Shear-Viscosity Behavior near the Double Critical Point of the Mixture 3-Methylpyridine, Water, and Heavy Water

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We have measured the shear viscosity of ternary mixtures of 3-methylpyridine, water (H_2O), and heavy water (D_2O) as a function of temperature for ten different concentrations, some of which were very near the double-critical-point concentration of this mixture. The exponent to describe the power-law divergence in temperature of the viscosity nearly doubles as the concentration approaches the double-critical-point concentration.

Binary fluid systems exhibiting a consolute temperature and phase separation have been studied extensively with regard to their critical phenomena properties. One usually encounters systems which unmix with cooling below an upper critical solution temperature. Some mixtures of hydrogen-bonding liquids, however, display reentrant behavior wherein the two phases reenter the one-phase region when the temperature is lowered below a lower critical solution temperature. Such closed-loop mixtures have been studied theoretically by Anderson and Wheeler,[1] and Walker, Vause, and Goldstein.[2] These latter workers have pointed out that if the miscibility loop were somehow closed, the upper and lower critical solution points would coalesce to a double critical point where the critical exponents of certain thermodynamic or transport properties should double. Deerenberg, Schouten, and Trappeniers[3] and Kortan *et al.*[4] have given evidence for exponent doubling in a gas-gas and liquid-crystal system, respectively, but no published results exist for a binary-fluid system near its closed-loop double critical point (DCP).[5] In this report we present shear-viscosity measurements near such a DCP and analyze these measurements to examine possible exponent doubling.

The system we have studied is a mixture of water, heavy water, and 3-methylpyridine (3MP) whose phase behavior was originally studied by Cox.[6] He found that the D_2O-3MP solution exhibits a closed loop with a lower critical solution temperature of 38.5 °C at 28-wt.% 3MP and an upper critical solution temperature of 117 °C at 34-wt.% 3MP. Cox also gives data for a solution of 30-wt.% 3MP in which the ratio of H_2O to D_2O is varied to cause an eventual disappearance of the miscibility loop at 78 °C. From these data we infer that a double critical point lies roughly near $X_{DCP} = 15.5\%$, 76.7%, and 7.8% mol% of D_2O, H_2O, 3MP, respectively, and $T_D = 78$ °C. While this system is a ternary system, Gulari, Chu, and Woerman[7] and Knobler and Scott[8] have shown that ternary systems of deuterated and nondeuterated isobutyric acid and water displayed binary-solution behavior in the one-phase region.

Our solutions were made up from doubly distilled H_2O, D_2O obtained from Aldrich Chemical Company with isotopic purity of 99.8%, and 3MP which was distilled over CaH_2 and collected over molecular sieves. Two stock solutions of H_2O-3MP and D_2O-3MP were made up at 29.9 wt.% 3MP each, which according to Cox's data should be near the critical concentration of 3MP. By mixing these two solutions, various ratios of H_2O to D_2O could be obtained for experimentation while the weight percent of 3MP was held constant (although the mole fraction varied). Phase separations near the DCP showed volume ratios as large as 10:1 indicating that in this region we were not on the critical concentration. Thus, one sample (solution 5) was altered by addition of a small amount of 3MP in an attempt to get closer to the DCP. All mixing and filling operations were done volumetrically under dry nitrogen.

Three viscometers were used. They were glass Poiseuille-flow type with volumes ~ 2 cm^3. They were calibrated relative to water for temperatures from 20 °C to 80 °C. Temperature control was achieved by immersing a viscometer in a stirred water bath which was thermostated to ± 0.01 °C. Flow times were measured with a stopwatch. Densities of the solutions necessary to convert kinematic to shear viscosity were obtained gravimetrically from 20 °C to 80 °C using a 5-cm^3 pycnometer. We feel our shear viscosity precision is better than $\pm \frac{1}{2}\%$. Phase separation temperatures were determined visually to ± 0.05 °C.

