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The lamellar-to-vesicle phase transition by shear experiments

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Abstract. It is shown that the transformation of an L_3 -phase to an ionically charged L_α -phase with stacked bilayers can be induced by the hydrolysis reaction of an ester. This process takes place on a time scale of minutes with ethyloxalate as an ester and occurs spontaneously. If this low-viscous L_α -phase is subjected to shear it is transformed into a highly viscous vesicle phase (onion phase). The structural changes during this transformation process have been monitored by conductivity, rheology and small angle neutron scattering (SANS) experiments. We observed that the transformation occurs in several steps. For low shear rates the transformation time τ decreases linearly with the shear rate ($\tau\dot{\gamma} = \text{constant} \equiv 2000$) while for higher shear rates a different mechanism occurs.

1. Introduction

Amphiphilic molecules spontaneously self-assemble in aqueous solution into a variety of microstructures. The equilibrium properties of these structures are well known but little is understood about the kinetics of the structural transitions. In particular the dynamics of the transformation process of the bilayer–vesicle transition under flow is not understood. Diat *et al* have come up with an orientation rheogram which they assumed would be generally valid [1]. They have shown that prolonged steady shear in a couette cell causes a dynamic transition from the L_α -phase to ‘onions’ (multi-lamellar vesicles (MLV)). In some other studies the L_α -vesicle transition was not observed [2]. Instead, it was observed that the bilayers orient themselves at first to a parallel position to the wall, then to a perpendicular one and finally again to a parallel one with increasing shear rate. For charged L_α -phases, the bilayer transition from perpendicular to parallel was not observed. Moreover, at the highest available shear rate of 6000 s^{-1} small unilamellar vesicles (SUV) were obtained [3]. Finally, it was found for the surfactant aerosol OT (sodium-1,4-bis(2-ethylhexyl)sulphosuccinate) (AOT) system that the shear rate is not the critical parameter for the transformation but the wall shear stress [4]. In this paper it also was shown that the MLV form an ordered state under shear.

In most of the investigations no detailed studies were made about the mechanisms of the various phase transformations. In general it was observed that a stationary state for a given shear rate is reached only after a long time [5]. The results show that there is plenty of room for new experiments which could lead to a more consistent picture. With this investigation we intend to do this. For the measurements we used an L_α -phase which was prepared in the well defined bilayer L_α -state. Prior to its formation, the L_α -state had not been exposed to shear. The described results have the advantage over previous investigations that the results do not depend on the preparation history of the samples [6]. All measurements were carried out on a well defined virgin L_α -phase.

2. Experimental

2.1. Sample preparation

The tetradecyldimethylaminoxide (C_{14} DMAO) was a gift from Clariant GmbH and was recrystallized twice from acetone before use. Diethyl oxalate and hexanol were purchased from Merck in p.a. purity. For the measurements all the samples were prepared in the same way. We produced a large amount of a L_3 -phase with 100 mM C_{14} DMAO and 250 mM hexanol [7]. This phase was mixed with the appropriate amount of diethyl oxalate to obtain the final charge density of the L_α -phase. Within the next 10 min diethyl oxalate 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 classic multidomain L_α -phase which consists of stacked bilayers.

2.2. Measurements

The controlled stress measurements were carried out in a Bohlin CS 10 rheometer with a couette geometry. Before all measurements a sample of the L_3 -phase was mixed with diethyl oxalate (10 mM), stirred and quiescently kept in the rheometer for 4 hours. The conductivity was measured in a basic couette cell similar to the ones already described to perform light, neutron or x-ray scattering [8]. These measurements were performed with a conductivity meter, type If 3000 (WTW, Weilheim, Germany). Neutron scattering experiments were performed at the Risø National Laboratory in Roskilde, Denmark. The scattering data were collected on a two-dimensional (2D) detector covering a range of momentum transfer q from 3×10^{-3} to $7.5 \times 10^{-2} \text{ \AA}^{-1}$ and corrected for background and empty cell scattering. The shear experiments were performed in a couette cell that has already been described in detail [9].

