The Viscosity Anomaly Near the Lower Critical Consolute Point[1]

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Shear viscosity measurements for a critical mixture of 3-methylpyridine + heavy water near a lower critical consolute point are reported. The background contribution was determined from viscosity measurements of mixture at a noncritical composition. In the entire investigated temperature range $T_c - T \leqslant 15.6$ K, the viscosity of the critical mixture exceeds the background contribution, and the critical enhancement is important. The increase of the viscosity near critical is found in the temperature range $T_c - T \leqslant 1.82$ K. The critical exponent $y = 0.0415 \pm 0.002$ and the wave number $Q = (0.40 \pm 0.07)$ nm^{-1} are determined.

KEY WORDS: critical behavior; lower critical solution point; mixture; viscosity; water; 3-methylpyridine.

1. INTRODUCTION

The shear viscosity η exhibits weak divergence approaching the critical point from the one-phase region. Renormalization group [1] and mode-coupling [2, 3] theories predict the η divergence as

$$\eta = \eta_0 (Q\xi)^z F \tag{1}$$

where η_0 is the background viscosity, ξ is the correlation length, z is a universal critical exponent, Q is a system-dependent wave number, and F is a crossover function. Theoretical estimates for z give values from $z \approx 0.052$ [4] to $z \approx 0.065$ [5]. The second z value seems to be in better agreement with experimental data [6-9]. The connection between the range of viscosity critical behavior and values of system-dependent

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parameters based on molecular structure and intermolecular interaction is of special interest in view of recent investigations of the critical behavior of electrolytes [10, 11]. However, difficulties with a determination of the background contribution and an ambiguity of crossover from critical to noncritical behavior resulted in insufficient information for such analysis.

Viscosity measurements for the binary mixture of 3-methylpyridine (MP) with heavy water (HW) in an extended region near the lower critical consolute point are reported in the present paper. The viscosity of this mixture has been studied in Refs. 12 and 13, but the background contribution was determined from the same critical sample far from the critical temperature. We found the critical enhancement to viscosity is significant in wide temperature range, so the background contribution should be determined from the samples with a noncritical concentration.

2. EXPERIMENT

2.1. Method

The kinematic viscosity measurements were performed with a quartz Cannon–Tilting-type capillary viscometer. The capillary had a length $l = 0.125$ m and an internal radius $R = 3.2 \times 10^{-4}$ m. The volume flowing through the capillary was $V = 5.4 \times 10^{-6}$ m^3, and the mean value of the height of the fluid meniscus during an experiment was $h = 0.145$ m. The capillary tube had a sharp bottom opening which makes the surface-tension effects negligibly small [14]. The viscometer was calibrated with proanalysis toluene [15] and with double-distilled water [9] in the temperature range 289.15 K $< T <$ 343.15 K, taken into account the "inlet" correction, which was found to be nearly 0.3%. The efflux time t was measured with a stopwatch from five to seven times at every temperature, and it varied in the range 190 s $< t <$ 255 s. The upper bound of the random error is 0.1%, while a systematic error of 0.3% was estimated from the control measurements of the viscosity of heavy water and several other simple fluids. The viscometer was immersed in a carefully insulated water thermostat (volume of 0.02 m^3) with a long-time temperature stability of ± 0.005 K.

The densities of the mixtures were measured as a function of temperature with a pycnometer. The pycnometer was calibrated and provided density measurements with a systematic uncertainty of no more than ± 0.3%.

2.2. Experimental Results for the Critical Mixture

The viscometer was filled with a mixture of MP + HW with mass fraction of MP, $C_c = 0.2997 \pm 0.0005$ in accordance with Ref. 16. The kinematic

viscosity was measured for 78 temperatures in the range 297.15 K $< T <$ 312.69 K and demonstrated critical enhancement of the viscosity in the temperature range 310.81 K $< T <$ 312.69 K.

In order to determine shear viscosity values, we performed density measurements for the critical sample and found the temperature dependence of the density $\rho(T)$ represented successfully by the equation

$$\rho(T) = 0.983688 + 1.153 \times 10^{-3}T - 3.01 \times 10^{-6}T^2 \tag{2}$$

The temperature dependence of the shear viscosity $\eta = \tilde{v}\rho$ (where $\tilde{v}$ is the kinematic viscosity) is presented in Fig. 1.