The shear viscosity η is known to follow a power-law behavior near a critical point given by[9]

$$\eta = \eta_0(T) t^{-x}, \qquad (1)$$

where $\eta_0(T)$ is the background viscosity, $t = |T - T_c| T_c^{-1}$ is the reduced temperature, T_c is the critical temperature, and x is the critical exponent. To find η_0 for each solution, we first fitted the $X(D_2O) = 0.0$ data, which had the weakest anomaly, with a modified Arrhenius equation, $\eta = \eta_0 \exp[-A/(T - T_0)]$. By starting at 10 °C and fitting to progressively more data, good fits were obtained until $T > 35$ °C when chi-squared values began to increase. This indicated the
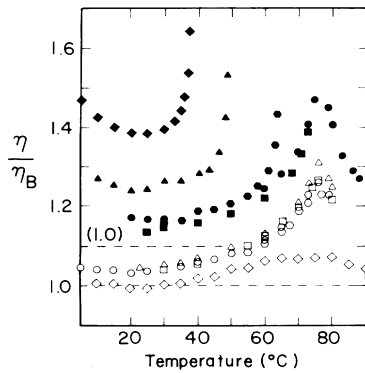
FIG. 1. Graph of η/η_B vs T where η_B was found from the fit to solution 10 data in the range $10\,^\circ C \leqslant T \leqslant 35\,^\circ C$. $\eta_B = 0.0294\exp[587.4/(T-157.3)]$. The symbols mean the following: filled lozenges, solution 1; filled triangles, solution 2; filled hexagons, solution 3; filled squares, solution 4; filled circles, solution 5; open triangles, solution 6; open circles, solution 7; open squares, solution 8; open hexagons, solution 9; and open lozenges, solution 10. Values of η/η_B for solutions 1–5 have been shifted upward by 0.1 for clarity.

singular part of the viscosity was significant in these large-T data. This fit gave us a background viscosity, which we call η_B, for the $X(D_2O) = 0.0$ solution. It also gave a singular part which was symmetric about $\sim 76\,^\circ C$ for this solution which could be inferred as necessary from the symmetric behavior of the other solutions as seen in Fig. 1. Figure 1 shows that the nonsingular parts of our data showed a linear correlation with D_2O concentration with slope roughly equal to the viscosity difference between pure H_2O and D_2O at $25\,^\circ C$. Hence η_0 for each solution was determined from the η_B fit multiplied by the appropriate scaling factor determined from Fig. 1. Solutions 1 and 2 show curvature at low T in Fig. 1 and so η_0 was also determined independently. The exponents found this way increased by 10% and 1%, respectively, over those given below.

We shall approach the analysis in a purely empirical manner to find how well and under what conditions Eq. (1) can represent the data. To fit our data with Eq. (1) for the systems that had a two-phase region, we varied T_c to linearize the double-log graphical representation of Eq. (1). The exponent is the negative slope of this graph. While in an ideal case one would determine T_c experimentally, an effective critical temperature, T_c^*, may be used[10] when the system is off loaded as ours was. T_c^* should not vary greatly from the separation temperature, T_{sep}, and it should be in the two-phase region.

Figure 2 graphically displays our results for fitting to Eq. (1) to obtain linearization for the five solutions which phase separated. One can see that not only does
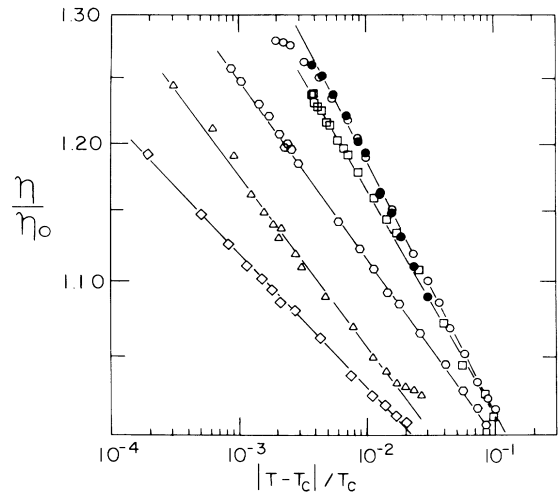

FIG. 2. Log-log plot of the viscosity anomaly for the closed-loop solutions. The symbols mean the following: open lozenges, solution 1; open triangles, solution 2; open hexagons, solution 3; open squares, solution 4; and open circles, solution 5. Open symbols are data for $T <$ lower critical solution temperature, filled symbols are for $T <$ upper critical solution temperature. Approximate error is represented by symbol size.

the anomaly increase for a given $t = |T - T_c^*|T_c^{*-1}$ as the concentration nears the DCP concentration, but the slope magnitudes and hence x increase as well.

