Turbidity of deuterated isobutyric acid and heavy water in the one-phase region near the critical solution point

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We have measured the total light scattered from a mixture of deuterated isobutyric acid and heavy water (deuterium oxide, D₂O) near its upper critical solution point. The resulting turbidity was measured in a reduced temperature region 10⁻⁶ < t < 10⁻⁵, where t = (T - T_c)/T_c and T_c is the critical solution temperature, in a sample close to the critical composition. This completely deuterated mixture near its critical point exhibits similar properties to the undeuterated mixture and the turbidity can be explained using an Ising model. When the critical exponents ν and γ were fixed at the values predicted from renormalization-group theory, the amplitude ∆γ of the correlation length was determined to be 0.343 ± 0.024 nm, while the amplitude of the turbidity τₐ was (3.51 ± 0.03) × 10⁻⁵ cm⁻¹, which seem consistent with two-scale-factor universality predictions.

INTRODUCTION

The effect of deuteration on the binary fluid mixture isobutyric acid and water has been investigated in the one- and two-phase regions by a number of people. The coexistence curve¹ and turbidity² for the undeuterated mixture found this system to obey the exponent and amplitude relations predicted by renormalization-group theory.³ The effect of isotope exchange has also been investigated by several authors⁴-¹⁰ who have looked at the coexistence curve in the two-phase region, and the correlation length in the one- and two-phase regions. They observe normal critical point behavior in the one-phase region but more complicated phenomena in the two-phase region where isotope effects provide a ternary system. Only one investigator¹¹ has measured the totally deuterated system, for which the coexistence curve was found to behave normally. The mixture of deuterated isobutyric acid in heavy water is particularly interesting because of the complementary information on the partially deuterated mixtures and the undeuterated system. This article presents the first measurement of light scattering in the totally deuterated mixture of isobutyric acid and water. The results will be compared to the undeuterated and partially deuterated isobutyric acid and water systems previously reported. Finally, the amplitude prediction from two-scale-factor universality will be discussed.

Modern theories of critical solution points have been very successful in explaining a wide variety of observed phenomena in low molecular weight fluid mixtures.³ In particular, the critical exponents experimentally measured in binary fluid mixtures are found to be universal and to agree with the renormalization-group predictions for the Ising model (space dimension d = 3 and order parameter dimension n = 1).³ Renormalization-group theory has also been used successfully to relate amplitudes that describe phenomena near a critical solution point. Two-scale-factor universality predicts a universal relationship among the amplitudes B of the coexistence curve, χ₀ of the osmotic compressibility, and ∆γ of the correlation length. These amplitudes are defined by:

\[ \xi = \xi_0 t^{-\nu}, \quad T > T_c \]

(1)

\[ \phi - \phi_c = B t^\beta, \quad T < T_c \]

(2)

and

\[ \chi = \chi_0 t^{-\gamma}, \quad T > T_c \]

(3)

where φ is the volume fraction of one component in the upper or lower phase, φ_c is the critical composition, χ is the osmotic compressibility, t is the reduced temperature \( t = (T - T_c)/T_c \), and β, ν, and γ are universal critical exponents predicted from the n = 1 (Ising) model to be 0.325, 0.63, and 1.241, respectively. It has been shown¹³-¹⁴ that the amplitudes can be related by

\[ R = \xi_0 \left( \frac{B}{k_B T_c \chi_0} \right)^{1/3} = 0.65 - 0.67 \]

(4)

with a predicted¹³-¹⁴ value of 0.65-0.67 for the three-dimensional Ising model. Experiments in liquid-gas systems¹⁵ and undeuterated liquid mixtures²⁶-²⁷ have confirmed this value within experimental error. The values of ∆γ and χ₀ can both be determined, in principal, by turbidity measurements as described later.

The turbidity τ is the inverse of a effective extinction length and is defined by \( \tau = (1/L) \ln(I_0/I) \), where L is the length of the scattering medium, I is the transmitted light intensity, and I₀ the incident light intensity. The turbidity is caused by light scattering from concentration fluctuations in the fluid mixture near the critical point. By assuming Ornstein–Zernike scattering, which has accurately explained the angular distribution of scattered light near a critical point, an expression for the turbidity can be obtained. A small asymmetry in the forward direction caused Fisher¹⁸ to introduce a critical exponent η whose value is small \( (\eta = 2 - \nu/\nu \sim 0.030) \), resulting in a negligible effect on the turbidity at the level of current experiments.¹⁶,¹⁹ The
The deuterated isobutyric acid came from Merck, Sharpe, and Dohme in Canada and was at least 94 at. % deuterated by mass spectrometric analysis. Deuterium oxide came from the Aldrich Chemical Co. and was 99.96 at. % deuterated. The sample was prepared by S. Greer at the University of Maryland, sealed in a quartz ampoule, and loaned to our lab for the purpose of this study. Using a sample prepared at the same time as that used for the coexistence curve study helps allow the critical amplitudes obtained from this experiment to be meaningfully combined with those from the coexistence curve. This mixture is somewhat sensitive to contamination from water vapor in the air and precautions were taken when the fluids were transferred into the optical cell (described later) just before the start of our experiment. The effect of minute impurities on the critical point is principally seen as a shift in the critical temperature, with negligible effects on the critical composition, amplitude, or exponents.

