

Shear Effects in a Micellar Solution Near the Critical Point¹

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This paper is concerned with rheological properties of a phase-separating mixture in the presence of macroscopic shear flow. Specifically, we have investigated the shear viscosity of a nonionic micellar solution in shear-induced quasi-stationary states, where a dynamical balance between the growing concentration domains and the suppression by shear is established. During the phase separation, when concentration domains of the two phases with viscosity difference are formed, the measured viscosity of all mixtures as a function of temperature is found to satisfy to a good approximation a novel rheological equation proposed by Onuki. In addition, we have determined that the observed characteristic temperature related to the crossover from the shear-affected regime to the shear-unaffected regime depends on the shear rate as S^ν , with $\nu = 1 - \nu z \approx 0.51$, where ν and z are universal critical exponents associated with the range and decay rate of the critical fluctuations. This power law dependence on S , expected for a mixture at the critical composition, appears to be valid also for all off-critical mixtures.

KEY WORDS: critical phenomena; micellar solution; phase separation; rheology; viscosity.

1. INTRODUCTION

Much attention has been directed lately to shear-induced effects on the critical fluctuations associated with order parameters and on phase-separating

¹ Paper presented at the Fourth Asian Thermophysical Properties Conference, September 5–8, 1995, Tokyo, Japan.

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concentration domains. Extensive theoretical and experimental studies of shear-induced phenomena have been reported during the last two decades [1]. Near a critical mixing point fluid mixtures exhibit large concentration fluctuations characterized by a long-range correlation length $\xi = \xi_0 \varepsilon^{-\nu}$ with a universal value of $\nu \simeq 0.63$ where ξ_0 is a system-dependent length and $\varepsilon = |T - T_c|/T_c$ is the reduced temperature distance between the critical temperature T_c and the actual temperature T . The lifetime t_ξ of the fluctuations is given by $t_\xi = 6\pi\eta\xi^3/k_B T$, with η being the shear viscosity satisfying a dynamical scaling law of the form $\eta \sim \xi^x$ [2]. Here $x \simeq 0.065$ is again a universal exponent. Since t_ξ diverges strongly as ξ^z with a dynamical scaling exponent $z = 3 + x$ in the vicinity of a critical mixing point, these fluctuations can be greatly affected by shear sufficiently close to T_c . Moreover, phase separation occurs and bicontinuous or percolating inhomogeneous concentration domains emerge and grow with the coarsening process as $R \sim (\sigma/\eta) t$, when a critical mixture is brought into a thermodynamically unstable state inside the phase boundary. Here R is the effective size of the concentration domain and σ the surface tension. A remarkable result is that in this region the spinodal ring, observed by light scattering from a phase-separating mixture, under shear becomes strongly anisotropic due to the presence of significantly elongated concentration domains along the direction of flow [3]. Because of critical-point universality such a phenomenon, arising from a coupling between phase separation and macroscopic flows, is sometimes referred to as critical-point rheology [4, 5]. Thus, the investigation of flow-induced effects in fluid mixtures near a critical point is a very interesting subject, which may be expanded in range of interest to nonlinear rheological behaviors in terms of dynamical scaling.

Furthermore, the critical behavior of self-assembling microstructured fluids such as amphiphilic mixtures has been elucidated in terms of critical-point universality [6]. Amphiphilic compounds are characterized by possessing two molecular groups which differ greatly in their solubility, for example, a hydrophilic group which tends to be water soluble and hydrocarbon insoluble. As a consequence of their dual nature—the presence of both polar and nonpolar portions in the same molecule—micelles are formed in either aqueous or hydrocarbon solvents. Their surface activity, i.e., the ability to solubilize other fluids, arises from the cooperative association of relatively large number of small detergent-like amphiphilic molecules. This nature renders micelles both important and useful in numerous technical and biological processes. Phase separation into two isotropic micelle-poor and micelle-rich phases can be observed in a water-rich region by raising the temperature. In this paper we present results of an experimental investigation of the rheological properties

of a micellar solution when, near the critical mixing point, the concentration domains formed during phase separation are subjected to shear.

2. PROCEDURE

A common family of nonionic amphiphilic alkyloxyethylene glycol monoether is often referred to as C_iE_j . In the present work we investigated mixtures of $C_{10}E_4$ + water in Couette flow. The measurements were performed with a rotational Zimm–Crothers viscometer as the shearing cell, while a provision was made to observe simultaneously light scattered by the solution. The critical properties of $C_{10}E_4$ + water mixtures, as well as a description of the experimental apparatus, have been reported in a previous publication [5]. Here we describe only the essential details. The shearing cell consists of concentric cylinders made of Pyrex and contains the sample mixture between the two vertical coaxial cylinders that was subjected to shear. Our viscometer was calibrated with pure water; the shear rate S and the viscosity η were measured with an absolute accuracy of 2% in S and 3% in the viscosity η . However, since all measurements were obtained under the same instrumental conditions, the relative errors in S and η relevant for the analysis in the current work are 0.2 and 0.4%, respectively.

