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Viscosity Measurements near a Critical Point Using a Novel Torsion Oscillator[1]

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A torsion-oscillator viscometer has been constructed for the measurement of the viscosity of fluids near both liquid–vapor and liquid–liquid critical points. This viscometer has a resolution of $\pm 0.2\%$ and operates at a low frequency (0.6 Hz) and a very low shear rate (0.05 Hz). Thus, it can be used closer to critical points than other viscometers before encountering the non-Newtonian phenomena associated with critical slowing down. This viscometer was used to study the viscosity anomaly near the consólute point of mixtures of methanol and cyclohexane along paths of constant pressure and paths of constant volume at temperatures spanning the range $10^{-5} < (T - T_c)/T_c < 10^{-2}$. The data are consistent with a simple, power-law divergence of the viscosity with a multiplicative background characterized by an apparent exponent $y \approx 0.041$. Recent theoretical estimates for y are near 0.033. If the data are to be fit with the theoretical value of y, one must simultaneously restrict the range of the data and introduce additional unphysical parameters into the fitting function.

KEY WORDS: critical point; cyclohexane; methanol; torsion oscillator; viscometer; viscosity.

1. INTRODUCTION

As the consolute point of a binary liquid mixture is approached, the correlation length (ξ), i.e., characteristic size of the composition fluctuations within the mixture, diverges according to the power law:

$$\xi = \xi_0 t^{-\nu} = \xi_0 t^{-0.63} \tag{1}$$

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[Here, $t = (T - T_c)/T_c$ is the reduced temperature measured from the critical temperature.] The characteristic lifetime of composition fluctuations (τ) also diverges. This lifetime can be estimated using the mutual diffusion coefficient (D):

$$\tau = \xi^2/D = (\xi_0^2/D_0)\, t^{-1.92} \tag{2}$$

In order to measure the shear viscosity close to a consolute point without disrupting the characteristic fluctuations, the angular frequency, ω, of the measurement must satisfy the inequality $\omega\tau < 1$ and the shear rate, S, must satisfy the inequality $S\tau < 1$. If the frequency inequality is violated, non-Newtonian viscoelastic behavior can be expected [1]. If the shear-rate inequality is violated, one expects both non-Newtonian behavior and an apparent change in the critical temperature itself [2].

In order to make more stringent tests of theories of transport properties near critical points, we have constructed a novel torsion-oscillator viscometer. This instrument, in its present form, has a resolution of 0.2% and operates at a low frequency (0.6 Hz) and a very low shear rate ($0.05\ \mathrm{s}^{-1}$). In contrast, typical capillary viscometers have shear rates of $100\text{–}1000\ \mathrm{s}^{-1}$.

We have used this new viscometer for a preliminary study of the viscosity anomaly near the consolute temperature of mixtures of methanol and cyclohexane. The data were taken at the critical composition approaching T_c from above along a path of nearly constant volume and along a path of nearly constant pressure. The data in the temperature range $10^{-5} < (T - T_c)/T_c < 10^{-2}$ can be represented by an empirical function consistent with the expected power-law divergence of the viscosity:

$$\eta = A e^{Bt} t^{-y} \tag{3}$$

Here A, B, and y are fitted to the data. Both the constant-volume and the constant-pressure data are consistent with an apparent exponent $y = 0.041$. In contrast, recent theoretical estimates [3] for y are near 0.033. At present, we have no certain explanation for the difference between the experimental and the theoretical values for y; however, we are planning more sophisticated tests of the mode-coupling theory of transport properties in the critical region using both the present viscosity data and recent optical studies of the relaxation of concentration fluctuations in the same binary liquid mixture [4]. A review of the theory and other experiments, some of which find a similar discrepancy in y, has been recently completed by Sengers [5].

We estimate that the condition $\omega\tau = 1$ occurs for a methanol–cyclohexane sample at $t = 10^{-5}$. Our viscometer can be used without any modification whatsoever to study the viscosity anomaly near the liquid–vapor critical point of a fluid such as xenon. There, we would expect to encounter the condition $\omega\tau = 1$ at $t = 10^{-6}$ [in order to make this estimate, the diffusion coefficient in Eq. (2) must be replaced with the thermal diffusivity]. In fact, on earth, gravitationally induced density gradients will limit the resolution of xenon viscosity measurements to $t > 10^{-4}$.

