ nm derived from the shear viscosity and dynamic light-scattering measurements.

**ACKNOWLEDGMENTS**

Financial support by the Deutsche Forschungsgemeinschaft, Bonn, and the VolkswagenStiftung, Hannover, is gratefully acknowledged.