In a typical experiment, we started with the sample at a temperature about 1 K below the phase-separation temperature T_p and raised the temperature while maintaining a constant shear stress. The appearance of the spinodal ring around the directly transmitted central spot of the laser beam passing through a near-quiescent portion of the mixture indicates when the temperature has passed through the phase-separation temperature. Further heating raises the temperature of the mixture to a characteristic value at which we observe strongly anisotropic scattering perpendicular to the flow direction from the sheared portion of the mixture [7]. To determine these crossover temperatures, experimental runs were performed for four off-critical mixtures at constant composition. Measurements of the effective viscosity in the unstable region inside the phase boundary were performed in quasi-stationary states of the phase-separating critical and off-critical mixtures as a function of the temperature for shear rates S higher than $S \sim 10 \text{ s}^{-1}$, while the shear rate S was still lower than the relaxation rate $1/t_{\xi'}$ of the concentration fluctuations with correlation length ξ' . Here ξ' denotes the correlating length in the coexisting phases because the mixture is now located inside the coexistence curve.

3. RESULTS

The viscosity of a quiescent critical mixture satisfies a power law of the form

$$\eta/\eta^{\text{B}} = (Q_0 \xi)^x = A \varepsilon^{-\phi} \quad (1)$$

with $A = (Q_0 \xi_0)^x$ and $\phi = vx \simeq 0.04$ [7]. Here v^{B} is a regular part of the viscosity and Q_0 a system-dependent constant. For $t_\xi \gg S^{-1}$, the fluctuations are affected significantly by shear, while a shear rate has a negligible effect on the lifetime of the fluctuations for $t_\xi \ll S^{-1}$. One distinguishes between a strong-shear regime corresponding to $St_\xi > 1$ and a weak-shear regime corresponding to $St_\xi < 1$. The crossover between the shear-affected and the shear-unaffected regime corresponds to $St_\xi = 1$. The dependence of the reduced crossover temperature $\varepsilon_s(S) = [T_s(S) - T_c]/T_c$ corresponding to $St_\xi = 1$ inside the phase boundary is given by

$$\varepsilon_s(S) = \varepsilon_0 S^p \quad (2)$$

with $p = 0.51 \pm 0.03$, in accordance with the theoretically expected value $p = 1/vz$ for the one-phase region [4, 8]. It is noted here that the characterization of the shear effect as weak or strong refers to its effect on critical fluctuations, not on concentration domains in the process of phase separation. According to our experimental observations, upon a further increase in temperature to the crossover temperature T_s , the system enters the weak-shear regime and strong forward scattering appears [9]. This implies that the phase-separating domains are concentration inhomogeneities that are stronger in concentration contrast, and they produce much intense and forward scattering in the form of a sharp streak perpendicular to the flow direction, indicating the onset of highly elongated concentration domains, sometimes referred to as a *string phase* [1]. Such large elongation of concentration domains occurs even in the weak-shear regime.

In the present study we examined the validity of Eq. (2) for $C_{10}E_4$ + water mixtures with off-critical concentrations from $C \simeq 0.018$ to 0.026, where C is the mass fraction of $C_{10}E_4$. Here we define $T_{p,s}(S)$ as the characteristic crossover temperature associated with the mixtures with off-critical concentrations. In Fig. 1 we show that the values measured for these crossover temperatures collapse onto a single curve with a slope of 0.51, when plotted in terms of $\varepsilon_{p,s}(S) = [T_{p,s}(S) - T_p]/T_c$. At the critical concentration, i.e., when $T_p = T_c$, the crossover temperature $T_{p,s}(S)$ is identical to $T_s(S)$ in Eq. (3). The experimental results obtained for a critical mixture as a function of the shear rate S are indicated by the filled circles