In this paper, we describe the viscometer, the procedures followed in using it, the reduction of the data to viscosity, and finally, a preliminary analysis of our results concerning mixtures of methanol and cyclohexane.

2. APPARATUS

The viscometer is a low-frequency torsion oscillator similar to ones used by other investigators to measure fluid viscosities accurately [6] but with several unique modifications appropriate for a nearly critical sample. The hollow oscillating bob containing the sample was made of two pieces of 304 stainless steel welded together to form a cylinder whose inside diameter and height were both 38 mm. Its robust wall thickness (4 mm) allowed sample pressures in excess of 10 MPa. Figure 1 shows the bob hung in the innermost thermostat shell. The external features of the bob are a pin vise on the axis for attachment of a quartz or metal torsion fiber and a thick vane. The vane is a moving electrode for capacitive motion detection. A miniature high-pressure valve is built into the vane on the bob's axis and closes off the 1.5-mm-diameter entrance hole.

The three features of our viscometer important for the critical point are (i) the surrounding thermostat, (ii) the restriction of the oscillator to low amplitudes (5×10^{-4} radian) to attain low shear rates, and (iii) a means for stirring the sample.

Temperature stability is achieved by actively controlling the temperatures of the outer and inner stages of the three-stage thermostat. Since the oscillator bob is thermally coupled to the inner shell chiefly by radiation, it is essentially a fourth passive stage of the thermostat. Temperature gradients on the bob introduced by the surrounding shell can be reduced to less than $10\ \mu\mathrm{K} \cdot \mathrm{cm}^{-1}$.

The restriction of the oscillation amplitude to less than 1 mradian has several secondary advantages. First, a capacitive scheme for motion detection can be used, allowing a compact thermostat without windows. Second, centrifugal effects, namely, parabolic curvature of the sample's surface and secondary flow within the sample, become negligible. Third, the detection electrodes are convenient for electrostatically exciting torsional oscillations.

The electrode system consists of the thick vertical vane (see Fig. 1) and a lower, stationary electrode. The lower electrode consists of two posts, each with a vertical face 1 cm^2 in area and positioned 180° apart. This configuration is sensitive to the desired torsion oscillation and insensitive to pendulum-like motion. The thermostat must be evacuated to reduce viscous damping of the torsional oscillations by gas between the capacitor plates. A liquid nitrogen-cooled sorption pump maintained a pressure of 0.1 Pa without vibration. The empty oscillator has a Q of 8×10^4.

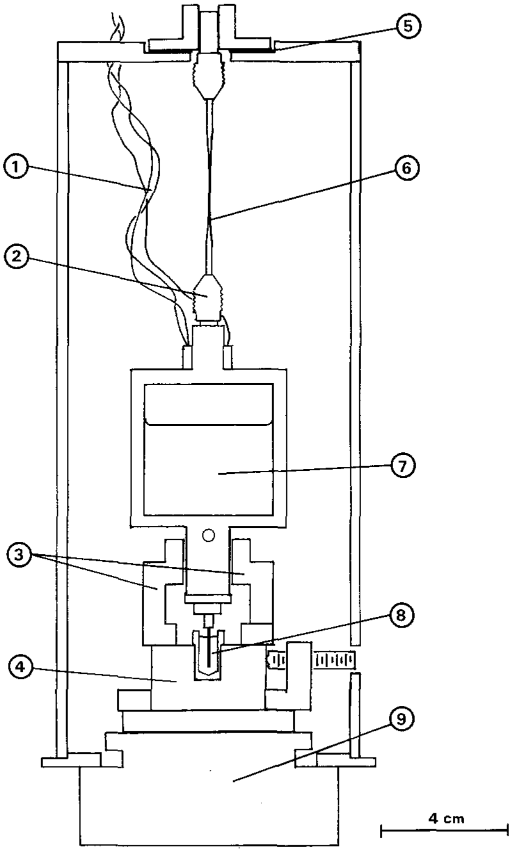

Fig. 1. The torsion oscillator hung inside the innermost thermostat shell. The following features are identified: 1, fine wires for electrical contact to thermistor and bob; 2, pin vise clamp to grip quartz rod; 3, stationary electrode for excitation and detection of bob motion; 4, translation stage for electrode positioning; 5, sapphire disks for electrical isolation; 6, torsion fiber drawn from 1-mm-diameter quartz rod; 7, liquid sample; 8, needle immersed in oil cup to reduce nontorsional oscillations; 9, rotational stage for electrode positioning.