Our light-scattering cell is a commercial (Spectrocell) optical glass cell with a cylindrical design 22 mm in diameter and a path length of 5.00 cm. It has a fill tube which was heated and drawn closed to seal the sample. The optical cell was filled with a 88.5 mole % D$_2$O sample transferred in air over a 2 min period from the sealed quartz ampoule. The critical composition was determined by Greer to be 88.2 mole % of D$_2$O, which is very close to the composition used in our experiments.

The temperature of the cell was controlled by immersion in a well-stirred, filtered water bath, as described previously. A pair of optical glass windows was sealed to an insulated, cylindrical tank that housed the water, optical cell, stirrer, temperature control, and filtering attachments. The temperature was coarsely controlled by a separate circulating bath passing water through a sealed copper tube in the optical tank, and finely controlled with a Tronac PTC-41 to give ±0.2 mK maximum excursions over an hour and a long term stability less than 1 mK. The temperature was monitored with a Thermometrics thermistor in a separate ac bridge to an accuracy of ±10 mK and a precision of ±0.2 mK.

The optical system was designed and refined to optimize the precision and accuracy of the light-intensity measurements which allowed the turbidity to be determined. The optics have been fully described and were modified by adding a laser power amplitude controller that provided an incident intensity that varied less than 0.1% long term and 0.02% short term.

The low-power laser beam ($\lambda_0 = 632.8$ nm) traveled through the water bath where the cell was oriented with the
Experimental RESULTS

The procedure of taking intensity measurements with the cell in and out of the beam path corrects for reflected and absorbed light from the bath, but not for reflected light from the cell windows. The turbidity due to reflections from the cell windows can be calculated from the refractive indices of the cell windows, water, and the fluid mixture. The refractive index of the deuterated isobutyric acid and water solution was measured by a beam-displacement technique and found to be 1.381 ± 0.007. Water and the optical glass windows had refractive indices of 1.333 and 1.52, respectively. The contribution to the measured turbidity due to the reflectance at normal incidence is then 0.0026 ± 0.0001 cm⁻¹ for the optical glass cell. The turbidity τ due to reflectance from the cell windows is subtracted from the measured turbidity at each temperature to obtain the absolute turbidity \( \tau \) of the deuterated isobutyric acid and heavy water mixture:

\[
\tau = -\frac{1}{L} \ln \left( \frac{I_1}{I_2} \right) - \tau_r,
\]

where \( I_1 \) and \( I_2 \) are the ratios of the transmitted to reference intensities with and without the cell in the beam, respectively. A rather long (5 cm) path length cell was used because of the small amount of light scattering which occurs in this system.

Two effects were used to determine the onset of phase separation. The first was a large increase in the turbidity as the temperature was decreased in small (1-3 mK) steps toward \( T_c \). Since the turbidity changes slowly with temperature close to, but above, \( T_c \), a sudden turbidity increase signals the formation of large concentration fluctuations—the precursor of a second phase. When such an increase was observed, the system was held at the temperature for 1-2 d to look for the second indicator of phase separation: the appearance of two liquid phases separated by a distinct meniscus, which appeared to divide the phases equally in our cell. The phase-separation process takes several hours when very close to the critical temperature (< 1 mK) and can be easily observed, the system was held at the temperature for 1-2 d to observe the phase separation. The first fit allowed the five parameters \( \xi_0, \tau_0, \tau_r, \nu, \gamma, \) and \( T_c \) to all be adjusted in Eq. (5). A properly weighted fit utilizes both the experimental uncertainty in the turbidity \( \delta \tau \) given in Table I, and the propagated uncertainty in the reduced temperature. The error in the reduced temperature corresponds to the 1.0 mK uncertainty in the critical temperature. A nonlinear fit described in Bevington was used to determine the parameter values. The errors in the parameters take into account the correlated errors in the parameters, and are quoted in our results at the 99% confidence interval.

