

Critical Dynamics of a Sheared Micellar Solution¹

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We have investigated the dynamic behavior of a nonionic micellar solution of tetra-ethylene glycol *n*-decylether (C₁₀E₄) in water near its critical point in the presence of shear. The non-Newtonian behavior of the viscosity η can be represented by $\eta/\eta^* = [1 + a(S\tau_c)^2]^{-\omega}$, where η^* is the viscosity in the absence of shear, S is the shear rate, τ_c is the lifetime of the critical fluctuations, a is a system-dependent constant, and $\omega = 0.02$. In addition, we have found that, before attaining a steady state, the sheared mixture undergoing phase separation shows significant shear-dependent rheological effects due to the presence of concentration domains.

KEY WORDS: critical dynamics; micellar solution; shear effects; spinodal decomposition; viscosity.

1. INTRODUCTION

Amphiphilic compounds are characterized by the feature that the molecules contain two chemical species that differ greatly in their solubility. Often one of the chemical species is a water-soluble hydrophilic group and the other chemical species is hydrophobic. As a consequence of the frustration arising from having both polar and nonpolar molecular components, these molecules find it difficult to phase-separate at macroscopic scales and thus amphiphilic compounds tend to form self-assembling mesoscopic ("micelle") structures. A simple micelle consists of a spherical aggregate of a few nm in diameter with the polar portions of the molecules on its surface and

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the hydrocarbon chains forming a micelle core. This type of micelle can exist in isotropic liquid phases at concentrations as low as a few percent amphiphiles in water. Phase separation into a micelle-poor phase and a micelle-rich phase can be observed by raising the temperature. The minimum temperature of this phase-separation curve as a function of composition is the lower critical mixing point of the micellar solution [1-3].

Sufficiently close to the critical point the viscosity η of fluids exhibits a weak enhancement of the form $\eta \propto \xi^x$ with $x \simeq 0.06$ [4-6]. Here ξ is the correlation length of the order-parameter fluctuations, which diverges as $\xi = \xi_0 \varepsilon^{-\nu}$, where $\varepsilon = |T - T_c|/T_c$ is the reduced difference between the actual temperature T and the critical temperature T_c and where $\nu = 0.630$ is the usual universal critical exponent of the correlation length of Ising-like systems. In the presence of macroscopic flows the fluctuations may be affected strongly by shear if the lifetime $\tau_\xi = 6\pi\eta\xi^3/k_B T$ of the fluctuations, where k_B is Boltzmann's constant [7], becomes larger in magnitude than the characteristic time associated with the flow process; this leads to non-Newtonian behavior [8]. Onuki and Kawasaki [9] investigated theoretically the non-Newtonian effects as well as a shift of the critical temperature resulting from such flow processes. Subsequently Onuki [10] considered rheological effects in a phase-separating fluid, where a dynamical balance between the growth of concentration domains and their deformation against capillary forces associated with the interfacial tension can be achieved. During recent years a significant body of theoretical and experimental work has been devoted to shear-induced critical phenomena [8-19].

In this paper we consider the behavior of the viscosity of a micellar solution near its critical mixing point in the presence of flow. Micellar solutions are sensitive to shear, so that experiments with micellar solutions can contribute to our understanding of shear-induced critical dynamics.

2. EXPERIMENTS

The experiments have been performed with a solution of tetra-ethylene glycol *n*-decylether ($C_{10}E_4$) in water at its critical composition. The phase behavior of this micellar solution has been investigated by Lang and Morgan as a function of concentration and temperature [1]. It has been verified that $C_{10}E_4$ + water belongs to the same critical-point universality class as ordinary fluids and fluid mixtures [1, 6, 20-22]. The relevant critical-exponent values are summarized in Table I.

The viscosity measurements were obtained with a rotational viscometer constructed so as to allow simultaneous observations of light-scattering patterns formed by forward-scattered light [8, 23]. The critical mixture located between two vertical cylinders separated by an annular gap of

Table I. Critical Power Laws

Osmotic susceptibility	$\chi \propto c^\gamma$	$\gamma = 1.25 \pm 0.02$
Correlation length	$\xi \propto c^{-\nu}$	$\nu = 0.63 \pm 0.01$
Viscosity	$\eta \propto \eta^0 c^{\alpha} \xi^{\beta} \propto c^{\alpha - \beta \nu}$	$\alpha = 0.065 \pm 0.008$ $\beta = 0.041 \pm 0.005$
Lifetime of fluctuations	$\tau_c \propto \xi^z$	$z = 3.04 \pm 0.08$

(1.00 ± 0.04) mm was subjected to a shear stress produced by driving the rotation of the inner cylinder with an electrically induced magnetic field whose strength could be varied continuously. Details of the experimental method will be presented elsewhere [4]. In addition a provision was made to quench the mixture by a sudden change of the pressure *P*. This pressure was applied to the mixture in the viscometer by dry nitrogen. The pressure dependence of the critical temperature *T_c* was found to be *dT_c/dP* = (10.7 ± 0.4) mK · bar⁻¹.