The capacitance of the electrode gap is measured with a commercial capacitance bridge whose voltage is a negligible perturbation on the oscillator's motion.

The third feature necessary for critical-point experiments is a means for stirring the sample between runs. We used a heater below the bob to mix the sample via convection.

3. EXPERIMENTAL PROCEDURE

To measure the viscosity of methanol–cyclohexane mixtures at nearly constant pressure, the bob was loaded at room temperature, under nitrogen, from syringes containing the pure components as received from the manufacturers [7]. The composition of the mixtures was determined by weighing (29.04% methanol by mass). For measurements at nearly constant volume, the components were first weighed. They were degassed by two freeze–thaw cycles. Finally, they were distilled, under vacuum, into the bob. A very small adjustment to the loading was made with the bob at 37°C. The valve was opened momentarily while the filling port was filled with cyclohexane. This ensured that the bob was completely filled at atmospheric pressure at a temperature of 8°C below the value of T_c at vapor pressure. The bob was installed in the thermostat and then warmed 5°C above T_c and mixed by convection.

Viscosity data were taken as the bob containing the sample cooled toward the inner shell temperature (typically 10 mK below T_c) over a period of 5 to 20 h. During this time period, a cycle lasting about 4 min. was repeatedly used to measure the decrement, time, and temperature at several locations.

The capacitance waveform is approximately a damped sine wave, distorted by the $1/x$ dependence of the electrode capacity on the gap, x. We measured the peak-to-peak voltages of this waveform, corrected the data for nonlinearity, and fit the voltages to Eq. (4) to obtain the decrement.

4. REDUCTION OF DATA TO VISCOSITY

Figure 2 is a display of the decrement data and indicates the various conditions under which the data were taken. The ordinate is the decrement, Δ, defined by the decrease in oscillator amplitude Θ per period, τ, namely,

$$\Theta(t) = \Theta(0)\exp(-t\Delta/\tau) \tag{4}$$

The lower three curves correspond to runs where the oscillator was loaded to 1/7, 1/3, and 2/3 of the total volume of 43 cm^3. For these different

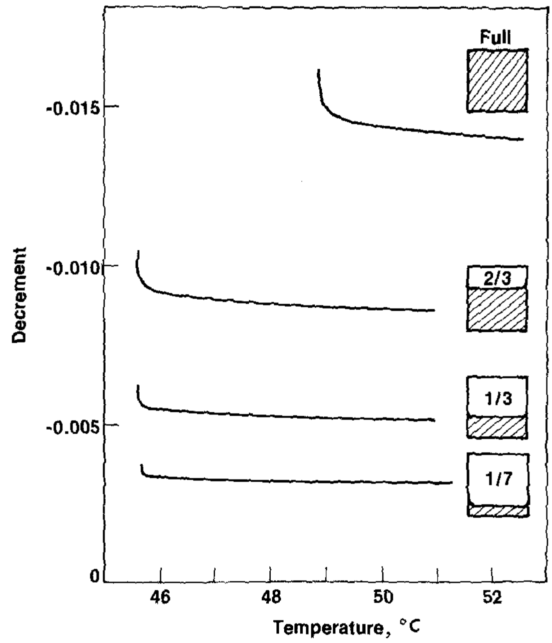

Fig. 2. Oscillator decrement data for four different loadings of methanol–cyclohexane. Decrement is defined by Eq. (4).

loadings, the critical temperatures all fell into a band 70 mK wide near 45.6°C.

The upper curve in Fig. 2 shows that the completely filled bob yields a value of T_c, which is 3.3°C higher than the other loadings. This shift in T_c is caused by the rise in pressure within the bob as it is heated from the fill temperature (37°C) toward T_c. The shift in T_c which we observe is within 10% of that which we estimated from independent measurements via the relation:

$$T_c(P) - T_c(0) = dT_c/dP_c(\partial P/\partial T)_v[T_c(P) - T_{\text{fill}}] \qquad (5)$$

We obtained dT_c/dP_c from Ref. 8. We estimated $(\partial P/\partial T)_v$ from the thermal expansion of the mixture at vapor pressure [8, 9] and the isothermal compressibilities of methanol and cyclohexane [10].

The decrement data were analyzed as follows. First, the critical temperature, T_c, was defined as the temperature of the highest decrement. The discrete nature of the decrement measurements causes T_c to be uncertain by 0.3 to 0.5 mK, the interval between successive measurements.

