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Non-linear rheology and flow-induced transition of a lamellar-to-vesicle phase in ternary systems of alkyldimethyl oxide/alcohol/water

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Abstract The time-dependent transformation of an ionically charged lamellar phase (L_α -phase) into a vesicle phase under the influence of shear is investigated using rheological and conductivity measurements. The L_α -phase consists of the zwitterionic surfactant tetradecyldimethylaminoxide (C_{14} DMAO), hexanol, oxalic acid and water. The experiments were carried out on the L_α -phase in a well defined state. It was prepared by a special route from the neighbouring L_3 -phase that consists of 100 mM C_{14} DMAO, 250 mM hexanol and 5 mM oxalicediethylester (OEE). The OEE hydrolyses in the L_3 -phase to oxalic acid and ethanol. The result is a virgin L_α -phase which consists of stacked bilayers and which has not been exposed to shear. When this low-viscous phase is subjected to shear it is transformed into a highly viscous vesicle phase. The transformation of the L_α -phase into vesicles

under constant shear was monitored by recording the viscosity and conductivity with time.

It is observed that at least three different time constants can be distinguished in the transformation process. The conductivity passes through a minimum (τ_1) in the direction of shear. The viscosity first passes through a minimum (τ_2) and then over a maximum (τ_3). It is concluded that τ_1 belongs to the complete alignment of the bilayer parallel to the wall, τ_2 to the beginning of the break-up of the bilayers to the vesicles and τ_3 to the complete transformation of the L_α - to the vesicle phase. When the shear rate was varied, it was noted that the product of the time constants and shear is constant.

Key words Tetradecyldimethylamine oxide · Lamellar phase · Onion phase · Complex fluids · Rheopex behaviour

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Introduction

It is well known that amphiphilic molecules in aqueous solutions form different types of aggregates. Of much general interest in surfactant science is the structure and the dynamic behaviour of these aggregates because they can control the properties of the fluids in a desired fashion. The lamellar phase (L_α) has attracted attention in many investigations. In its ideal, and therefore simplest, form the L_α -phase consists of infinite planar bilayers of one or more amphiphilic components inter-

calated with water and stabilized by the competition of long range (10–500 nm) intermembrane interactions (Israelachvili 1991), hydration and repulsive forces (Porte et al. 1986) which can be of electrostatic or steric origin. In general, a conventional lamellar phase has a tendency to transform into a vesicle phase when the bilayers are charged with ionic surfactants. Recently Roux et al. (1993) observed that the shearing of a lyotropic lamellar phase leads to the formation of multilamellar vesicles (MLV) (onion phase) and they have shown that technological handling and size control

of vesicles is possible by exposing the vesicle phases to different shear rates. Richtering et al. (1996, 1997) detected a transition to a state where the MLV are disordered in the direction of flow, which can be characterized by a butterfly type pattern at low scattering angles in small angle neutron scattering; it has also been found at least in one case that the transition was not brought about by a certain shear rate but by a characteristic shear stress (Bergenholtz and Wagner 1996). On the other hand, our group recently discovered a novel technique of inducing phase transitions in surfactant systems in-situ by a chemical reaction (Hoffmann et al. 1998). An uncharged L_3 -phase has been transformed to a charged L_α -phase by the hydrolysis of a small ester. We also studied shear effects during the preparation of dilute vesicle phases and found a transition from MLV into small unilamellar vesicles (SUV) at higher shear rates (Bergmeier et al. 1997).

Here we report on a series of experiments relating to the structural changes in aggregates which affect the symmetric sponge phase, L_3 , the lamellar phase, $L_{\alpha h}$ and the vesicle phases MLV and SUV, as a function of shear rate. For the experiments we used the phases from tetradecyldimethylamine oxide and hexanol. Our goal was to study the time dependent transformation of the classic L_α -phase with stacked bilayers to the vesicle phase under constant shear. We used the virgin ionically charged L_α -phase that is produced by a chemical reaction and that has not been exposed to shear prior to the experiments. To the best of our knowledge this is the first time that such time-dependent measurements are reported on a well defined L_α -phase. In this investigation we are using oxalic diethyl ester (OEE) instead of formic methyl ester (FME) for the preparation of the L_α -phase. The hydrolysis of the OEE is faster than the hydrolysis of FME. For this reason we do not have to wait so long for the start of the shear after the L_3 -phase has been mixed with the ester and more measurements can be carried out per unit time. We show that at least three different time constants can be distinguished in the whole transformation process. For low shear rates the transformation times τ decrease linearly with the shear rate ($\tau \dot{\gamma} = \text{const}$) while for higher shear rates a different mechanism occurs.