3. Results and discussions

3.1. Conductivity data

The L_α -phase at rest shows a high conductivity because some of the bilayers are aligned perpendicularly to the wall and the charged species can pass easily from one electrode to the other without hindrance. With shear the bilayers are aligned parallel to the wall and the conductivity decreases to its lowest value (τ_1). In this state (figure 1) the ions have to get across all the bilayers. This value of κ could allow us to determine a permeability of the bilayers. The double log plot shows a break at a second characteristic time (τ_2) where there is an equilibrium between vesicles and bilayers, then passes over a small maximum and a small minimum (τ_3) where all the bilayers have been transformed to vesicles and finally reaches a stationary state (τ_4). The results are summarized in table 1.

At this point it is noteworthy to mention that the conductivity data for the given system did not show any evidence for a state in which the bilayers would be aligned perpendicular to the wall. Such a stationary transition state has been proposed by several groups on the basis of small angle neutron scattering (SANS) data [10]. The conductivity data in the x -direction are reflected very well by the conductivity data in the z - and in the y -directions. The minimum (maximum) for the x -direction correspond to a maximum (minimum) in the z - and y -directions. For comparison the conductivity data for the y -direction are shown in figure 2. Here the conductivity data were replotted against the deformation parameter, $\tau\dot{\gamma}$. In this dimensionless plot the data fall on the same master curve. We find a linear shift of the time constants with increasing shear rate (Inset in figure 2).

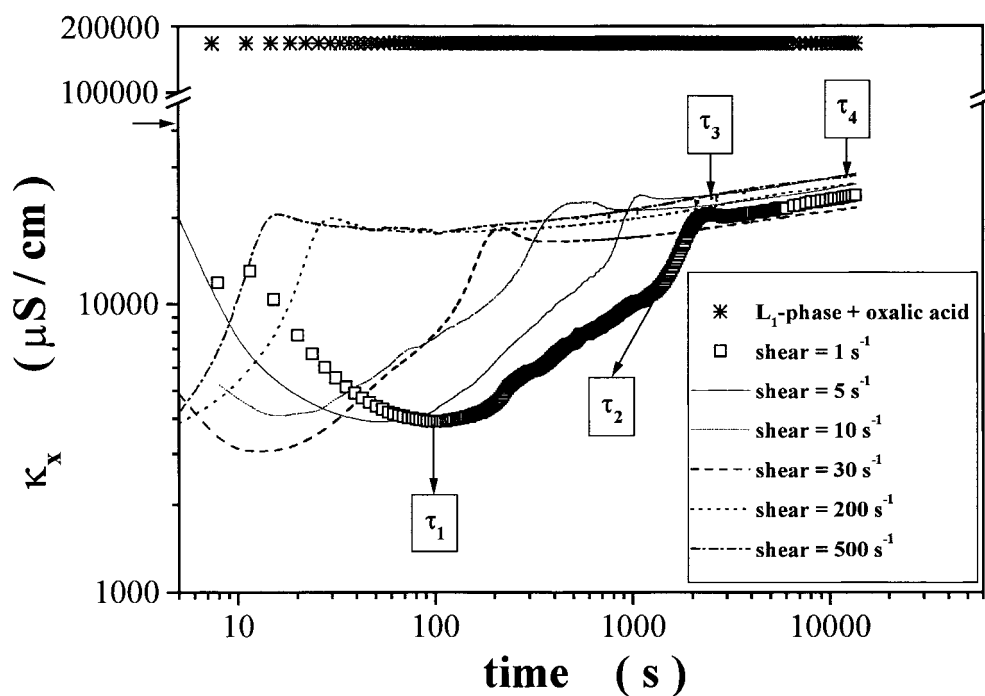


Figure 1. Electrical conductivity recorded in the shear direction from the sample 100 mM C₁₄DMAO, 250 mM hexanol, water and 10 mM diethyl oxalate at different shear rates. The symbols at the top shows the conductivity for a L₁-phase from the system 100 mM C₁₄DMAO and 50 mM hexanol.

Table 1. The time constants τ_1 , τ_2 and τ_3 (time to align the multidomains L _{α} -phase, time at which the L _{α} -phase has completely been transformed to multilamellar vesicles and the time to reach equilibrium, respectively) obtained from the rheological (A) and electrical conductivity (B) measurements.