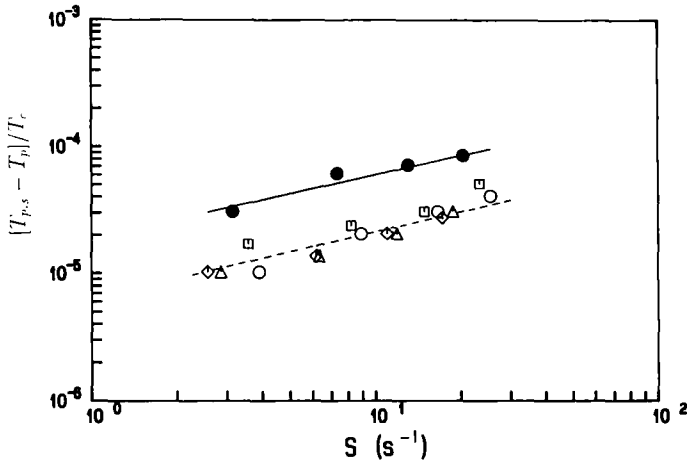


Fig. 1. Plots of the reduced temperature distance $[T_{p,s} - T_p]/T_c$ as a function of S for the critical mixture with $C \approx 0.022$ m.f. (filled circles) and four off-critical mixtures with $C \approx 0.018$ m.f. (open circles), $C \approx 0.020$ m.f. (squares), $C \approx 0.024$ m.f. (triangles), and $C \approx 0.026$ m.f. (diamonds), respectively, where the solid and dashed lines represent a slope of $p = 1/\nu \approx 0.51$.

in Fig. 1 and the solid line represents Eq. (3) with $\epsilon_0 \approx 1.9_4 \times 10^{-5}$ and $p \approx 0.51$. The dashed line is given by

$$\epsilon_{p,s} = \epsilon_{p,0} S^p \tag{3}$$

with a slope identical to $p = 0.51$ obtained for the critical mixture and $\epsilon_{p,0} = (\xi'_0/\xi_0)^{1/\nu} \epsilon_0 \approx 0.34\epsilon_0$. The present result indicates that the shear dependence of the characteristic crossover temperature for a mixture with an off-critical concentration is the same as that for a mixture with the critical concentration, while the prefactor differs in accordance with $(\xi'/\xi)^{1/\nu}$ as derived from a tentative scaling. Our result is essentially compatible with that obtained by Fujioka et al. [10] for semidilute polymer mixtures.

Beyond $T_{p,s}(S)$ inhomogeneous concentration domains appear which are deformed significantly by the shear. Our previous experiments have indicated that shearing of a phase-separating critical mixture results in the formation of a nearly stationary string-like phase, namely, a dynamically stationary two-phase state, in which the concentration domains are stable and elongated but do not resist shearing resulting again in Newtonian behavior [5]. Remarkably a quasi-stationary state can be achieved, accompanied by the formation of string-like domains ordered in space along the flow direction, suggesting that the phase separation may be stopped by shear. In the case of phase-separating mixtures of $C_{10}E_4$ + water, this

happens for shear rates larger than $S \simeq 10 \text{ s}^{-1}$, while the system should be located in a region referred to as a weak-shear region according to the usual hydrodynamic equations [4]. Since at a temperature above T_c the system consists of two coexisting mixture phases whose concentrations differ by $C_2 - C_1 \propto \varepsilon^\beta$, with the coexistence-curve exponent $\beta \simeq 0.35$, the difference in the viscosity between the domains increases as the concentration difference increases upon raising the temperature. Here C_1 and C_2 are the concentrations of $C_{10}E_4$ in the dilute phase and the concentrated phase at the coexistence curve. Very recently, Onuki extended his theory [4] of rheological properties of mixtures near a critical point to the more general case of phase-separating concentration domains having a viscosity difference. It is considered that the velocity fields associated with the phase-separating two phases, which determine the domain structure as well as the associated volume fraction, are asymmetric. He has suggested a novel rheological property of the phase-separating Newtonian-like fluid mixtures by considering the condition of bicontinuity of the concentration domains [11]. The viscous stress ηS associated with the domain must balance at the interface. This leads to $R_1/\eta_1 \sim R_2/\eta_2$, where the subscripts 1 and 2 denote the quantities associated with the less viscous phase and the more viscous one, respectively. The macroscopic shear S can be related to S_1 and S_2 by $(R_1 + R_2) S \sim R_1 S_1 + R_2 S_2$, leading to