Experimental

Sample preparation

The tetradecyldimethylamine oxide (C_{14} DMAO) was a gift from Hoechst Co. and was recrystallized twice from acetone before used. The oxalic diethyl ester and 1-hexanol were purchased from Fluka in p.a. quality and were used without further purification. The water was doubly distilled. For the measurements all the samples were prepared in the same way. We produced a large amount of a L_3 -phase consisting of 100 mM tetradecyldimethylamine oxide (C_{14} DMAO) and 250 mM hexanol. The L_3 -phase is a low viscous

fluid and was mixed with the appropriate amount of oxalic diethyl ester to obtain the final ionically charged L_α -phase. We used conditions in which 10% of C_{14} DMAO were protonated. The OEE is soluble in the L_3 -phase without destroying it. Immediately after mixing the OEE with the L_3 -phase the sample was filled into the rheometer. Within the next 10 min oxalic diethyl ester hydrolyses to oxalic acid and ethyl alcohol. The oxalic acid protonates the aminoxide and this causes the L_3 -phase to be transformed to a classical multidomain L_α -phase which consists of stacked bilayers. The L_α -phase when measured with oscillatory mode is a low viscoelastic liquid which is very shear sensitive.

Measurements

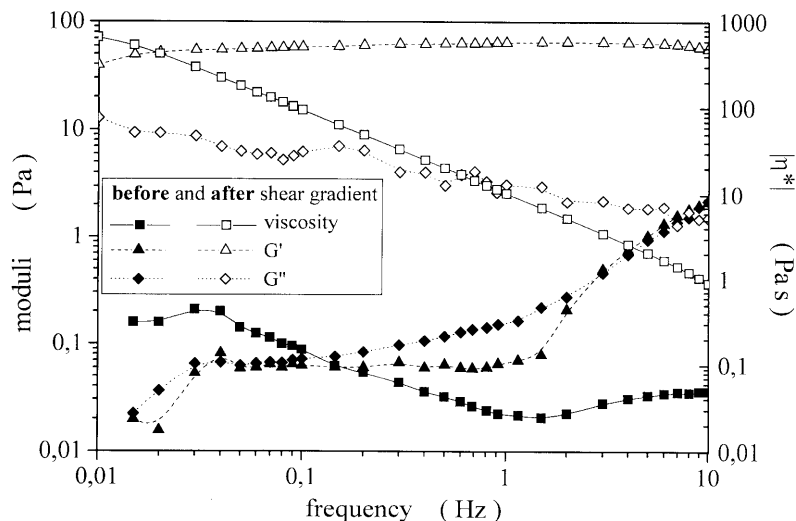
The controlled stress measurements were realized in a Bohlin CS 10 rheometer with a coaxial cylinder geometry. For all measurements samples were kept in the rheometer at rest for 4 hours. We used a chamber of controlled humidity to avoid evaporation of the sample during the measurements. We observed that there was reproducibility of data. Conductivity measurements were performed with a conductivity meter, type LF3000 (WTW, Weilheim, Germany), that measures the conductivity with a precision of better than 0.5%. The apparatus was calibrated with 10 mM KCl solution. We used a basic couette cell similar to the ones already described to perform light, neutron or X-ray scattering. Depending on the localization of the electrodes we can measure the conductivity in the three different directions (shear, velocity and vorticity) with respect to flow.