The critical temperature T_c of the sample was determined by visual observation of the critical opalescence followed by separation of the mixture into two liquid phases. Note that at a temperature slightly higher than T_c in the strongly stirred and macroscopically homogeneous mixture,
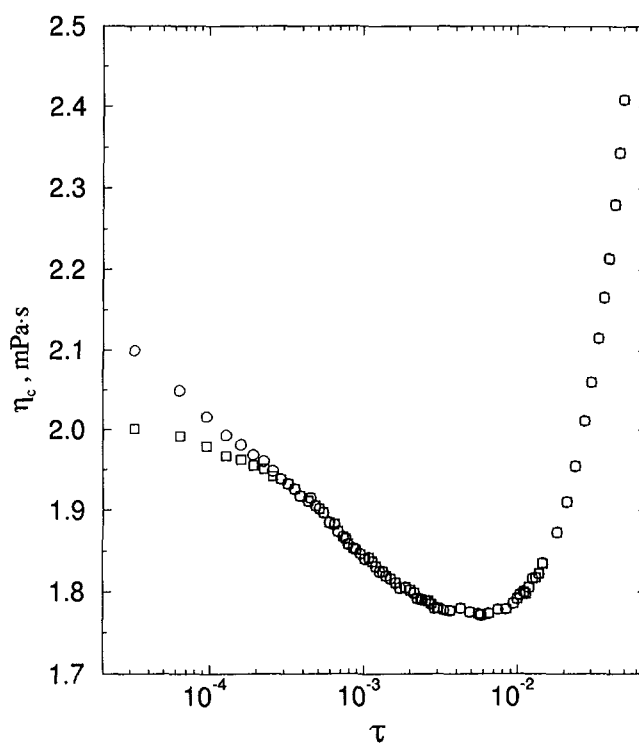

Fig. 1.   The experimental shear viscosity data of the critical mixture (squares) and data corrected for shear using Eq. (3) (circles).

we observed a sharp decrease in efflux time. For our sample, we found the critical solution temperature to be equal to $T_c = 312.69 \pm 0.005$ K. The accuracy of the T_c determination is limited by long-time temperature stability of the bath.

2.3. Correction for the Influence of Shear

The viscosity measurements may be affected when the decay time of the concentration fluctuations becomes comparable to the inverse rate of shear, S^{-1}. The influence of shear for the lower critical consolute temperature as well as the upper critical temperature appears in the extension of the one-phase region on the phase diagram, and deceleration of the critical divergence of viscosity when the critical temperature is approached. From Fig. 1, one can see that several experimental points in the range of the reduced temperature $\tau \leqslant 3 \times 10^{-4}$ ($\tau = (T - T_c)/T_c$) demonstrate the above-mentioned tendency and the correction for shear seems to be important for these data. Approaching T_c, the rate of shear produces two effects. The first effect was considered by Oxtoby [17]. It concerns the decrease in the shear viscosity due to shear, $\eta(S)$, in comparison with the viscosity at zero shear rate $\eta(S = 0)$:

$$\eta(S = 0) = \eta(S)/[1 - \Delta(\lambda)] \tag{3}$$

where the correction $\Delta(\lambda)$ for small shear ($0.1 < \lambda < 20$) is given by

$$\Delta(\lambda) = 0.0214 + 0.0266 \log \lambda + 0.0078(\log \lambda)^2 \tag{4}$$

λ is a dimensionless parameter, which is related to the shear rate value S by the relation,

$$\lambda = \frac{\eta \xi^3 S}{k_B T} \tag{5}$$

where k_B is the Boltzmann constant. The shear rate S is a transverse velocity gradient, and in a capillary viscometer, it may be estimated as [9]

$$S = \frac{4\rho g h R}{15 \eta l} \tag{6}$$

where g is the acceleration due to gravity. The shear rate S changes with temperature, due mainly to the change in shear viscosity and, in our case, varies within the limits $490 \text{ s}^{-1} < S < 553 \text{ s}^{-1}$. The parameter λ diverges

strongly near the critical point due to divergence of the correlation length ξ. In our case, the viscosity changes along the critical isochore and the correlation length varies with reduced temperature τ as

$$\xi = \xi_0 \tau^{-\nu} \tag{7}$$

where $\nu \approx 0.63$ is the critical exponent and ξ_0 is the amplitude of the correlation length. For a mixture of MP + HW near the lower critical solution point, the ξ_0 value was found from light scattering measurements [18]: $\xi_0 = 0.443$ nm. The values of the parameter λ indicate that eight experimental points close to T_c should be corrected for the influence of shear. The corrected values of shear viscosity η_c using Eq. (3) are presented in Fig. 1. As we can see from Fig. 1, the data corrected for shear following the Oxtoby formalism lies approximately on a straight line and the second correction [19] seems to be needless.