The viscometer was calibrated with pure water as the calibration fluid. The shear rate *S* was calculated from the measured angular velocity of the inner cylinder and the radii of the inner and outer cylinders. The viscosity *η* and the shear rate *S* were determined with an absolute uncertainty of 3% and 2%, respectively. However, since all measurements were obtained under the same instrumental conditions, the relative uncertainties in *η* and *S* are only 0.4% and 0.2%, respectively; these are the uncertainties relevant for the analysis of the temperature and shear-rate dependence of the viscosity.

3. RESULTS

We have measured the viscosity of the micellar solution at the critical concentration as a function of the shear rate *S* at various temperatures close to *T_c*. Onuki and Kawasaki [9] predicted that at the critical temperature *η* should depend weakly on *S* as *S*^{-ω} with ω = α/z = 0.021. As reported in a previous paper, we have indeed observed a small but noticeable dependence of the viscosity on the shear rate *S*, such that at *T* = *T_c*, *η* = *η*₀ *S*^{-ω} in the range 2.7 ≤ *S* ≤ 36 s⁻¹ with *η*₀ = (3.22 ± 0.02) mPa · s and ω = 0.021 ± 0.003, in excellent agreement with the theoretical prediction [8].

To include the shear-rate dependence of the viscosity at temperatures close to *T_c* we consider a scaling law of the form

$$\eta/\eta^* = [1 + aX^2]^{-\omega/2} \tag{1}$$

where *X* = *Sτ_c*. This scaling law was originally suggested to us by Seki [25] and has also been proposed by Douglas [17]. In Eq. (1) *η*^{*} is

treated as the viscosity in the absence of shear, which can be represented by [6]

$$\eta^*/\eta^B = (Q_0\xi)^x = A\varepsilon^{-\phi} \quad (2)$$

where $A = (Q_0\xi_0)^x$ is a system-dependent constant and η^B is a background viscosity. In the present analysis we have identified this background viscosity with the experimental viscosity $\eta^B = 2.73 \text{ mPa}\cdot\text{s}$ observed at $T_c - T = 1.22 \text{ K}$. The scaling law as given by Eq. (1) satisfies the expected boundary condition that for $X \rightarrow 0$ the first derivative of η with respect to X should vanish. For $X \gg 1$, Eq. (1) implies $\eta/\eta^* \propto X^{-\omega}$. Thus at a fixed temperature, i.e., at a fixed value of τ_ξ , $\eta/\eta^* \propto S^{-\omega}$. On the other hand, at a fixed value of the shear rate S , Eq. (1) yields $\eta/\eta^* \propto \tau_\xi^{-\omega} \propto \xi^{-x}$, which approaches a constant value at T_c , since η^* diverges as ξ^x . The scaling law given by Eq. (1) implies that at very small values of X the viscosity will approach the value η^* in the absence of shear.

In Fig. 1 we have plotted logarithmically our experimental values of η/η^* as a function of the scaling parameter $X = S\tau_\xi$. The data cover a range from $X = 0.0092$ to $X = 680$ and collapse approximately onto a single curve. The solid curve in Fig. 1 represents the scaling law (1) with $a = 0.02$ and $\omega = 0.02$. We conclude that the observed non-Newtonian viscosity may be represented by a simple function of the product of the shear rate S and the lifetime τ_ξ of the fluctuations.

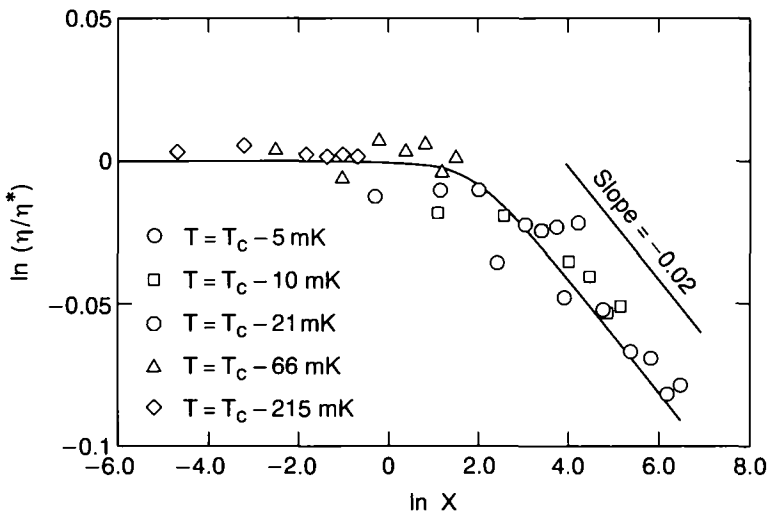


Fig. 1. Log-log plot of the viscosity ratio η/η^* as a function of $X = S\tau_\xi$, where S is the shear rate and where $\tau_\xi = 6\pi\eta^*\xi^3/k_B T$ is the lifetime of the critical concentration fluctuations.

