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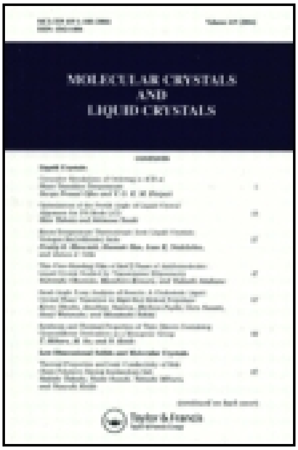

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Influence of Electrostatic Interactions on the History Dependent Rheology of Surfactant Hexagonal Phases

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INFLUENCE OF ELECTROSTATIC INTERACTIONS ON THE HISTORY DEPENDENT RHEOLOGY OF SURFACTANT HEXAGONAL PHASES

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The time-dependent response of hexagonal phases of nonionic and anionic surfactant systems to stepped strain has been investigated. It was found that the rheology of the anionic system is very sensitive to the degree of the surfactant charge screening. Two types of transitions were detected: strain-induced, i.e. transitions associated with the yielding of most of the domains of the system when their energy becomes close to the yield energy, and noise-induced, i.e. yielding of most of the domains of the system due to domain coupling. It was found that the transitions in the nonionic system are mostly associated with strain-induced yielding events, while noise-induced yielding plays an important role in the process of domain rearrangement/fusion in anionic systems. Consequently only long-range forces provide a sufficient domain coupling for noise-induced yielding to take place.

Keywords: electrostatic interactions; SGR model; stepped strain; surfactant hexagonal phase

INTRODUCTION

Ordered mesophases attract much attention due to their rich rheology. However, the effect of intermolecular forces on the rheology of surfactant ordered mesophases seems not to have been studied systematically.

The results obtained for the lamellar phase of the AOT/water system revealed a distinct concentration dependence of the rheological material functions of the system [6]. It has been shown that the minimum of the concentration dependence of the elastic modulus and shear viscosity of the system corresponds to the minimum in coulombic interactions between

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double layers and, consequently, between microdomains of the lamellar phase. The rheology of the AOT/water lamellar phase was also reported to be very sensitive to the addition of salt or hydrocarbons, which causes a decrease in the elastic modulus of the system [2].

The dynamics of an "onion" state of a lamellar phase in ionic surfactant systems also depends on of degree of the surfactant charge screening. Systems with high salt content experience a transition from monodisperse multilamellar vesicles with no long-range order, to a state with long range order, and then to an ordered state of much bigger vesicles, with an increase of shear rate [3,4]. On the other hand, in salt-free systems the "onion" size is not shear rate dependent [5].

In the present paper we attempt to establish the role of electrostatic interactions on the rheology of a surfactant hexagonal phase. For this purpose we investigated the stepped strain response of a nonionic system and an anionic system with various degrees of surfactant charge screening.

EXPERIMENTAL PROCEDURE

We investigated the quaternary system of sodium dodecyl sulfate (SDS) (BDH Laboratory Suppliers, England, 99% purity), pentanol, brine (or water) and cyclohexane. Systems with 0.5 and 0.4 M brine were used. In all systems the polar solvent/SDS weight ratio was equal to 2.5 while the cyclohexane and pentanol content was 65 and 4 wt.% of the total weight of the mixture respectively for the system with 0.5 M brine, 61.5 and 4.7% for the system with 0.4 M brine, and 34 and 8% for the salt-free system.

We also investigated a binary system of hexaethylene glycol monododecyl ether ($C_{12}E_6$) (Fluka, Switzerland, >98% purity), water with 50 wt.% content of the surfactant. At the above compositions all these systems are reported to display swollen hexagonal phases at room temperature [6,7], and we confirmed this by polarising microscopy.

The rheological measurements were performed in a Couette geometry on a strain-controlled Bohlin VOR rheometer (BRS VOR 7:9, Sweden). The Couette cell consisted of a fixed inner cylinder of 7 mm radius and a rotating outer cylinder, with a 0.7 mm sample gap.