The data shown in Table I can be analyzed using a properly weighted least-squares fit where the parameters \( \xi_0, \tau_0, \tau_r, \nu, \gamma, \) and \( T_c \) can all be adjusted in Eq. (5). A properly weighted fit utilizes both the experimental uncertainty in the turbidity \( \delta \tau \) given in Table I, and the propagated uncertainty in the reduced temperature. The error in the reduced temperature corresponds to the 1.0 mK uncertainty in the critical temperature. A nonlinear fit described in Bevington was used to determine the parameter values. The errors in the parameters take into account the correlated errors in the parameters, and are quoted in our results at the 99% confidence interval.

The critical temperature was allowed to vary within the range determined from observation; however, the other parameters did not change within experimental error, principally because the points close to \( T_c \) are not weighted strongly nor does the turbidity change rapidly in this region. The resulting values of the parameters are given in Table II, along with the uncertainties in the parameter values at the 99% confidence interval. The data reported in Table I were well explained by an \( n = 1 \) Ising model as shown by the three fits in Table II.

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### Table I. Absolute turbidity \( r \) in the one phase region of deuterated isobutyric acid in heavy water as a function of temperature \( T \) or reduced temperature \( t = (T - T_c)/T_c \). \( T_c \) is the critical temperature taken as 315.343 K for runs 1-3 and 315.333 K for run 4. The absolute turbidity corrects the measured turbidity for the light reflected from the cell windows.

<table>
<thead>
<tr>
<th>( T, K )</th>
<th>( r ) ( \text{cm}^{-1} )</th>
<th>( \delta r ) ( \text{cm}^{-1} )</th>
<th>( T, K )</th>
<th>( r ) ( \text{cm}^{-1} )</th>
<th>( \delta r ) ( \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>315.3000</td>
<td>1.7032E-03</td>
<td>0.02430</td>
<td>0.00008</td>
<td>315.3758</td>
<td>1.040E-04</td>
</tr>
<tr>
<td>315.3100</td>
<td>1.4476E-03</td>
<td>0.01099</td>
<td>0.00012</td>
<td>315.3703</td>
<td>8.66E-05</td>
</tr>
<tr>
<td>315.3200</td>
<td>1.3864E-03</td>
<td>0.02956</td>
<td>0.00013</td>
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<td>5.6312E-03</td>
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<td>0.00018</td>
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<td>6.50E-05</td>
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<tr>
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<td>1.1692E-03</td>
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<td>0.00025</td>
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<td>0.00027</td>
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<tr>
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<td>0.00025</td>
<td>315.3534</td>
<td>3.30E-05</td>
</tr>
<tr>
<td>315.3700</td>
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<td>0.04712</td>
<td>0.00030</td>
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<td>2.54E-05</td>
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<tr>
<td>315.3800</td>
<td>6.0661E-04</td>
<td>0.06638</td>
<td>0.00060</td>
<td>315.3510</td>
<td>2.74E-05</td>
</tr>
<tr>
<td>315.3900</td>
<td>4.7124E-04</td>
<td>0.08296</td>
<td>0.00028</td>
<td>315.3502</td>
<td>2.28E-05</td>
</tr>
<tr>
<td>315.4000</td>
<td>3.8697E-04</td>
<td>0.09793</td>
<td>0.00014</td>
<td>315.3489</td>
<td>1.87E-05</td>
</tr>
</tbody>
</table>

### Table II. Parameter values resulting from fitting Eq. (5) to the absolute turbidity data in Table I. All fits were to the entire set of data which covered the reduced temperature region \( 10^{-6} < t < 10^{-4} \). A constant background turbidity \( r_b \) was used to account for scattering far from the critical solution temperature \( T_c \). Errors on the parameters are at the 99% confidence interval as described in the text. \( \chi^2/N \) is the reduced chi squared as defined in Ref. 25. Fit 2 shows the parameter values giving the best fit to the data.

<table>
<thead>
<tr>
<th>Fit Points</th>
<th>( \nu )</th>
<th>( \gamma )</th>
<th>( g_0 ) ( \text{nm} )</th>
<th>( r_b ) ( \text{cm}^{-1} )</th>
<th>( \chi^2/N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>0.024 ± 0.009</td>
<td>1.19 ± 0.21</td>
<td>4.04 ± 0.03</td>
<td>0.424 ± 0.22</td>
</tr>
<tr>
<td>2</td>
<td>89</td>
<td>0.63</td>
<td>1.241</td>
<td>3.51 ± 0.03</td>
<td>0.343 ± 0.024</td>
</tr>
<tr>
<td>3</td>
<td>89</td>
<td>0.63</td>
<td>1.241</td>
<td>4.35 ± 0.10</td>
<td>0.47 ± 0.05</td>
</tr>
</tbody>
</table>
to the fits, it was not possible to accurately determine the critical exponents from this experiment.