Results and discussion

Rheological data

We present dynamical rheograms for the unsheared low viscous L_α -phase and for the MLV in Fig. 1. The results show that the viscoelastic parameters in the two samples vary by almost a factor of 100. Detailed measurements of the vesicle phase that have been carried out before have actually shown that the phase behaves like a Bingham fluid with a yield stress value (Hoffmann et al. 1994). Figure 2 shows an apparent viscosity curve for the L_α -phase that is exposed to a shear gradient of 1 s^{-1} . For other shear rates we obtained similar curves. We found that the viscosity at first is slowly decreasing with time and then abruptly increasing and reaching a “pseudo” stationary state, this means that the system keeps changing in a well controlled manner for long times before it reaches the stationary state. When the shear rate was varied we observed that with increasing shear rate the increase of η in the curves is shifted to shorter times. In order to analyze the curves in a more quantitative way, we determine two time constants (τ_2 and τ_3) from this graph and three (τ_1 , τ_2 and τ_3) from the conductivity data. The time constant τ_1 is the time to reach the minimum of the conductivity in the direction of shear. τ_2 is the time to reach the minimum of the viscosity in Fig. 2. It should be noted that τ_1 and τ_2 are not the same and differ by a factor of 5. Finally, τ_3 is the time where the viscosity has reached its maximum value. τ_1 corresponds to the alignment of domains of the

Fig. 1 Rheogram of the sample 100 mM C_{14} DMAO/250 mM hexanol/water with 10 mM oxalic diethyl ester after the hydrolysis reaction at 25 °C before and after shearing



L_{α} -phase into the direction of flow. τ_2 corresponds to the beginning of the transition of the bilayers to vesicles and τ_3 corresponds to the time at which the whole sample has been transformed to vesicles. By comparing then the time constants with the shear rates we find that the product of τ and $\dot{\gamma}$ is a constant ($\tau_1\dot{\gamma} \approx 100$, $\tau_2\dot{\gamma} \approx 1000$ and $\tau_3\dot{\gamma} \approx 6000$) (inset of Fig. 2).

In Fig. 3 we have recorded viscosity values for which the shear rate was first increasing and then decreasing with time. The parameters were adjusted so we observed the vesicle phases for the highest shear rate, after that we decreased the shear rate with time. The data clearly show two regimes, at first a shear-thinning region at low shear rates and then a second shear-thinning region at high shear rates. The first region belongs to the stacked

bilayer phase and the second to the MLV phase, in between of the two regions the viscosity passes over a maximum. This is located at a well defined shear rate, $\dot{\gamma}_c$. We can define the shear rate of the maximum as the critical shear rate involved with structural changes. At low shear rates, the sample behaves like a plastic fluid. With increasing shear rate, some of the bilayers break up by shear and form vesicles that are more viscous than extended bilayers (Hoffmann et al. 1994; Montalvo et al. 1998). Above the maximum, most of the bilayers form MLV and the phase now behaves in the same way as the $L_{\alpha 1}$ -phase. For decreasing shear rates the plot shows that the sample remains in the viscoelastic state that is due to the MLV. In the previous investigation (Bergmeier et al. 1997) we have actually shown that the

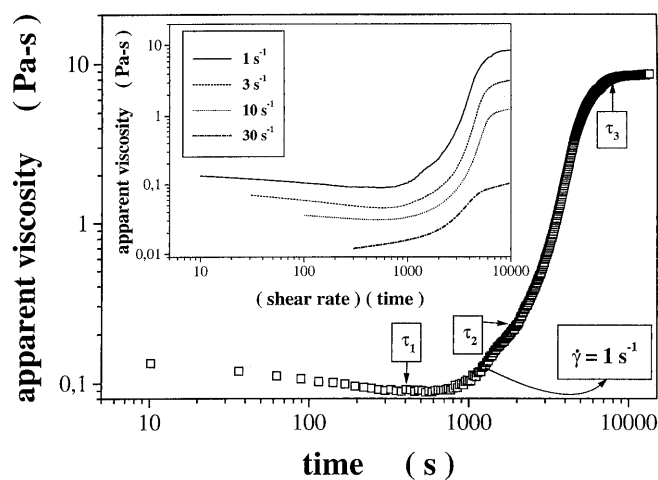


Fig. 2 Apparent viscosity of the sample 100 mM C_{14} DMAO/250 mM hexanol/10 mM OEE in water measured after the hydrolysis reaction with a constant shear gradient of 1 s^{-1} . Inset: a master curve at different deformations $\tau \cdot \dot{\gamma}$