We have also investigated the effects of shear at temperatures above the critical temperature. In a first set of experiments we observed the forward light scattered from the sheared mixture in the gap between the inner and outer cylinders of the viscometer as a function of temperature. Starting at a temperature below T_c , we raised the temperature slowly at a finite value of the shear rate S . The light-scattering pattern would remain essentially unchanged at $T \geq T_c$ until a characteristic temperature $T_0(S)$ was reached, where a strongly anisotropic scattering pattern with spikes in the direction perpendicular to the flow would appear [8]. This observation can be explained by the formation of "string phases" with highly anisotropic concentration domains in the form of long tubes oriented parallel to the flow [24, 26]. We have observed the same phenomenon in an ordinary liquid mixture near the critical point [23]. The temperature difference $T_0(S) - T_c$ is not to be identified with a shift $T_c(S) - T_c$ in the critical temperature, but is appreciably larger [23]. In reduced units the new characteristic temperature $T_0(S)$ in our micellar solution depends on the shear rate S as [8]

$$\varepsilon_S(S) \equiv [T_0(S) - T_c]/T_c = \varepsilon_0 S^p \quad (3)$$

with $\varepsilon_0 = (1.35 \pm 0.11) \times 10^{-5}$ and $p = 0.51 \pm 0.03$ in the range $2.7 \leq S \leq 36 \text{ s}^{-1}$. The value of the exponent p agrees with the value $p = 1/\nu_c = 0.52$ for the shear-rate dependence of the critical temperature $T_c(S)$ [11, 12, 27]. Since the process of phase separation is suppressed at $T_c \leq T \leq T_0(S)$, we were also able to measure the viscosity at these temperatures. The viscosity measured at $T \simeq T_0(S)$ could be represented by

$$\eta \propto S^{-\omega} \quad (4)$$

with $\omega = 0.021 \pm 0.004$ in the reduced-temperature range $2.39 \times 10^{-5} \leq \varepsilon_S(S) \leq 8.21 \times 10^{-5}$ corresponding to $2.7 \leq S \leq 36 \text{ s}^{-1}$. The ratio η/η^* was approximately equal to 1.02 ± 0.02 in this range.

To study the effect of shear on the actual phase-separation process we quenched the system into states that effectively correspond to a temperature larger than $T_0(S)$. At a given S we would raise the temperature to $T_0(S)$ at an elevated pressure $P = P_0 + \Delta P$, where P_0 represents atmospheric pressure and $\Delta P = 1.96 \text{ bar}$, and then apply a pressure quench to $P = P_0$. If we assume that $dT_0(S)/dP = dT_c/dP$, these pressure quenches correspond to effective temperature quenches $T - T_0(S) = 21 \text{ mK}$. At shear rates ranging from $S \simeq 0.2$ to 38 s^{-1} we measured the viscosity η as a function of the time t after the quench. In Fig. 2, we have plotted $\Delta\eta/\eta^* = (\eta - \eta^*)/\eta^*$ as a function of the logarithm of the product St , where η^* is the viscosity expected in the two equilibrium phases in the absence of shear.

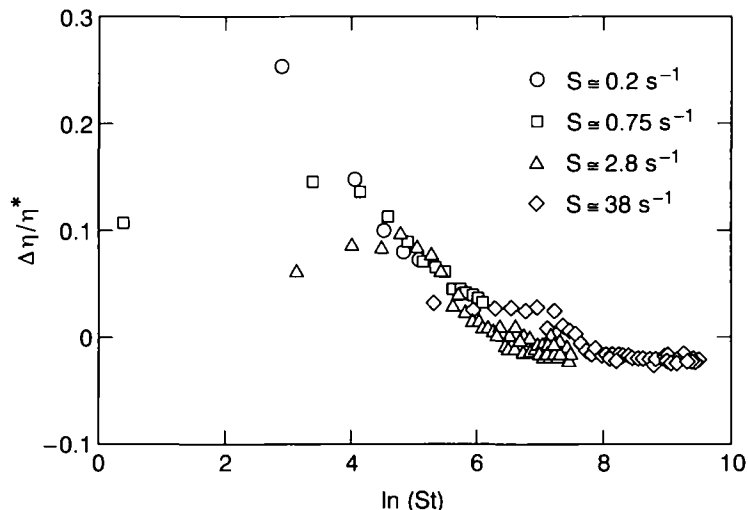


Fig. 2. The effective viscosity enhancement $\Delta\eta/\eta^*$ as a function of the product of the shear rate S and the time t after a pressure quench corresponding to $T - T_0(S) \approx 21$ mK.

We note that the decrease of $\Delta\eta/\eta^*$ with increasing St is roughly similar for the various experimental runs. Hence, we find that a steady state with $\Delta\eta/\eta^* = 0$ is reached faster as the shear rate becomes larger. In addition we find that the sheared mixture undergoing phase separation shows large shear-dependent rheological effects before the steady state is reached, as earlier suggested by Onuki [10] and observed in some previous experiments [28].

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