$$\eta \sim 1/[\phi_1/\eta_1 + \phi_2/\eta_2] \quad (4)$$

where ϕ_1 and $\phi_2 = 1 - \phi_1$ are the total volume fractions of water-rich and $C_{10}E_4$ -rich concentration domains. By considering the symmetric features of the physical properties at the critical point, we take the prefactor in Eq. (4) to be unity. In Fig. 2, we show the viscosities measured for the critical and off-critical $C_{10}E_4 + \text{water}$ mixtures at a fixed shear rate S . To compare our result with Eq. (4) predicted by Onuki, we need to evaluate that the viscosities and the associated volume fractions are identical to the isothermal values at the two-equilibrium phases at the phase boundary. The background viscosities η_1^B and η_2^B along the two branches of the coexistence curve were evaluated from measured values of the viscosity as a function of the concentration at a fixed temperature of $T_c - T \simeq 1 \text{ K}$ on the basis of numerical data of the coexistence curve reported by Lang and Morgan [12]. In the temperature range studied here the background viscosity is insensitive to the temperature variation, amounting to less than 0.5%. Having determined the background contributions to the viscosity, we evaluated the critical viscosities η_1 and η_2 as $\eta_1/\eta_1^B = \eta_2/\eta_2^B = A\varepsilon^{-\phi}$ with $A \simeq 0.74$ and $\phi \simeq 0.04$ [7]. Typical differences in the estimated viscosities for η_1 and η_2 for the critical mixture $C_{10}E_4 + \text{water}$ were $\eta_2/\eta_1 \simeq 2.1$ at

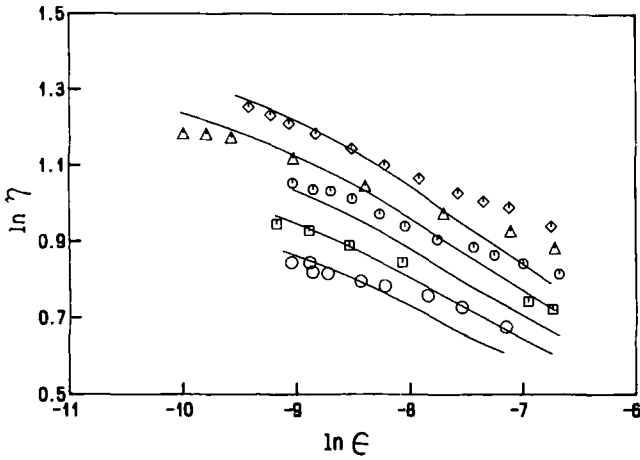


Fig. 2. Plots of the effective viscosity η as a function of $\varepsilon = [T - T_c] / T_c$ for the mixtures with $C \approx 0.018$ m.f. (circles), $C \approx 0.020$ m.f. (squares), $C \approx 0.022$ m.f. (octagons), $C \approx 0.024$ m.f. (triangles), and $C \approx 0.026$ m.f. (diamonds). The solid lines denote the calculated viscosity η , deduced from Eq. (4), as a function of ε for the mixtures with the corresponding concentrations.

$\varepsilon \approx 5.45 \times 10^{-5}$ and $\eta_2/\eta_1 \approx 5.5$ at $\varepsilon \approx 8.17 \times 10^{-4}$. The volume fraction ϕ_1 was calculated from [13]

$$\phi_1 = \left[X_1 \frac{M_w}{\rho_w} + (1 - X_1) \frac{M_s}{\rho_s} \right] (X_2 - X) \left/ \left[X \frac{M_w}{\rho_w} + (1 - X) \frac{M_s}{\rho_s} \right] (X_2 - X_1) \right. \tag{5}$$

where ρ_w and ρ_s are the densities, and M_w and M_s the molecular weights of pure water and pure $C_{10}E_4$ respectively. X is the mole fraction of the sample mixture, and X_1 and X_2 are the mole fractions of $C_{10}E_4$ in the dilute and the concentrated phases. Because $C_{10}E_4 + \text{water}$ is a nearly density-matched mixture, we set $\rho_s = \rho_w$. For the critical and four off-critical mixtures we have calculated ϕ_1 as a function of the temperature from Eq. (5) and, hence, the effective viscosity from Eq. (4). The effective viscosities thus obtained for the critical and the four off-critical mixtures are shown by the solid curves in Fig. 2. In spite of possibly large errors in calculating the viscosities and the corresponding volume fractions, the typical difference between the measured and the calculated effective viscosities is at most about 15%.

In summary, we have examined rheological properties of phase-separating nonionic micellar solutions under macroscopic shear flow. It has

been established that the shear-dependent characteristic temperatures for the critical and off-critical mixtures vary as S^p , with $p = 1/\nu z \simeq 0.51$ derived from the dynamical scaling. The effective viscosity of a phase-separating mixture in a quasi-stationary state under shear can be represented by the equation of Onuki derived from the bicontinuous condition that the shear stresses should balance at the interface when the emerging two phases have different viscosities.

ACKNOWLEDGMENTS

The authors are indebted to D. Ito and T. Tabata for valuable experimental assistance. We thank Professor A. Onuki for enlightening comments on the subject. The research at Gunma University and at Tokyo University of Agriculture and Technology was supported by the Ministry of Education, Science and Culture under Grant 07454089 (K.H.) and Grant 06453056 (H.U. and K.H.), and the research at the University of Maryland by the National Science Foundation under Grant D-9215128.

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