2.4. Determination of the Regular Part

In order to extract the critical part of the shear viscosity from the experimental data, the background viscosity should be determined in a range far from T_c. Much of the ambiguity is due to lack of knowledge about the range of the critical enhancement, which may extend over 20 K from T_c [8, 11]. Moreover, the form of the background temperature dependence is not well known, especially for associated liquids such as aqueous solutions. Therefore, the viscosity for noncritical compositions with mass fraction of MP, $C_1 = 0$, $C_2 = 0.0998 \pm 0.0005$, $C_3 = 0.1994 \pm 0.0005$, $C_4 = 0.4003 \pm 0.0005$, were measured in the temperature range 297.15 K < T < 313.15 K. The measurements for the mixtures with higher concentration of MP are useless for our purpose due to the nonmonotonic dependence of the viscosity upon concentration of an organic component in aqueous solutions. (See, e.g., Ref. 9).

The measurements for noncritical mixtures were carried out at 20 temperatures for four mixtures and are presented in Table I. The noncritical viscosity data η_0 for a mixture with critical composition, $C_c = 0.2998$, were estimated using a quadratic approximation in concentration and temperature:

$$\eta_0 = 4.64711 - 0.12570(T - 273.15) + 0.00119(T - 273.15)^2 \tag{8}$$

The estimated values of η_0 are also given in the last column in Table I. The viscosity temperature dependence for mixtures of critical and noncritical compositions, together with the constructed background data for critical composition, is shown in Fig. 2. The shear viscosity of the critical mixture

Table I. Shear Viscosity η of 3-Methylpiridine + Heavy Water Mixtures with Different Mass Fractions C_i ($i = 1,..., 4$) of 3-Methylpyridine and Estimated Background Viscosity for Critical Mixture C_c

T (K)	n (mPa·s)				
	$C_1 = 0.$	$C_2 = 0.0998$	$C_3 = 0.1994$	$C_4 = 0.4003$	$C_c = 0.2997$
297.15	1.128 ± 0.001	1.471 ± 0.001	1.954 ± 0.002	2.706 ± 0.002	2.3146
298.15	1.101 ± 0.001	1.433 ± 0.001	1.899 ± 0.002	2.627 ± 0.002	2.2488
299.15	1.072 ± 0.001	1.389 ± 0.001	1.846 ± 0.002	2.558 ± 0.002	2.1889
300.15	1.050 ± 0.001	1.355 ± 0.001	1.794 ± 0.002	2.483 ± 0.002	2.1219
301.15	1.026 ± 0.001	1.320 ± 0.001	1.751 ± 0.002	2.401 ± 0.002	2.0591
302.15	1.000 ± 0.001	1.284 ± 0.001	1.700 ± 0.002	2.330 ± 0.002	1.9991
303.15	0.981 ± 0.001	1.254 ± 0.001	1.656 ± 0.002	2.267 ± 0.002	1.9491
304.15	0.964 ± 0.001	1.225 ± 0.001	1.615 ± 0.002	2.200 ± 0.002	1.8934
305.15	0.942 ± 0.001	1.191 ± 0.001	1.578 ± 0.002	2.140 ± 0.002	1.8434
306.15	0.924 ± 0.001	1.165 ± 0.001	1.538 ± 0.002	2.083 ± 0.002	1.7934
307.15	0.901 ± 0.001	1.136 ± 0.001	1.502 ± 0.002	2.033 ± 0.002	1.7506
308.15	0.879 ± 0.001	1.104 ± 0.001	1.467 ± 0.001	1.981 ± 0.002	1.7078
309.15	0.861 ± 0.001	1.082 ± 0.001	1.434 ± 0.001	1.932 ± 0.002	1.6650
310.15	0.842 ± 0.001	1.055 ± 0.001	1.404 ± 0.001	1.889 ± 0.002	1.6307
311.15	0.826 ± 0.001	1.034 ± 0.001	1.371 ± 0.001	1.841 ± 0.002	1.5893
312.15	0.809 ± 0.001	1.007 ± 0.001	1.344 ± 0.001	1.804 ± 0.002	1.5550
313.15	0.791 ± 0.001	0.984 ± 0.001	1.320 ± 0.001	1.765 ± 0.002	1.5222

exceeds the constructed background in the entire temperature range. This indicates that the critical enhancement is significant for a critical mixture of MP + HW in a wide temperature range (more than 20 K from critical temperature). Therefore, the background contribution estimated from data on the critical mixture [13] may not be adequate and it exceeds our background by ≈15%. Note that viscosity data of the mixture 2-butoxyethanol + water are apparently not influenced by a critical contribution up to $T_c - T = 11$ K [9]. Comparison of experimental results on aqueous solutions of 2,6-lutidine [20], isobutyric acid [8], butoxyethanol [9], and 3-methylpyridine [this paper] indicates that the range of a critical enhancement increases with a decrease in the absolute value of the solution viscosity.