$\dot{\gamma}$ (s ⁻¹)	τ_1 (s)	(A) τ_2 (s)	(B) τ_2 (s)	(A) τ_3 (s)	(B) τ_3 (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
20		68		222	
30	14		122		214
200	18		22		41
500	9		9		14
1000					12

3.2. Rheological results

In figure 3 a time dependent rheogram is shown when the L _{α} -phase is exposed to constant shear rates and the apparent viscosity is recorded. We find that the viscosity slowly decreases with time and then abruptly increases until a maximum is reached. In order to analyse the curves in a more quantitative way, we determine two time constants from this graph. The time constant τ_2 , that is the time to reach the minimum in the viscosity and the time constant τ_3 , which is the time to reach the maximum. When these time constants are determined at

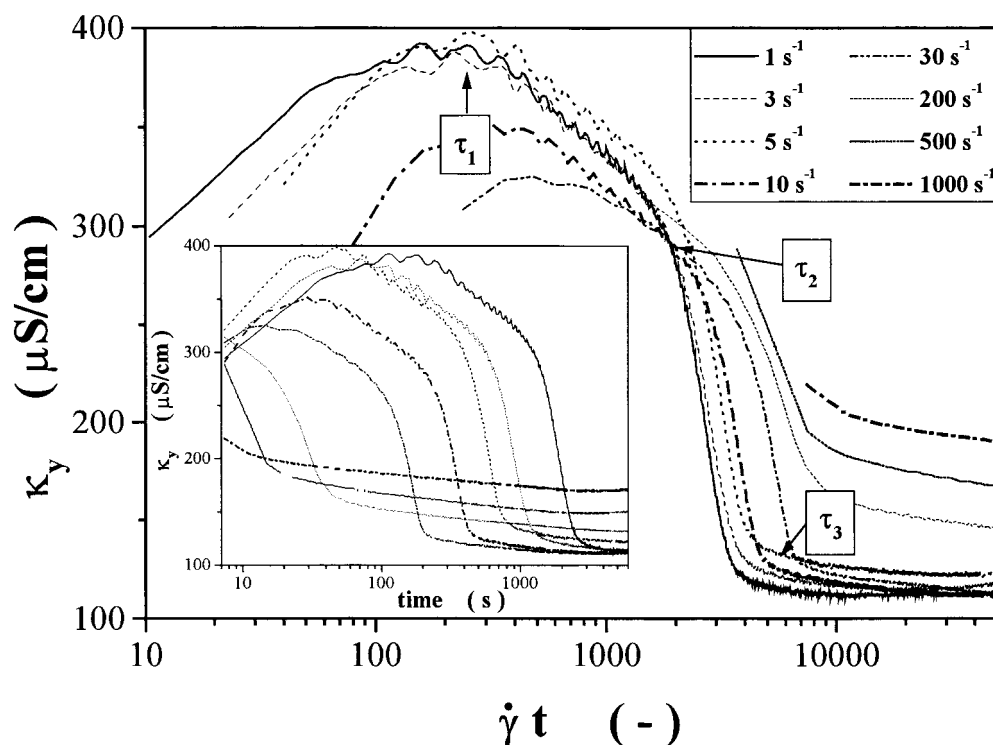


Figure 2. Master curve of the electrical conductivity for the system at various shear gradients in the flow direction and at 25 °C plotted against the deformation $\dot{\gamma}t$. Inside the graph the conductivity curves made in the flow direction for the L_{α} -phase that were exposed at different shear gradients are given as a function of time.

different shear rates we find that the product of τ and $\dot{\gamma}$ is a constant ($\tau_2\dot{\gamma} \approx 2000$ and $\tau_3\dot{\gamma} \approx 5000$).

It is interesting to note from the curves that the viscosity never reached a stationary state. Under shear the system keeps changing in a well controlled manner for long times. We also carried out viscosity measurements in which the shear rate increased with time (inset figure 3). The parameters were adjusted to such a level so we could observe MLV for the highest shear rate, after that we decreased the shear rate again with time. The data show clearly that the transformation that we have obtained with increasing shear is irreversible and does not go back.