The last two fits in Table II use the exponents fixed at their theoretical values of $\nu = 0.63$ and $\gamma = 1.241$. The data were best fit by the parameters in Eq. (5) having the values $\tau_0 = (3.51 \pm 0.03) \times 10^{-6} \text{ cm}^{-1}$, $\xi_0 = (0.343 \pm 0.024) \text{ nm}$, and $\tau_0 = (1.97 \pm 0.22) \times 10^{-3} \text{ cm}^{-1}$. It is necessary to include $\tau_0$ as a variable parameter, even though its value is small, as shown by the relatively large reduced chi square when $\tau_0 = 0$ in the last fit.

Our determination for $\xi_0$ and $\tau_0$ are compared to the values others have determined for the undeuterated or partially deuterated mixture isobutyric acid and water in Table III. In the one-phase region, the partially deuterated system has a value of $\xi_0$ which seems independent of the original deuteration of the hydroxyl ion in isobutyric acid. However, the partially deuterated system has a significantly lower value of $\xi_0$ than either the undeuterated mixture or the completely deuterated system reported here. While the values of $\xi_0$ for the undeuterated and completely deuterated system agree within experimental error, the value of $\tau_0$ is much larger in the former system than in the latter. Since the amplitudes $\tau_0$, $\xi_0$, and $B$ are universally related through Eqs. (4) and (6), a larger $\tau_0$ (with a similar $\xi_0$) should mean a larger value of $B$ in the undeuterated than in the completely deuterated system. However, Greer found just the opposite—that $B$ increases on deuteration. This can still be consistent with two-scale-factor universality if the refractive index dependence on composition appearing in Eq. (6) is much larger in the undeuterated than completely deuterated system. While data exist for isobutyric acid, water, and heavy water, only the density has been reported for completely deuterated isobutyric acid. Even estimates for the refractive index variation on composition using, say, the Lorentz–Lorenz relation require refractive index data which have not appeared in the literature. Thus, it is not possible to verify two-scale-factor universality in this system at this time.

**SUMMARY**

From transmitted light-intensity data in the one-phase region of completely deuterated isobutyric acid and heavy water, the turbidity was well determined in the reduced temperature range $10^{-6} < t < 10^{-2}$. Although the data could not accurately determine the critical exponents, when the Ising model values of $\nu = 0.63$ and $\gamma = 1.241$ were used, the best fit to the data gave amplitudes $\xi_0 = (0.343 \pm 0.024) \text{ nm}$ and $\tau_0 = (3.51 \pm 0.03) \times 10^{-6} \text{ cm}^{-1}$. The amplitude $\xi_0$ of the correlation length is effectively the same as that found in the undeuterated isobutyric acid and water system but larger than in partially deuterated systems. Two-scale-factor universality could not be directly tested in this system.

**ACKNOWLEDGMENTS**

Professor Sandra Greer kindly provided the sample and helpful discussions. The work was supported in part by the National Science Foundation under Grant No. CHE-87-22034. One of us (L.W.D.) would like to thank the Pew Charitable Trust Fund as administered by The College for partial support of her research. D. T. J. thanks the Henry Luce III Fund for Distinguished Scholarship as administered by The College for release time.

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**TABLE III. Values of the parameters $\tau_0$ and $\xi_0$ are compared for the undeuterated system isobutyric acid (iba) and water, partially deuterated isobutyric acid with the hydroxyl ion deuterated (COOD) or not (COOH) with heavy water, and the completely deuterated isobutyric acid (d-iba) and heavy water.**

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_0 \left(10^{-6} \text{ cm}^{-1}\right)$</th>
<th>$\xi_0 \left(\text{nm}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>iba + H$_2$O</td>
<td>10.8 ± 0.2</td>
<td>0.3625 ± 0.0065*</td>
</tr>
<tr>
<td>iba(COOD) + D$_2$O</td>
<td>3.51 ± 0.03</td>
<td>0.343 ± 0.024*</td>
</tr>
<tr>
<td>iba(COOH) + D$_2$O</td>
<td>0.313 ± 0.016</td>
<td>0.315 ± 0.0015*</td>
</tr>
<tr>
<td>d-iba + D$_2$O</td>
<td>3.51 ± 0.03</td>
<td>0.315 ± 0.007*</td>
</tr>
</tbody>
</table>


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