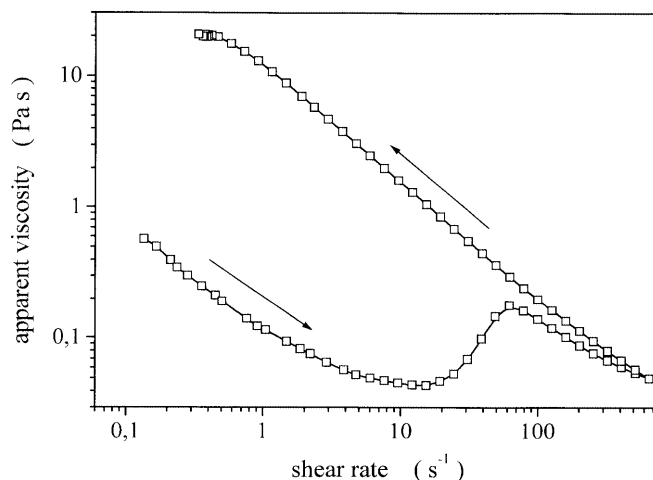


Fig. 3 Steady-state viscosity shear rate. Above a critical shear rate, $\dot{\gamma}_c = 10 \text{ s}^{-1}$, the solution exhibits an abrupt increase in the steady-state viscosity at 25 °C. In the experiment $\dot{\gamma}$ increased linearly with time, the highest shear rate was reached in 20 min

two states can be kept for a year without observing any obvious changes. It is thus difficult to decide which of the states is the thermodynamically stable one.

Conductivity data

We measured the conductivity in three different directions (velocity, vorticity and shear) as a function of shear gradient. As for the viscosity we found continuous changes for the conductivity with time. The largest changes were observed in the x -direction, that is the direction of the shear gradient. Figure 4 shows the conductivity measurements in shear and velocity directions (x and y , respectively) exposed to a shear gradient of 1 s^{-1} . Both curves presented a similar shape. The $L_{\alpha 1}$ -phase at rest, in the shear direction, shows high conductivity because some of the bilayers are aligned perpendicular to the wall. When the shear starts the bilayers are aligned parallel to the wall and the conductivity in the shear direction decreases while it increases in the other direction. These conductivity values could allow us to determine the permeability of the bilayers. The minimum in the x -direction (maximum in the flow direction) corresponds to the situation where the bilayers are completely aligned parallel to the wall, and the subsequent maximum (minimum in the shear direction) corresponds to the situation where all the bilayers have been transformed to vesicles. In the time between we have an equilibrium between vesicles and bilayers. With this assumption we have good quantitative agreement between the typical time constants that are determined from rheological and from conductivity measurements. The results are summarized in Table 1. It is noteworthy that the vesicles that are present when

Table 1 The time constants τ_1 , τ_2 and τ_3 (time to alignment of the multidomains, time at the beginning of the transformation and time to reach equilibrium, respectively) obtained from the rheological (^A) and electrical conductivity (^B) measurements

Shear rate (s^{-1})	τ_1^{B} (s)	τ_2^{A} (s)	τ_2^{B} (s)	τ_3^{A} (s)	τ_3^{B} (s)
1	108	1509	2452	5287	3428
3	44	665	710	1938	1217
5	29	244	422	813	789
10	29	232	300	641	446
30	14	–	122	–	214
200	18	–	22	–	41
500	4	–	9	–	14
1000	–	–	–	–	12

the L_{α} -phase has been completely broken up are not yet in equilibrium with the shear rate and that the time constant τ_4 to reach equilibrium takes very much longer.