3. ANALYSIS OF CRITICAL CONTRIBUTION

Shear viscosity data η divided by the background contribution η_0 were fitted by the following general equation:

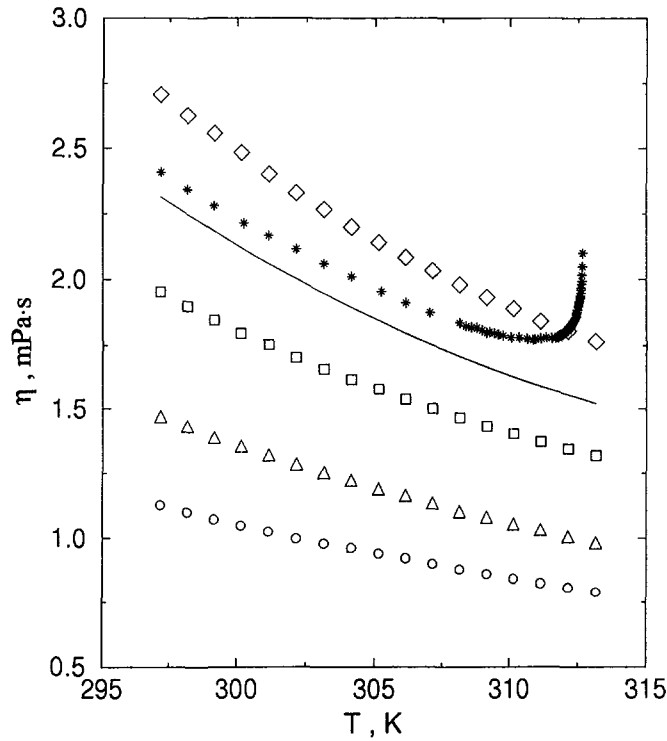$$\frac{\eta}{\eta_0} = A\tau^{-y}F \tag{9}$$

Fig. 2. Temperature dependence of the viscosity of mixtures of different compositions: $C_1 = 0$ (circles); $C_2 = 0.0998$ (triangles); $C_3 = 0.1994$ (squares); $C_4 = 0.4003$ (diamonds); $C_c = 0.2997$ (stars); constructed background contribution to viscosity of critical mixture $C_c = 0.2997$ (solid line).

with $A = (Q\xi_0)^{y/v}$ taken as a single adjustable parameter, $y = zv$, and F the crossover function. The function F was set equal to 1 (no crossover) or to a value corresponding to the first term of the Wegner correction-to-scaling to correlation length [21],

$$F = (1 + a\tau^{0.5})^{y/v} \qquad (10)$$

or to a value corresponding to the dynamic correction-to scaling [22],

$$F = 1 + a\tau^{0.7} \qquad (11)$$

where a is an amplitude of the correction. We also used a crossover function, derived from mode-coupling theory [23]. The critical temperature

was fixed at its critical value $T_c = 312.69$ K, while the critical exponent y was either a free parameter or set to theoretical predictions. The results of the fits are presented in Table II, where $\chi^2 = ((\eta/\eta_0) - (\eta/\eta_0)_{fit})^2/\sigma^2$ is the average deviation of fitted values $(\eta/\eta_0)_{fit}$ from experimental data (η/η_0) and $\sigma = 0.01$ mPa·s was imposed. The experimental data and several fitting curves are shown in Fig. 3. The value of $y = 0.0327$ ($z = 0.052$) is found inappropriate. The exponent $y = 0.04095$ ($z = 0.065$) fits the data well close to the critical point, but evidently deviates from experimental data far from the critical point. Including the correction with Wegner exponent Δ improves the fit and gives the value of $y = 0.0441$ ($z = 0.070$). The dynamic correction [22] from Eq. (11) leads to the best fit over the entire temperature range, but the fit of near-critical data becomes worse. The crossover function [23] derived from mode-coupling theory represents the viscosity data with Eq. (25) [23] better in the limiting case in which the effect of the background decay rate on the viscosity is neglected. The corresponding fit ($N = 15$) in Table II shows that the value of $y = 0.0399$ ($z = 0.063$) is in the best agreement with theoretical predictions [5].