In the relaxation tests, a strain γ_0 was applied and the time dependence of the relaxation modulus $G(t) = \sigma(t)/\gamma_0$ was measured (here $\sigma(t)$ is the stress). Series of experiments with applied strains from 5 up to 100% were performed. In our experimental set-up 100% strain corresponds to $\gamma_0 = 0.15$, where the shear strain is defined as $\gamma = \theta(R_o + R_i)/2(R_o - R_i)$ with θ being the angular displacement of the outer cylinder and R_o and R_i being the radii of the outer and the inner cylinders of the Couette cell

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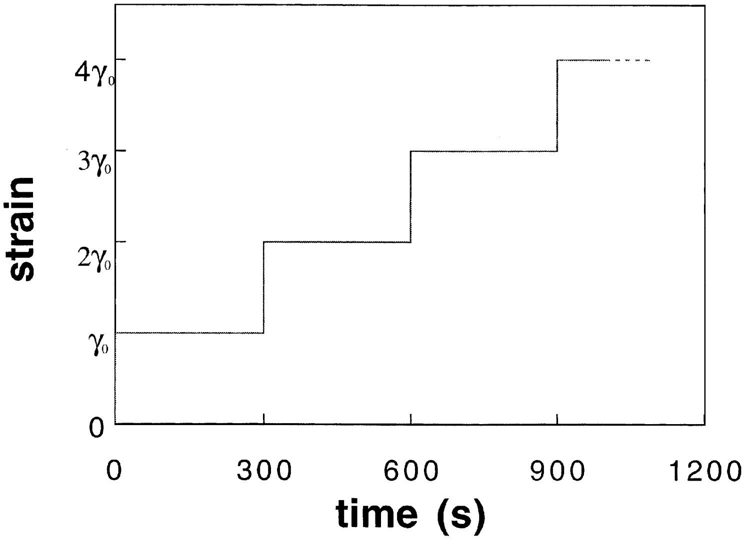

FIGURE 1 Time dependence of strain applied to the systems under investigation. The values for γ_0 are given in the text.

correspondingly. Each of the series of measurements consisted of 19 relaxation experiments lasting 300 s each with a strain rise time of 0.1 s (Fig. 1). Each successive relaxation measurement in the series started immediately after the previous one was finished. In other words the waiting time t_w, i.e. the time elapsed from the beginning of the first measurement in the series, had an increment of 300 s from measurement to measurement. All relaxation experiments were performed at 25 ± 0.2°C.

To avoid any pre-shearing of the samples, the anionic systems were cooled down to 2°C once loaded in the measuring system, while the nonionic system was heated up to 50°C (at these temperatures the samples are in isotropic states). After that the samples were heated up/cooled down to 25°C and left at this temperature for 4 hours or more before the measurements were performed. This procedure gave reproducible results. All experiments were repeated at least three times.

THEORY. THE SOFT GLASSY RHEOLOGY MODEL (SGR)

In the SGR model [8,9] the macroscopic sample is regarded as a combination of mesoscopic elements. Each element is assigned a local strain l, and a corresponding stress kl (k is an elastic constant), which describes deformations away from some local position of unstressed equilibrium

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relative to neighbouring elements. The local strain of an element is supposed to follow the imposed strain until it reaches its yield value l_y. At this point the element rearranges to a new configuration, where it is less deformed. Thus, yielding provides a mechanism of stress relaxation, while between yield events the material behaves as an elastic solid of spring constant k.

Yielding in the SGR model is regarded not as a purely strain-induced phenomenon, but as an "activated" process. A mesoscopic element strained by an amount l has a certain probability of yielding in a unit time interval. This rate is τ^{-1}, where the characteristic yield time for the element with a yield energy $E = 1/2\,kl_y{}^2$ is

$$\tau = \tau_0 \exp[(E - 1/2\,kl^2)/x] \tag{1}$$

where τ_0 is the "attempt" time and x is an activation factor, regarded as an effective "noise" temperature or, alternatively, as the typical energy available for the activated process. For $x < 1$ the theoretical flow curve, i.e. a macroscopic stress response to a steady shear rate, has a macroscopic yield stress (σ_y). This behavior is characteristic of a glass phase. If such a system is strained below σ_y, it ages, while if $\sigma > \sigma_y$, the system achieves a steady state and aging no longer occurs. In the so-called "transient" regime, $1 < x < 2$, aging is absent and the behavior of the system is dominated by yielding of the mesoscopic elements.