3.3. Results of the SANS

Some of the obtained SANS data are given in figures 4(a), (b), (c), and (d). In the first figure of that series we show the scattering pattern of a sample at the end of the hydrolysis reaction. The position of the correlation peak at $1.5 \times 10^{-2} \text{ \AA}^{-1}$ corresponds to an interlamellar distance between the bilayers of 420 Å. From that moment on when the cell had been completely assembled and put into position we recorded the scattering pattern every few minutes until the pattern did not change any more. The intensity profiles of the scattering patterns were scaled to the same irradiation period so they can therefore directly be compared with each other. Figure 4(b) shows the intensity profile for a sample which had been sheared for 30 s. with a constant shear rate of 10 s^{-1} . The pattern corresponds to the situation where most of the

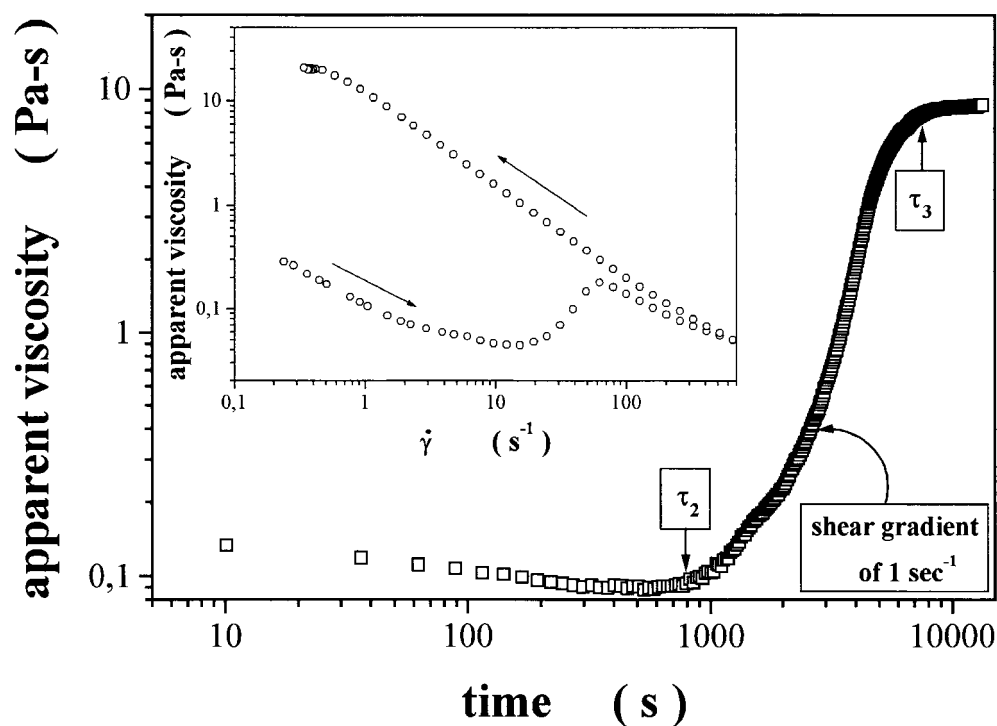


Figure 3. Apparent viscosity of the sample 100 mM C₁₄DMAO, 250 mM hexanol and water after the hydrolysis reaction and for a shear rate of 1 s⁻¹. Inside the graph of shear viscosity against shear rate where $\dot{\gamma}$ increased linearly with time, the highest shear rate was reached in 20 min.

bilayers have been aligned parallel to the walls of the couette system. In this state the sample shows no birefringence when viewed through crossed polarizers (homeotropic alignment).

During the next few minutes of constant shear a strongly anisotropic pattern develops with time. In figure 4(c) we show the pattern of this state in which some of the bilayers but not all of them are aligned in the shear plane that is perpendicular to the wall. A pattern of a sample which has been sheared for about 2 h is shown in figure 4(d). This state corresponds to MLV that have been deformed by shear. The intensity of the correlation peak disappears completely for very high shear rates. Under such conditions the anisotropy also disappears. Such a scattering pattern corresponds to a situation in which the MLV have been transformed to SUV.

From the development of the different scattering patterns for constant shear with time we may conclude that the systems develop with time the following structures: multidomains at rest, parallel domains, rotation of the director of the L_α-phase into the z-direction, transformation to MLV and transformation to SUV. The different states depend on the duration that the samples were exposed to different shear rates and in particular on the composition of the system like concentrations, alcohol chain length, charge density and so on.

