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Note

Shear Viscosity of the Binary Liquid Mixture 3-Methylpentane + Nitroethane Near the Consolute Point

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Shear viscosity measurements of a mixture of 3-methylpentane and nitroethane at the critical concentration are presented in the temperature range 0.005 K $\leqslant T - T_c \leqslant$ 13.93 K, where T_c is the consolute or critical temperature. The data agree with earlier measurements.

KEY WORDS: critical region; methylpentane; mixtures; nitroethane; viscosity.

Both liquid-gas and binary liquid systems exhibit anomalies for a vast variety of thermodynamic and transport properties in the critical regime [1]. In particular, the shear viscosity η has a power-law divergence given by

$$\eta = \eta_0 \epsilon^{-x_\eta} = \eta_0 \left(\frac{T - T_c}{T_c} \right)^{-x_\eta} \tag{1}$$

where η_0 is the viscosity amplitude and T_c is the critical temperature. The critical exponent x_η is found experimentally to be $x_\eta = 0.04$ [2], in good agreement with theory [3].

An accurate knowledge of the viscosity is needed to compare Rayleigh linewidth data of light quasi-elastically scattered from fluid systems near the critical point to the various dynamical theories of critical point fluctuations [4]. One attractive system for these studies is the binary solution of 3-methylpentane and nitroethane which, because of its small scattering

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cross-section, is not subject to the problem of multiple scattering. This system has been studied using light scattering by Sorensen et al. [5], Burstyn et al. [6] and Burstyn and Sengers [7]. While two sets of viscosity data exist in the literature for this system, they unfortunately do not agree, the data of Stein et al. [8] being ~3.2% larger than those of Tsai and McIntyre [9]. Because of this discrepancy, in order to interpret our light-scattering data [5], the author measured the viscosity for this system and found values ~7% larger than Stein et al. Communication regarding this problem with J. V. Sengers [10] has led me to remeasure the viscosity of this system. An error was found due to the overfilling of the viscometer in my first measurements; the new measurements, described below, agree quite well with those of Stein et al.

The mixture was made up under dry nitrogen from spectrographic grade 3-methylpentane and purified nitroethane. The mole concentration of the solution was 0.5003 ± 0.0004 nitroethane, which is comparable to the literature value of 0.500 [11].

The viscometer, a glass Poiseuille flow type, was held in a well-stirred 45 liter water bath and temperature controlled with a thermistor and heater feedback circuit to 0.01°C. The time t for roughly 3 cm^3 of liquid to flow down through the 10 cm long, 0.54 mm inside diameter capillary of the viscometer leads to the liquid viscosity by

$$\eta = A\rho t \qquad (2)$$

where ρ is the mass density of the liquid and A is the viscometer constant. Calibration to determine A was performed with the known viscosities and densities [12] of pure water and spectrographic grade methanol at a variety of temperatures. The values of A showed no systematics and were found to be $A = (8.173 \pm 0.02) \times 10^{-3}\ \mathrm{cp \cdot cm^3 \cdot g^{-1} \cdot s^{-1}}$.

The temperature of the bath was measured with a mercury thermometer to a precision of about 0.01°C and accuracy estimated to be 0.05°C. The critical temperature was determined by visual inspection for phase separation to be 26.52°C. This can be compared to the literature value of 26.456°C [11].

Data for the density of the mixture, necessary for evaluation of the viscosity in Eq. (1), were obtained from Greer and Hocken [13] in the range $26.5°\mathrm{C} \leqslant T \leqslant 31.5°\mathrm{C}$ and linearly extrapolated to 40.5°C, the upper limit of the flow measurements reported here. The accuracy of this extrapolation is estimated to be 0.1%.

Table I gives the viscosity as a function of the temperature T, the relative temperature $\Delta T = T - T_c$, where $T_c = 26.517 \pm 0.01°\mathrm{C}$, and the reduced temperature $\epsilon = (T - T_c)/T_c$. The estimated error in ΔT is ± 0.02°C. Errors contributing to the viscosity are the density, known to

Table I. Shear Viscosity of the Binary Mixture 3-Methylpentane and Nitroethane at Mole Concentration Nitroethane = 0.500[a]