There are two possibilities of yielding for the elements. If the element was strained up to the yield point, $1/2\,kl^2 \approx E$, it experiences a "strain-induced" yield event. On the other hand, an element with an energy much below the yield point can yield through activation dynamics once $E - 1/2\,kl^2 \approx x$ (a "noise-induced" yield event).

For the case of stepped strain applied to a system under investigation the expression for the relaxation modulus has been derived [10]. The relaxation modulus was found to depend on the measuring time $(t - t_w)$ as

$$G(t - t_w, \Delta t, n, \gamma_0) \propto \Gamma(x)[\exp(\gamma_0^2/2x)]^{2-x}(t - t_w)^{1-x} + \delta. \tag{2}$$

The correction factor δ in (2) is a function of the number of steps n, the step length Δt, and the amplitude of the applied strain γ_0, and $\Gamma(x)$ is a gamma-function. It has been shown that if the number of steps in strain and the amplitude of the applied strain are not too high the relaxation modulus could be approximated by a power function of the measuring time $(t - t_w)$:

$$G(t - t_w, t_w) \propto (t - t_w)^{1-x} \tag{3}$$

where t is the time elapsed from the beginning of the first measurement in the series and t_w is the time of strain application, the waiting time [10].

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The above approximation was found to be valid for the experimental procedure described in the experimental section for applied strains lower than 0.15 for all the measurements in the series, and the relation is valid for $\gamma_0 = 0.15$ up to the 14th step in strain [10].

RESULTS

It has been shown that anionic systems experience a number of strain and noise-induced transitions depending on the amplitude of the applied strain in the stepped strain experiments. We use the term "macroscopic transition" or "transition" for an almost simultaneous yielding of most of the elements of the system. While "local rearrangements" correspond to yielding of one or a small number of mesoscopic elements of the system. As was specified in [10], the transitions characterised by high relaxation modulus and low noise temperature before the transition have a mostly strain-induced mechanism and are therefore called strain-induced transitions, while those characterised by a low relaxation modulus and high x before the transition will be called noise-induced transitions. The details of the stepped strain response of the SDS/pentanol/cyclohexane/0.5 M brine system in the hexagonal phase are given elsewhere [10]. We would only like to mention here that the experimental results suggest that the transitions in the system are associated with rearrangement of domains with hexagonal symmetry when low strain is applied to the system and with monodomain formation when higher strain is applied.

Investigations of the relaxation in the SDS/pentanol/cyclohexane/brine system in lower ionic strength brine with almost the same spacing between cylinders, revealed that the system experiences similar transitions as in the higher ionic strength (0.5 M) case. However, the transitions induced by low strain, i.e. the transitions presumably associated with the rearrangement of domains, are shifted on the waiting time scale to shorter waiting times. For example, the transitions, induced by 20% strain, are shifted by 3000 s towards shorter waiting times in 0.4 M system. However, a decrease in the value of the applied strain results in a decrease in the transition time shift. A linear dependence of the shift of transition time on applied strain was observed (Fig. 2). Thus a 19.3% strain was found to produce exactly the same effect on the 0.4 M system as a 20% strain on the 0.5 M system.

Stronger electrostatic interactions in the system with the lower ionic strength of brine may be responsible for the observed shift in the transition times. Provided that in all systems the weight ratio of brine/SDS is the same, the screening of the SDS charge is different: the number of the excess counterions per SDS charge is 0.35 for the 0.5 M system, 0.28 for the 0.4 M system, and 0 for the salt-free system. Consequently, the

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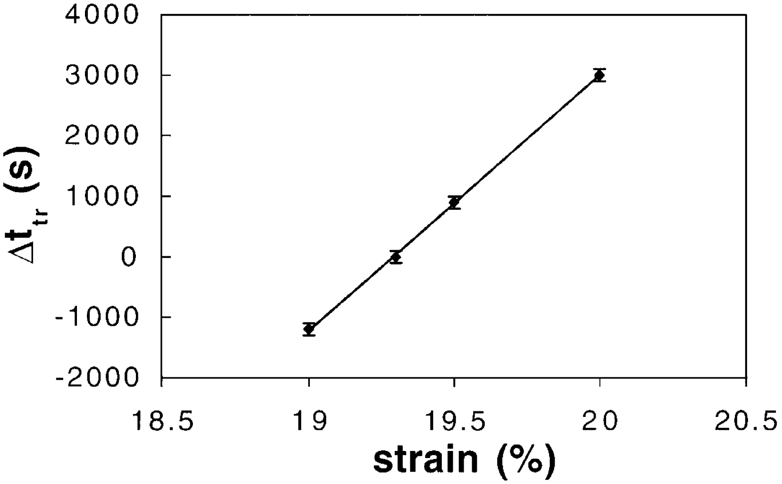