The conductivity data in the x -direction are reflected very well by the conductivity data in the other two directions. As for the viscosity data we find a linear shift of the time constants with increasing shear rate (inset of Fig. 5). Our data actually demonstrate very nicely that within a certain shear rate range the phases pass through exactly the same structural condition with time. In Fig. 5 conductivity data were replotted again versus the strain parameter, $\dot{\gamma}\tau$. The plot demonstrates that the data in quite an extensive shear rate range fall on the same master curve. Moreover the different time constants τ can be evaluated from the master curve. Figure 6 shows the shear viscosity at long times for the same sample; all the data were obtained in the equilibrium zone. As seen, we find a shear-thinning behaviour, characterized by $\eta \propto \dot{\gamma}^{-0.87}$, and the same scaling over a similar range of

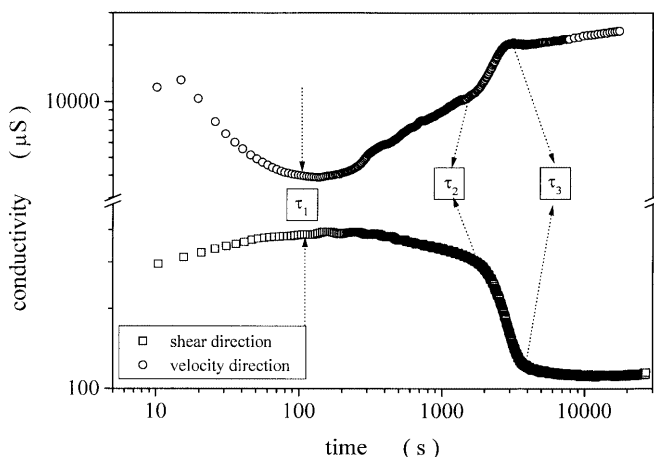


Fig. 4 Measurements of the electrical conductivity in shear and velocity directions at a shear rate of 1 s^{-1} at the end of the hydrolysis reaction

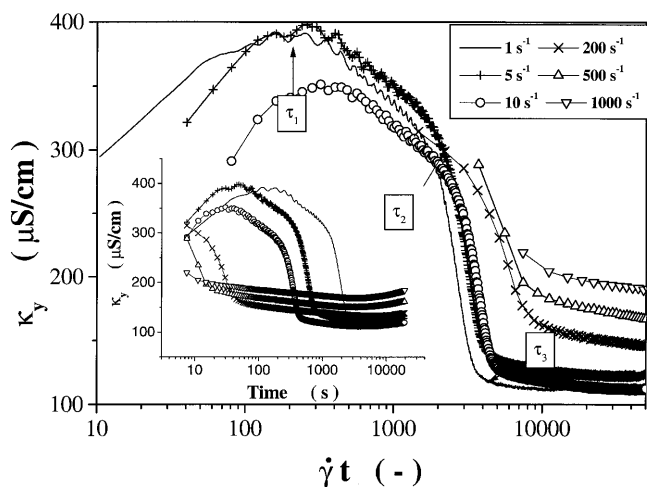


Fig. 5 Master curve for the conductivity measured in the velocity direction at different shear rates. Inset: the conductivity curves for the L_{α} -phase exposed to different shear gradients as a function of time