For runs where the bob was partially filled, care must be taken to account for the contribution to the decrement from flow in the curved meniscus region. On the assumption of complete wetting, the meniscus rises [11] 2.3 mm (the capillary length, a). This rise is not negligible compared with the liquid height (5–25 mm for 1/7 to 2/3 full).

The approximation we used to estimate the dissipation in the meniscus region, Q_m, is based on the dissipation per unit area, $Q(x)$, of an infinite oscillating plane [12] covered with a fluid layer of thickness x. We numerically computed the integral:

$$Q_m = C \int_0^a Q[x(z)]\, dz \tag{6}$$

where $x(z)$ is the meniscus profile as a function [13] of the height, z, and C is the circumference of the cylindrical interior of the bob. The value of the viscosity used in $Q(x)$ is obtained from our measurements in a self-consistent fashion.

When the bob was partially filled, additional smaller corrections were made for the dissipation in the vapor space and for changes in the liquid's height resulting from the formation of the meniscus, thermal expansion, and evaporation.

The decrement data are also corrected for the losses which are independent of the sample. These losses are determined from measurements made with the bob empty.

The final step was to convert the corrected decrements to viscosity values using experimental parameters and the theory derived by Newell and co-workers [14]. This was conveniently done by using the cubic working equation of Ref. 15. The liquid density is required for this conversion and was obtained from the excess volume data of Johnson [8] and the component data of Campbell and Anand [9].

Figure 3 (top) shows the viscosity of the mixture as a function of reduced temperature on a log–log plot. The lower band of points contains data from two runs at 1/3 full and two runs at 2/3 full, indicating the excellent consistency of the data. The one run at 1/7 full is not shown. However, it is consistent with the others to within 1% in the range $10^{-4} < t < 10^{-2}$.

The curve marked "full" in Fig. 3 (top) is data from three full runs. The cell loading for these runs was such that the bob was entirely filled with liquid above 37°C. Near T_c the pressure for these runs is above 11 MPa, the density is roughly 1% higher than the density at the vapor pressure, and the viscosity is about 8% higher than the viscosity at the vapor pressure and the same value of t.

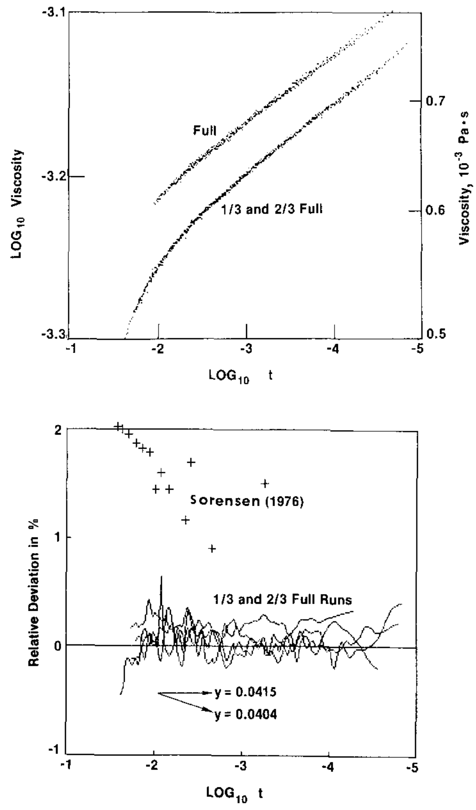

Fig. 3. Top: Log-log plot of methanol–cyclohexane viscosity (in Pa · s) versus reduced temperature. The runs for the full loading have higher viscosities due to their higher density. Bottom: Smoothed deviations of the data of the four runs at nearly constant pressure from Eq. (3) using the parameters in Table I. The arrows compare the apparent exponent (slope) for the nearly constant-pressure runs with the exponent for the nearly constant-volume runs (not shown). Capillary flow measurements by Sorensen consistently yield slightly higher viscosities than our measurements.

5. RESULTS FOR METHANOL–CYCLOHEXANE MIXTURES

Our aim in fitting the data was to find a simple analytic representation of the data consistent with theoretical expectations. It is now common to describe the viscosity divergence near T_c by a power law with an amplitude proportional to the noncritical viscosity [5, 16]. We found this approach to give a highly satisfactory fit using only three parameters. The parameters for Eq. (3), which are listed in Table I, represent the viscosity data within ±0.4% over three decades in reduced temperature. In Fig. 3 (bottom), we display the deviations of the data from this representation for the two runs at 1/3 full and the two runs at 2/3 full. Earlier data by Sorensen [17] [deviations from our Eq. (3)] for this same mixture using a capillary viscometer are also shown in Fig. 3 as an indication of the consistency ($<2\%$) of the new viscometer.