FIGURE 2 Strain-dependence of the transition time shift in the SDS/pentanol/cyclohexane/brine system with 0.4 M brine with respect to the transition times in SDS/pentanol/cyclohexane/brine system with 0.5 M brine submitted to 20% strain.

electrostatic repulsion between the cylinders is higher in the systems with lower ionic strength of brine. This suggests a higher cooperativity for domain rearrangement. The stronger correlation between the elements suggests also that less strain is required to produce the same transitions.

The above considerations relate to the transitions associated with domain rearrangements only, but not to those associated with monodomain formation. Contrary to the low strain case, positive shifts in transition times are observed when the 0.4 M or salt-free systems were submitted to high strain. However, linear dependencies of the transition time shifts on the applied strain were also observed (Fig. 3). Again we attempt to interpret these results from the point of view of the intercylinder, interdomain interactions.

In the case of low applied strain, stronger interdomain repulsion in the 0.4 M and salt-free systems induces stronger element (domain) coupling, because the rearrangement of a domain may lead to a decrease in the distances between the cylinders of this domain and those of the neighbouring ones. This induces an increase in the electrostatic repulsion between the yielded domain and the neighbouring ones and, consequently, leads to an increase in the probability of the neighbouring domain rearrangement. Provided that the Debye lengths in 0.5 M and 0.4 M systems do not differ much, the shift on the applied strain scale required to induce the transitions in both systems at the same waiting times is low, $\Delta\gamma_0 = 0.7\%$.

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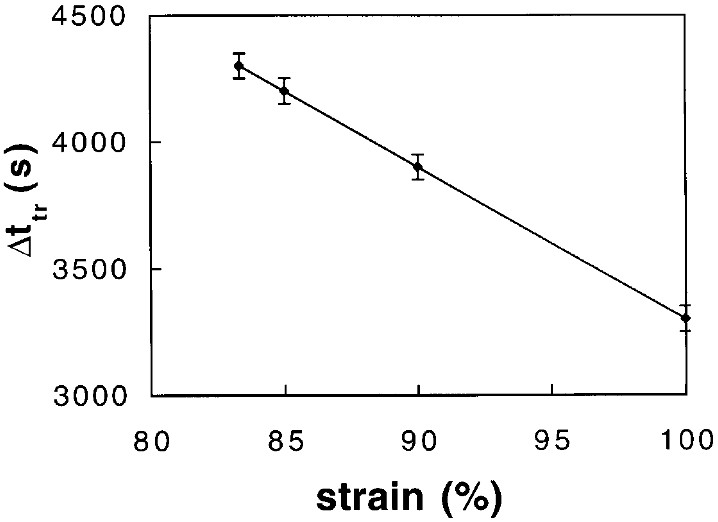

FIGURE 3 Strain-dependence of the transition time shift in the SDS/pentanol/cyclohexane/brine system with 0.4 M brine with respect to the transition times in the same system with 0.5 M brine submitted to 100% strain.

However, $\Delta\gamma_0$ is higher than 50% in the case of the high applied strain, i.e. when most of the domains presumably have the same orientation and the straining of the system induces a monodomain formation (Table I). Monodomain formation implies the annihilation of domain boundaries due to cylinder fusion. Consequently, in this case electrostatic repulsion along the cylinders rather than much weaker intercylinder repulsion plays the main role. Thus, the higher the repulsion along the cylinder is, i.e. the lower the SDS charge screening, the higher the strain that should be applied to induce monodomain formation. These effects are more pronounced in

TABLE I Dependence of the Properties of the SDS/Pentanol/Cyclohexane/Brine (water) System on the Ionic Strength of the Brine. Here h is the Thickness of Polar Solvent between the Cylinders and $\Delta\gamma_0$ is the Shift in Strain Required to Produce the Same Transitions at the Same Waiting Times as in the 0.5 M System

	0.5 M NaCl	0.4 M NaCl	Salt-free
h	2.5 nm	2.5 nm	2.5 nm
Debye length	0.4 nm	0.5 nm	1 μm
$\Delta\gamma_0$, low strain		– 0.7%	– 12%
$\Delta\gamma_0$, high strain		55%	127%

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the salt-free system. An almost tenfold increase in $\Delta\gamma_0$ compared to that in 0.4 M system is observed (Table I).