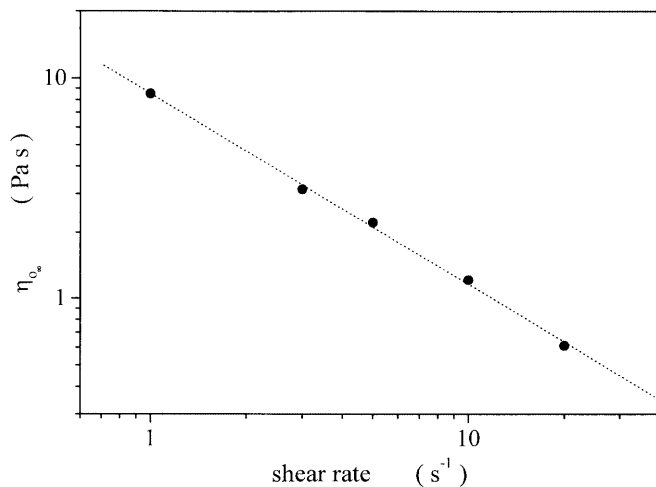


Fig. 6 Long time plot for rheological data at different shear rates

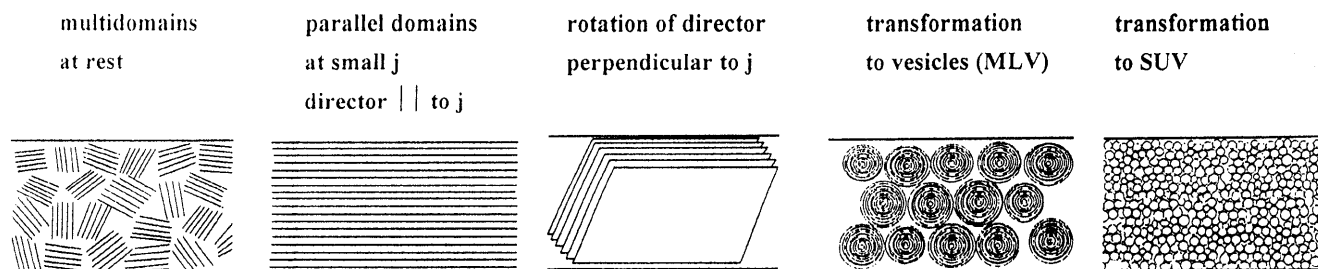
shear rates was observed by Roux et al. (1993) and by Bergholtz and Wagner (1996).

From the development of the different rheological and conductivity measurements for constant shear rate with time we may conclude that the system develops with time as sketched in Fig. 7. The different states that are shown in this sketch depend on shear rate and in particular on the composition of the system like concentrations, alcohol chain length and so on.

Possible mechanism for the results

It is noteworthy that the strain to pass from the aligned L_α -phase to the single phase vesicle state is independent of the shear rate. Besides there is never an abrupt change in the transformation process. This makes it likely that the whole process proceeds in a step-wise fashion. One possibility of how this could proceed is that the transformation occurs in a layer-by-layer fashion where

Fig. 7 Schematic representation of an L_α -phase under constant shear gradient with time. The state "three" is not obvious from the presented data. In this state the bilayers are oriented perpendicular to the walls of the couette cell. The state can clearly be seen by SANS measurements and has been included in the schematic sketch. This state evolves between τ_1 and τ_2



each layer has the thickness of a multilamellar vesicle. This means that given the gap width of the couette cell of 1 mm and a diameter of the MLV of about 2 μm , there would be about 500 layers. If we assume that the transformation to 1 layer requires the strain, $\dot{\gamma}\tau$. The whole process could require a strain of about 800. This estimate leads us to the correct time for the total transformation. The size of the MLV could be controlled by the ratio $\sqrt{K/B}$ (Panizza et al. 1996), where K is the bending constant and B is the compression modulus. This explanation is appealing since the time constants for the system are little dependent on chain length and on charge density. Since the length scale is determined by the ratio of the bending constant and the compression modulus, the length scale depends little on other parameters because both constants vary linearly with parameters like concentration and charge density. If this mechanism is valid, we would also have a simple method for the determination of K , because B and the size of the vesicles, with the characteristic length, ξ , can be determined.

Conclusions

Rheological and conductivity measurements have been used to monitor the transformation of an ionically charged L_α -phase to a multilamellar vesicle phase. A virgin L_α -phase that has not been exposed to shear was prepared by charging the bilayers of a sponge phase with hydrogen ions that are produced from the hydrolysis reaction of oxalic acid ethyl ester. The L_α -phase thus produced is of low viscosity and consists of stacked bilayers.

Under shear it transforms into a highly viscoelastic multilamellar vesicle phase that is stable for long times. At least three characteristic time constants can be distinguished in the transformation process under constant shear. The conductivity in shear direction passes through a minimum (τ_1) and then through a maximum (τ_2). The viscosity passes through a minimum (τ_2) and then reaches a flat maximum (τ_3). It was observed that all three time constants depend on the shear rate used and that the products of time constant with the shear rate were constant ($\dot{\gamma}\tau_1 \cong 100$; $\dot{\gamma}\tau_2 \cong 1000$; $\dot{\gamma}\tau_3 \cong 6000$). It is concluded that τ_1 corresponds to the

complete alignment of the multidomain L_{α} -phase, τ_2 to the beginning of the break-up of the bilayer to the vesicles and τ_3 to the complete transformation of the bilayers to the multilamellar vesicles.

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