Five of our solutions did not phase separate. To use Eq. (1) for these systems, T_c was replaced by T_m the
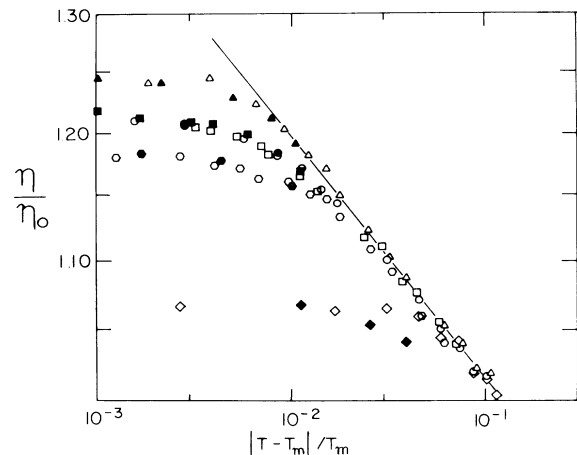

FIG. 3. Log-log plot of the viscosity anomaly for the no-loop solutions. The symbols mean the following: open triangles, solution 6; open circles, solution 7; open squares, solution 8; open hexagons, solution 9; and open lozenges, solution 10. Open symbols are data for $T < T_m \simeq 76.2\,^\circ C$, filled symbols are for $T > T_m$. Slope of the line is -0.073. Approximate error is represented by symbol size.

TABLE I. Parameters for the ten solutions studied. T_{sep} is the separation temperature if any, T_c^* is the critical temperature used in Eq. (1), T_m is the middle temperature which symmetrized the data, $\Delta T = 2|T_{sep} - 76\,°C|$ is the size of the miscibility loop, and x is the shear viscosity critical exponent.

Solution No.	Concentration (mole percent) 3MP	D_2O	H_2O	$T_{sep}(°C)$	T_c^* or $T_m(°C)$	$\Delta T(°C)$	x
1	8.40	91.6	0	37.3	37.36	78.5	0.038
2	8.07	52.8	39.1	48.4	48.5	56.4	0.050
3	7.78	18.7	73.6	63.75	64.0	25.7	0.051
4	7.76	13.0	79.3	72.74, 80.20	74.0	7.46	0.064
5	8.30	12.9	78.8	74.9, 78.45	75.0, 77.5	3.55	0.072
6	8.01	12.5	79.5	$\cdots$	76.25	$\cdots$	0.073
7	7.73	12.4	79.9	$\cdots$	76.0	$\cdots$	0.068
8	7.72	12.1	80.2	$\cdots$	76.0	$\cdots$	0.067
9	7.74	11.7	80.6	$\cdots$	76.45	$\cdots$	0.073
10	7.62	0	92.3	$\cdots$	76.0	$\cdots$	0.07

temperature at the middle of the anomaly that would yield a symmetric graph of η. That is, T_m was chosen so that when $\eta(T_1) = \eta(T_2)$, $T_1 - T_m = T_m - T_3$. Figure 3 displays these graphs. One should note a reasonably linear portion indicating power-law behavior far from T_m, and rounding off of this behavior, which all the curves must do since there is no phase separation, for smaller $|T - T_m|$.

The results of computer fits to Figs. 2 and 3 are summarized in Table I. Exponents were obtained from linear least-square fits to the linear portions of the graphs. The change in the critical exponent is quite dramatic. For the pure D_2O-3MP system which is far from the DCP, $x = 0.038$ which is consistent with both a variety of other experimental results,[11] which range from 0.029 to 0.043, and the theoretical predictions of 0.034 and 0.044[12] from mode-coupling theory and 0.041[13] from renormalization group calculations. The exponent increased as we approached X_{DCP} to 0.072 for the smallest-loop system. This is nearly double the normal experimental and theoretical values.

The nonseparating systems reinforce these results. T_m for these solutions, although they disagree with Cox's middle temperature of 78 °C, were all consistently within a few tenths of a degree of the average of 76.2 °C. Furthermore, the exponent of the linear portion of the curves is approximately 0.070 for each curve.

These results imply that the critical exponent for the shear viscosity doubled as we approached the DCP from either the closed-loop or no-loop direction. Furthermore, $T_{DCP} \simeq T_m$ played a prominent role as a symmetric temperature for the anomaly.

In conclusion we have found that the exponent describing the power-law divergence with temperature has increased from 0.038 to ~ 0.073 as the double

critical point of a ternary mixture was approached. Using the arguments of Gulari, Chu, and Woerman[7] and Knobler and Scott[8] this ternary system should act as a quasibinary system in the one-phase regime. Thus we interpret the behavior of the viscosity to indicate critical exponent doubling near the double critical point.

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