On the contrary to the case of anionic systems, in the nonionic system there are no transitions on the macroscopic level up to 100% strain. However, on the mesoscopic level some elements do experience rearrangements. At low applied strain the number of the yielded elements is low and the decrease in the macroscopic stress of the system due to yielding during the measurement is lower than the increase in stress at the beginning of the measurement. Consequently the macroscopic stress of the system increases with waiting time (Fig. 4). The number of the yielding elements increases with the applied strain. For the intermediate strain the decrease in stress due to yielding is almost equal to the increase in stress due to straining of the system and the relaxation modulus is almost independent of the waiting time (Fig. 5). For higher applied strain the number of elements yielded during the measurement is high enough to induce a decrease in stress which not only suppresses the external strain, but also lowers the macroscopic stress below its level at the end of the previous measurement. This results in a decrease in relaxation modulus with waiting

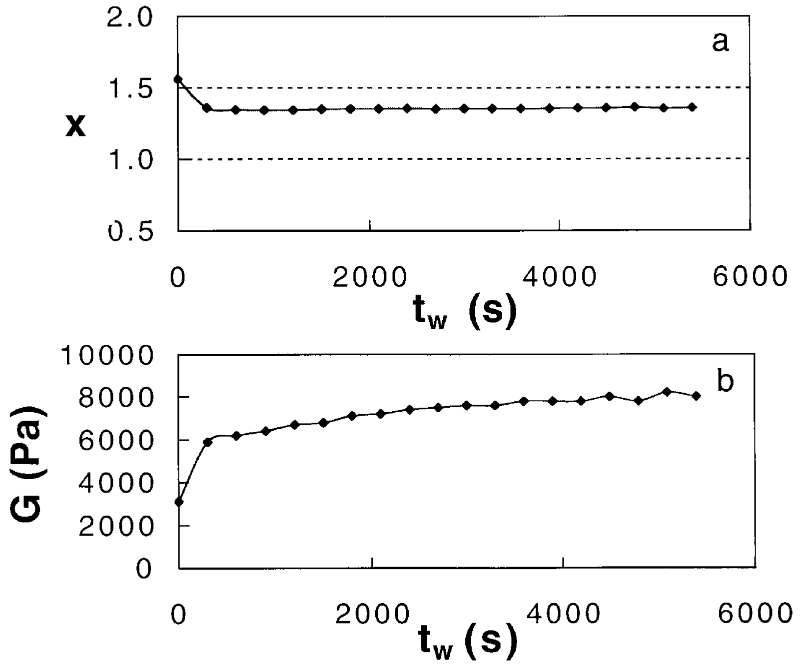

FIGURE 4 Waiting time dependence of (a) noise temperature x and (b) relaxation modulus $G(t - t_w = 1s, t_w)$ for the $C_{12}E_6$/water system submitted to 20% strain.

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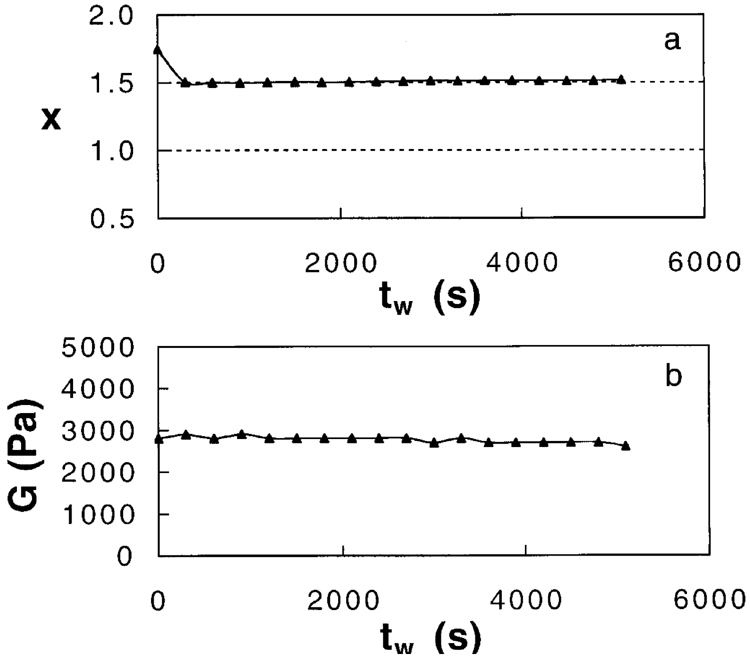