Also listed in Table I are the fit parameters for the runs with a completely full bob under constant-volume conditions. The deviations (not shown) for the full runs are as small as those for the partially filled runs. All three parameters in Table I change between the two sets of runs. The parameter A for the filled bob reflects the approximately 8% higher viscosity. The constant-volume constraint also reduces the parameter B (the noncritical temperature dependence of the viscosity) by 260%. The exponent, y, is expected to be the same whether on a constant-volume or a constant-pressure path. It differs between the two paths by only 2.6%.

The exponent y in Eq. (3) is the fitting parameter of greatest interest because it is thought to be universal and because there are two recent theoretical predictions that its value is near 0.033. Thus, our discussion of errors focuses on y.

We have examined the behavior of the goodness-of-fit χ^2 as a function of y (including the effects of correlations) for a specific data set. Standard tests suggest that the three-parameter fits are such that the exponent values obtained can be trusted (to ±0.0012, or ±3% of y) at a 95% confidence level. A similar confidence level is obtained by examining the range spanned by the four runs with a partially filled bob (±0.0008, or ±2.0% of y) or the range spanned by the three runs with a completely filled bob (±0.0003, or ±0.8% of y). Thus it appears that the difference between y for partially filled and y for completely filled runs is marginally significant; however, the difference between the experimental and the theoretical values of y is certainly significant.

Beyond questions of statistical uncertainty are questions of the validity of the model itself. Since the data are adequately described by three

Table I. Parameters for Eq. (3)

	A (Pa·s)	B	y
$P=$ constant	4.770×10^{-4}	-4.31	0.0415
$V=$ constant	5.149×10^{-4}	-1.66	0.0404

parameters, any elaboration of the model will not significantly improve the fit. Nevertheless, theoretical considerations indicate that additional nonanalytic terms may be present.

We considered the effects of the weak divergence in the thermal expansion [18] of methanol and cyclohexane. They were not large enough to account for the 2.6% difference in the viscosity exponent between the constant-pressure and the constant-volume runs.

If Eq. (3) were expanded about $t = 0$, it has the form

$$\eta = At^{-y}(1 + Bt + \cdots) \tag{7}$$

The "corrections" to the divergent term are arranged in ascending powers of t which differ by unity. It is known from experiment [19] and theory [20] that the expansion of thermodynamic properties near critical points contains noninteger corrections with exponents near 0.5 in addition to terms with integer exponents. It is a reasonable guess that these so-called "Wegner" corrections appear in the viscosity because they appear in the temperature dependence of the correlation length. We tried introducing such a term in Eq. (3) in the ad hoc fashion:

$$\eta = Ae^{Bt}t^{-y}(1 + Dt^{0.5}) \tag{8}$$

Four parameter fits of Eq. (8) to data from various runs resulted in values of D in the range $-0.2 < D < 0.2$ with uncertainties comparable to D. (This illustrates our statement that the data do not require a fourth parameter.) The addition of the fourth parameter D increased uncertainty in y, making irrelevant the small difference in y between the constant-pressure and the constant-volume runs. There is no value of D which is consistent with the data for our entire range of t and the theoretical value $y = 0.033$. By restricting the data of a typical (constant-pressure) run to the range $t < 10^{-3}$, Eq. (8) can be forced to agree with both the data and the requirement that $y = 0.033$ provided that the values $B = +20$ and $D = -2.8$ are chosen. The large, positive value of B and large magnitude of D lead us to believe that the ad hoc introduction of Wegner corrections into Eq. (8) is unable to reconcile the experimental and theoretical values of y in a physically meaningful way.

6. CONCLUSIONS

A novel viscometer has been described which is optimized for measurements near critical points. The viscosity data for both constant-volume and constant-pressure measurements yield essentially identical values of the exponent y, although the noncritical contribution to the viscosity is very different on the two paths. The experimental value $y = 0.041$ is significantly different from the theoretical value $y = 0.033$. We have attempted to reconcile the data with the theoretical value of y by simultaneously restricting the range of data ($t < 10^{-3}$) and introducting an additional term ($Dt^{0.5}$) into the fitting function. The large values of the fitting coefficients suggest that this approach is not physically meaningful.

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