Table II. Parameters Obtained for Different Crossover Functions with Critical Temperature Fixed at the Experimental Value, $T_c = 312.69$ K; The Values in Parentheses Were Set as Fixed Parameters in Fitting Eq. (9)

N	Crossover function	y	A	a	$Q(\text{nm}^{-1})$	χ^2
1	$F = 1$	(0.0327)	0.9489	—	0.822	2.04
2	$F = 1$	(0.04095)	0.9009	—	0.453	0.66
3	$F = 1$	0.03889	0.9127	—	0.514	0.48
4	Eq. (10)	(0.0327)	0.9608	4.78	1.045	1.06
5	Eq. (10)	(0.04095)	0.8956	−4.09	0.414	0.26
6	Eq. (10)	0.04407	0.8743	−2.11	0.331	0.16
7	Eq. (11)	(0.0327)	0.9540	−0.221	0.911	1.47
8	Eq. (11)	(0.04095)	0.8968	0.197	0.423	0.23
9	Eq. (11)	0.04351	0.8797	0.331	0.353	0.15
10	Eq. (2.23) [23]	(0.0327)			1.127	1.22
11	Eq. (2.23) [23]	(0.04095)			0.690	2.15
12	Eq. (2.23) [23]	0.0358			0.477	0.76
13	Eq. (2.25) [23]	(0.0327)			0.799	1.46
14	Eq. (2.25) [23]	(0.04095)			0.444	0.27
15	Eq. (2.25) [23]	0.0399			0.474	0.24
16[a]	Eq. (11)	(0.0327)	0.9042	−0.464	0.892	1.55
17[a]	Eq. (11)	(0.04095)	0.8392	0.726	0.419	0.23
18[a]	Eq. (11)	0.04343	0.8205	1.098	0.352	0.15

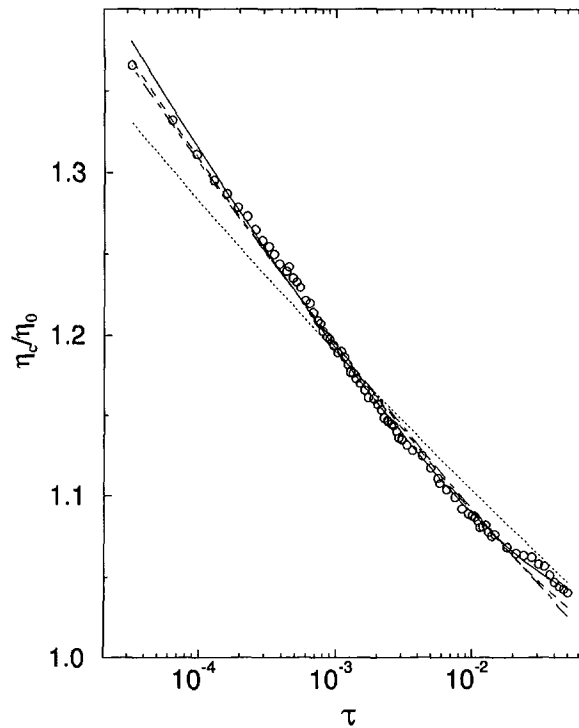[a] These sets were obtained with field variable τ'.

Fig. 3. Analysis of a singular contribution of the viscosity of the critical mixture. The experimental data points are represented by circles; fits 1, 3, 9, and 15 from Table II are shown by dotted, dotted-dashed, solid, and dashed lines, respectively.

However, this fit deviates from experimental data significantly (see dashed line in Fig. 3).

We also fitted our data using another field variable $\tau' = ((T_u - T)/T_u) \tau$, which is often used for mixtures of MP + HW [24] in order to take into account the closeness of the upper critical consolute temperature, $T_u \cong 390$ K. The results of fits for exponent y and wave number Q appear very similar to those for the usual field variable τ, and some of them are presented in Table II (sets 16-18).

We conclude that the value $y = 0.0395 \pm 0.0005$ represents best the viscosity data close to the critical point (see dotted-dashed and dashed lines in Fig. 3). The best fit of all the viscosity data is obtained in fit 9 with $y = 0.0435$. So the best value of y for our data is $y = 0.0415 \pm 0.002$ ($z = 0.0659 \pm 0.001$), which is lower than the value $z = 0.077 \pm 0.003$, obtained in Ref. 12 for our mixture MP + HW.

The wave number Q in the best fits 6 and 9 is $Q = (0.340 \pm 0.015)$ nm^{-1}. It is rather close to the value of Q for nitrobenzene + n-hexane [7] and for electrolytic mixtures [10, 11] and is two times larger than Q for a rather similar aqueous solution of 2-butoxyethanol [9]. The value of $Q = (0.50 \pm 0.03)$ nm^{-1} obtained in Ref. 12 for our mixture MP + HW is larger than we got, but it coincides with values of Q in fits 12 and 15 in Table II using the same crossover functions.

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