FIGURE 5 Waiting time dependence of (a) noise temperature x and (b) relaxation modulus $G(t - t_w = 1s, t_w)$ for the $C_{12}E_6$/water system submitted to 40% strain.

time (Fig. 6). We would like to stress that in spite of a considerable number of yielded elements during every measurement in the high strain regime, the number of yielding events at any moment of time is not high enough for the system to experience a transition as a whole.

It follows from Figures 5–7 that the noise temperature is independent of waiting time in all strain regimes and has a value of 1.2 in the low strain regime and $x = 1.5$ for $0.1 < \gamma_0 < 0.2$. Despite these high noise levels the system does not experience any noise-induced transitions, whereas a noise level of 1.2 was sufficient for the anionic system to experience noise-induced yielding. This indicates that although element coupling is responsible for noise-induced yielding the absolute value of the noise temperature does not directly describe the strength of the interelement interactions. The noise temperature rather reflects the degree of disorder in the system.

It appears that when there are no long-range interactions present in the system, even a high noise level is not a sufficient condition for a simultaneous yielding of most of the elements of the system. In other words although some of the elements could experience noise-induced yielding, these rearrangements remain local, not involving a sufficient number of

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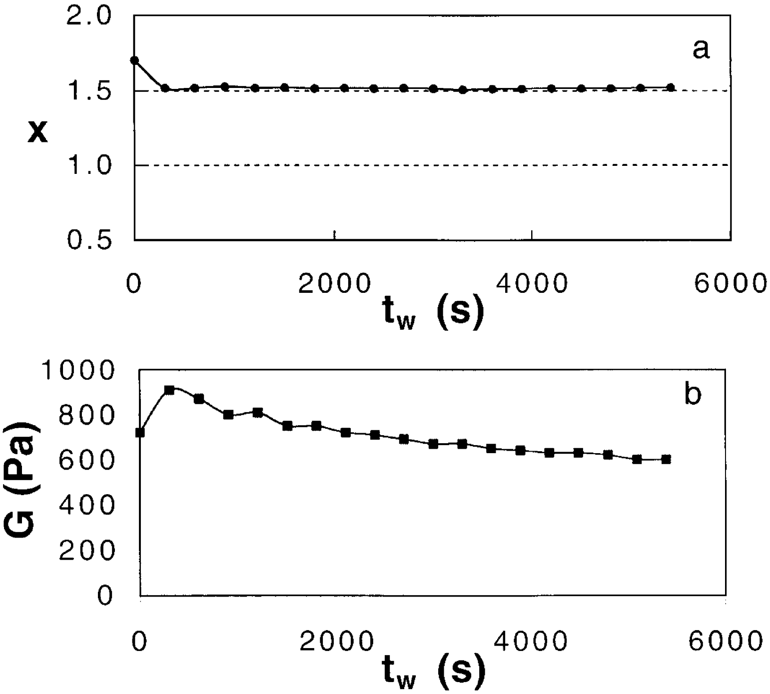

FIGURE 6 Waiting time dependence of (a) noise temperature x and (b) relaxation modulus $G(t - t_w = 1s, t_w)$ for the $C_{12}E_6$/water system submitted to 100% strain.

elements for a macroscopic transition to take place. Consequently, only long-range interactions provide a mechanism for macroscopic noise-induced yielding.

According to the experimental data for an applied strain lower than 0.2 the nonionic system does not undergo any macroscopic transitions. However, as was pointed out above, some of the elements experience rearrangements during each measurement at least in the intermediate and high strain regimes. In spite of these rearrangements the degree of disorder remains high, $x = 1.5$, indicating that there is no uniform orientation of the domains at any moment of time.