Preliminary measurements on the influence of these parameters have shown that the typical time constants in the whole transformation process are little influenced by these parameters.

4. Conclusions

A dilute ionically charged L_α-phase can be prepared from a L₃-phase with the help of hydrolysis reactions occurring in the L₃-phase. When such a virgin L_α-phase is exposed to constant shear

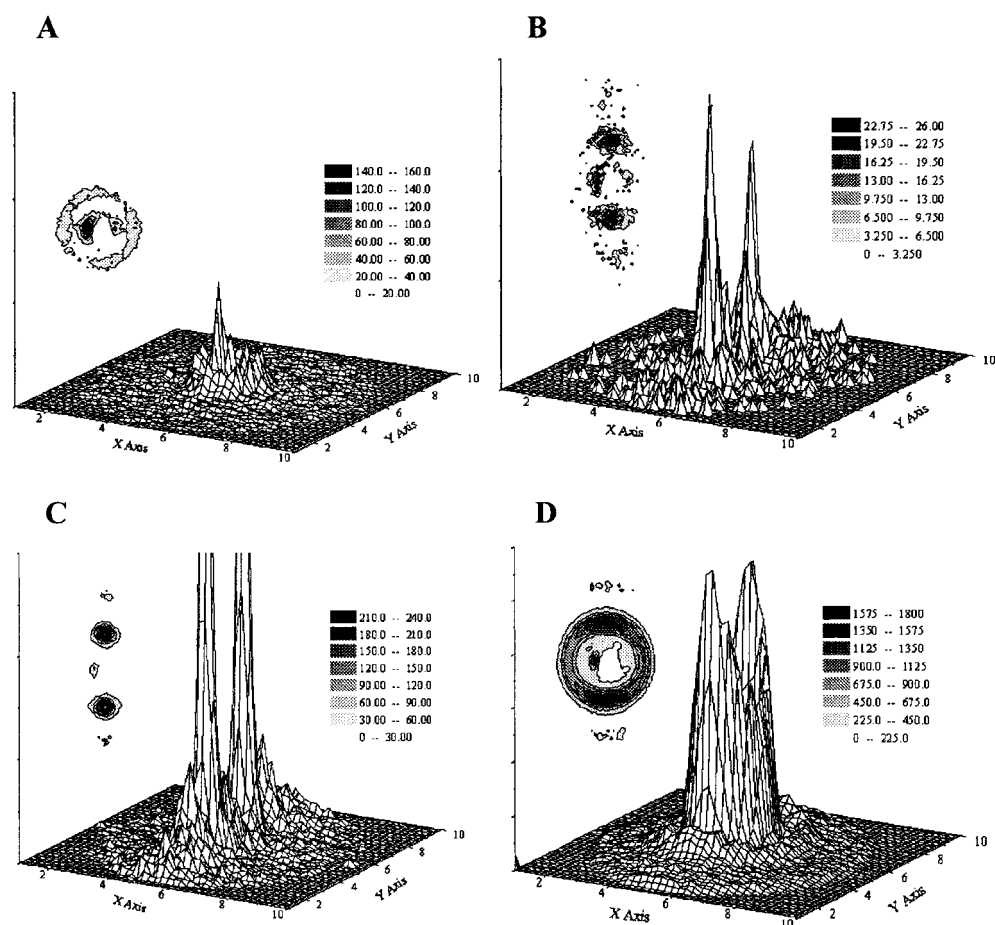


Figure 4. Neutron scattering patterns of the sample 100 mM C₁₄DMAO, 250 mM hexanol and water with 10 mM diethyl oxalate at 25 °C using a 'radial beam' geometry. The intensities are scaled to the same scattering time.

it is transformed to a vesicle phase. The transformation is associated with shear thickening. The whole transformation proceeds in a long process during which several states can clearly be distinguished by conductivity, rheology and SANS measurements. Under constant shear all bilayers in the multidomain L_α-phase are first aligned parallel to the walls of a couette system and then perpendicularly. The vesicles are finally formed from the perpendicular state of alignment. The different states are even reached for shear rates as low as 1 s⁻¹. The duration times for the formation of the different states depend on the shear rates and decrease linearly with shear rate. The different states are thus reached for a constant deformation.

Acknowledgments

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