T (°C)	ΔT (°C)	ϵ	η (cp)
26.522	0.005	1.66×10^{-5}	0.504
26.539	0.022	7.3×10^{-5}	0.495
26.572	0.055	1.8×10^{-4}	0.486
26.61	0.094	3.1	0.477
26.63	0.117	3.9	0.480
26.66	0.14	4.7	0.470
26.68	0.16	5.3	0.469
26.73	0.21	7.0	0.466
26.77	0.25	8.3	0.465
26.86	0.34	1.13×10^{-3}	0.460
26.88	0.36	1.2	0.459
26.98	0.46	1.53	0.457
27.02	0.50	1.67	0.448
27.07	0.55	1.84	0.446
27.15	0.63	2.1	0.443
27.22	0.70	2.3	0.441
27.30	0.78	2.60	0.439
27.41	0.89	2.97	0.436
27.60	1.08	3.60	0.432
27.83	1.31	4.37	0.428
27.85	1.33	4.44	0.427
28.06	1.54	5.14	0.424
28.22	1.70	5.67	0.422
28.63	2.11	7.04	0.416
28.89	2.37	7.91	0.413
29.19	2.67	8.91	0.410
29.43	2.91	9.71	0.408
29.74	3.22	1.07×10^{-2}	0.406
30.00	3.48	1.16	0.403
30.37	3.85	1.28	0.399
30.86	4.34	1.45	0.396
30.86	4.34	1.45	0.396
31.14	4.62	1.54	0.394
31.67	5.15	1.72	0.391
32.11	5.59	1.87	0.389
32.61	6.09	2.03	0.384
33.02	6.50	2.17	0.382
33.89	7.37	2.46	0.377
34.61	8.09	2.70	0.373
35.16	8.64	2.88	0.370
35.87	9.35	3.12	0.367
36.67	10.15	3.39	0.362
37.29	10.77	3.59	0.360
37.78	11.26	3.76	0.358
38.27	11.75	3.92	0.356
39.00	12.48	4.16	0.352
39.79	13.27	4.43	0.350
40.45	13.93	4.65	0.347

[a] $\Delta T = T - T_c$, $\epsilon = (T - T_c)/T_c$, $T_c = 26.517$°C.

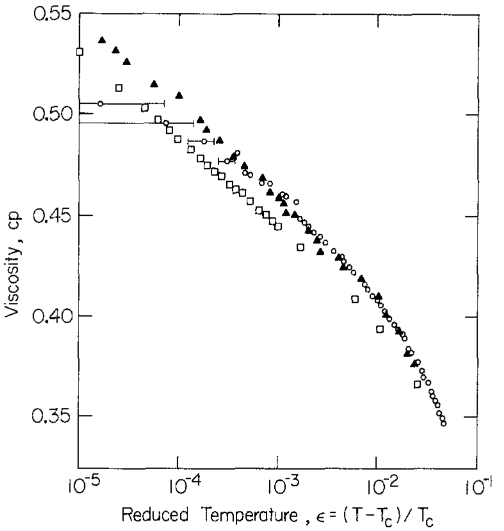

Fig. 1. Plot of the shear viscosity vs the reduced temperature. Data are plotted for: □, Tsai and McIntyre [9]; ▲, Stein et al. [8]; ○, data presented in this paper.

0.1% or better, the coefficient A, determined to 0.25%, and the variation of t over several timings, usually good at 0.2%. Thus, the error in viscosity is about ±0.3%. Within $\Delta T \lesssim 0.5°C$, the variation in flow times t was somewhat larger, so the corresponding error in the viscosity may be closer to ±0.6%.

Figure 1 displays data of the present work (open circles) versus the logarithm of the reduced temperature. The data of Stein et al. [8] and Tsai and McIntyre [9] are plotted as well for comparison. As can be seen, data of the present work agree quite well with those of Stein et al. throughout nearly the entire range of temperature and seem to exclude those of Tsai and McIntyre. The three points for which $\epsilon \leqslant 1.8 \times 10^{-4}$, i.e., $\Delta T \leqslant 0.05°C$, however, seem to match Tsai and McIntyre better. These data were taken at the limit of the temperature control of the author's apparatus; they also showed more scatter in the flow time than the rest of the data and so may not reflect the true viscosity. Better temperature control is necessary to improve the comparison for $\Delta T < 0.05°C$.

In conclusion, this new viscosity measurement agrees quite well with the earlier measurements of Stein et al. in the range $0.05°C \leqslant \Delta T \leqslant 7.0°C$ and not with those of Tsai and McIntyre. The current set of data extends to nearly $\Delta T = 14°C$. Interpretation of Rayleigh light-scattering measurements should use the data of Stein et al. as was done by Burstyn et al. [6].

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REFERENCES

1. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).
2. P. Calmettes, *Phys. Rev. Lett.* **39**:1151 (1977).
3. E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, *Phys. Rev. B* **13**:2110 (1976).
4. H. L. Swinney and D. L. Henry, *Phys. Rev. A* **8**:2586 (1973).
5. C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, *Phys. Rev. Lett.* **40**:777 (1978).
6. H. C. Burstyn, J. V. Sengers, and P. Esfandiari, *Phys. Rev. A* **22**:282 (1980).
7. H. C. Burstyn and J. V. Sengers, *Phys. Rev. A* **25**:448 (1982).
8. A. Stein, J. C. Allegra, and G. F. Allen, *J. Chem. Phys.* **55**:4265 (1971).
9. B. C. Tsai and D. McIntyre, *J. Chem. Phys.* **60**:937 (1974).
10. J. V. Sengers, University of Maryland, private communication.
11. A. M. Wims and D. McIntyre, *J. Chem. Phys.* **60**:937 (1974).
12. R. C. Weast, ed. *Handbook of Chemistry and Physics* (CRC Press, Cleveland, 1976), Vol. 57.
13. S. C. Greer and R. Hocken, *J. Chem. Phys.* **63**:5067 (1975).