On the other hand application of higher strain, $\gamma_0 > 0.2$, seems to eliminate the disorder leading to a formation of some uniform structure. We suppose that in this regime a formation of monodomain or a number of large uniformly oriented domains takes place. As in the case of the anionic system the relaxation modulus becomes very low after the transition and the noise temperature is close to unity indicating a high degree of order in the system (Fig. 7). However, in the nonionic system this transition is

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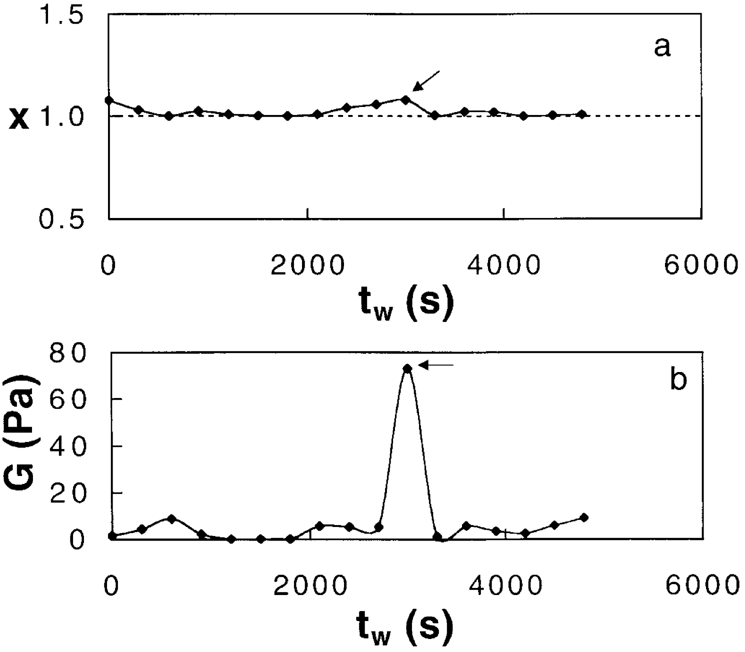

FIGURE 7 Waiting time dependence of (a) noise temperature x and (b) relaxation modulus $G(t - t_w = 1s, t_w)$ for the $C_{12}E_6$/water system submitted to 110% strain. Points highlighted by arrows correspond to the measurment, during which the transition takes place at $t - t_w = 270s$.

purely strain-induced (the noise temperature is independent of the waiting time and close to unity), while in anionic systems monodomain formation is mostly noise-induced (the noise temperature is high before the transition and drops almost to unity afterwards [10]).

The principal difference between nonionic and ionic systems with even well screened electrostatics is that the range of interactions in the nonionic system does not depend on the dynamics of the system. Although the Debye length, characterising the range of electrostatic interactions, is an equilibrium characteristic, determined by the average number of counter-ions in the ionic atmosphere of surfactant charges, the application of strain is likely to disturb the equilibrium in the system due to different mobility of the charged cylinders and low-molecular weight ions of the polar solvent. This could lead to a substantial fluctuation in surfactant charge screening resulting in a local change in the range of intercylinder electrostatic interactions and, in the case of a sufficient number of these fluctuations, could induce a macroscopic yielding event.

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CONCLUSIONS

Investigations of a hexagonal phase of an anionic surfactant have revealed that the higher the charge screening, the higher the strain required to induce rearrangement of the domains of the systems. On the other hand, the process of domain fusion requires a higher applied strain the lower the ionic strength of the polar solvent. The proposed model of these effects addresses the variation of the barrier height for the process of domain rearrangement and domain fusion due to the variation of the strength of inter- and intracylinder electrostatic interactions with ionic strength. In fact, according to SGR, there are three factors determining the probability of yielding for an element in a unit time interval. These are the yield strain (l_y), the elasticity of the elements (k), and the noise temperature (see Eq. (1)). The observed linear dependence of the transition time shifts on the applied strain in both low and high strain regimes suggests that the main factor is the change of the yield strain with ionic strength. However, the remaining two factors may also influence the transition time shifts. We leave the question of the influence of the elastic properties on the rheology of surfactant hexagonal phases for future investigation.

The nature of interactions between the domains of a hexagonal phase plays an important role in the rheology of the system. It was found that only long-range forces provide a sufficient domain coupling for noise-induced yielding to take place.

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