

Rheology of the lamellar liquid-crystalline phase in polyethoxylated alcohol/water/heptane systems

By F. Cordobés^{1*}, J.M. Franco² and C. Gallegos²

¹ Departamento de Ingeniería Química. Facultad de Química. Universidad de Sevilla.
c/Prof. García González s/n. Sevilla 41012, Spain. fcordobe@us.es

² Departamento de Ingeniería Química. Facultad de Ciencias Experimentales. Universidad de Huelva. Campus Universitario del Carmen, 21071, Huelva. Spain.
franco@uhu.es, cgallego@uhu.es

RESUMEN

Reología de la fase líquido-cristalina laminar en sistemas alcohol polietoxilado/agua/heptano.

En este trabajo se han estudiado las propiedades reológicas de una fase líquido-cristalina laminar contenida en un sistema alcohol polietoxilado/agua/heptano, mediante ensayos viscoelásticos lineales, estacionarios y transitorios. El efecto de distintas variables como la composición de tensioactivo y heptano sobre dichas propiedades reológicas ha sido analizado. El espectro mecánico obtenido de la fase laminar muestra en todos los casos una región «plateau» en el intervalo de frecuencias estudiado así como mayores valores de los parámetros viscoelásticos para valores intermedios de la concentración de tensioactivo y heptano, indicativo de un mayor desarrollo del entramado elástico estructural de dicha fase líquido-cristalina. Los ensayos de flujo estacionario y transitorio pusieron de manifiesto la existencia de estructuras inducidas por cizalla. En las curvas de viscosidad se obtuvieron diferentes regiones de variación potencial de la viscosidad frente a la velocidad de cizalla y, por tanto, distintos valores de índices de flujo. Las modificaciones de la microestructura de la fase líquido-cristalina laminar causadas por la cizalla, fueron confirmadas mediante el uso de microscopía de luz polarizada en un sistema de cizalla que incorpora un microscopio óptico. Las modificaciones estructurales parecen estar muy influenciadas por la velocidad de cizalla y, generalmente, la aplicación de elevadas velocidades de cizalla provoca el alineamiento de las bicapas de tensioactivo y la aparición de la clásica textura de «oily streaks» de la mesofase laminar. La presencia de vesículas se detecta en sistemas con alto contenido en heptano, como indica la textura detectada por microscopía de luz polarizada.

PALABRAS-CLAVE: Cristal líquido - Mesofase laminar - Reología - Viscoelasticidad - Viscosidad.

SUMMARY

Rheology of the lamellar liquid-crystalline phase in polyethoxylated alcohol/water/heptane systems.

Linear viscoelastic tests as well as transient and steady flow experiments were carried out on lamellar liquid crystalline samples of poly(oxyethylene) alcohol/water/heptane systems. The effect of surfactant and heptane concentrations on the rheological properties of the lamellar mesophase was investigated. The mechanical spectrum inside the linear viscoelastic regime shows, in all cases, a well-developed plateau region in the whole frequency range studied. The values of the dynamic functions were higher for intermediate surfactant or heptane concentrations indicative of a major development of the elastic network in the midrange of existence of the lamellar phase. Transient and steady flow experiments point out a shear-induced evolution of the lamellar microstructure. Different power

law regions with different values of the flow index were detected in the viscosity versus shear rate plots. These shear-induced structural modifications were confirmed by using polarizing microscopy in an optical shearing cell. Structural modifications appear to be highly influenced by shear rate. In general, applying relatively high constant shear rates, the alignment of the bilayers followed by the appearance of the «oily streaks» structure was observed. Appearance of shear-induced vesicles occurs at high heptane content, as indicates the texture of close-packed monodisperse spherulites detected by polarizing microscopy.

KEY-WORDS: Lamellar mesophase - Liquid crystal - Rheology - Viscoelasticity - Viscosity.

1. INTRODUCTION

Aqueous and non-aqueous solutions of nonionic surfactants (Tiddy, 1980; Robles-Vásquez, 1993; Dimitrova, 1995; Cordobés, 1997) may form different lyotropic liquid-crystalline phases as a result of interactions among association structures or micellar aggregates. These phases present static and dynamic properties related to the crystalline (long-range positional and orientational order, elasticity,...) and liquid states (viscosity, concentration fluctuations, etc.). Knowledge of the structure and dynamic properties of lyotropic phases is very important from both fundamental and practical points of view, especially considering their applications in the fields of detergents (Barnes, 1980), cosmetics (Comelles, 1994), pharmaceuticals (Müller-Goyman, 1987; Engström, 1990), emulsions and colloidal systems (Pilpel, 1987; Riego, 1988; Friberg, 1990), etc.

The phase diagrams of polyoxyethylene nonionic surfactants exhibit a succession of different lyotropic liquid-crystalline phases (Mitchell, 1983; Franco, 1995; Moros, 2001). The type of liquid-crystalline structure formed depends on the curvature adopted by the interface between the aggregates and the surrounding solvent. Lamellar, hexagonal and cubic phases are usually shown in these systems. The lamellar lyotropic phase, L_{α} , appears at rather high concentrations when the interface tends to be planar, although surfactant with more hydrophobic chains favors their appearance at low concentrations. This

phase consist of a simple one-dimensional crystal composed of alternating layers of water and surfactant bilayers with polycrystalline characteristics, i.e. comprised of small, micron-sized domains with intervening grain boundaries (Kilpatrick, 1994). This particular structure confers to this phase rheological properties clearly different from others. It is well known that the lamellar liquid crystalline phase shows lower values of the rheological functions than others lyotropic phases detected in nonionic surfactant/water phase diagrams (Moros, 2001; Muñoz, 1991).

Several aspects concerning the steady-state and transient flow behaviors of lamellar liquid-crystalline phase have been previously studied by different authors (Franco, 1995; Gallegos, 1987; Lockwood, 1987; Paasch, 1989; Roux, 1994). In these studies, the importance of the appearance of shear-induced structural defects in the rheological behavior of lamellar mesophases has been pointed out. First investigations about the effect of shear on the structure of a lamellar phase was analyzed by Diat et al. (Diat, 1993) in a quaternary system of anionic sodium dodecyl sulfate (SDS), pentanol, dodecane and brine. As shown, a multidomain L_{α} phase, which usually holds defects in the liquid-crystalline structure (Laüger, 1996), is aligned by shear into a state of orientated bilayers parallel to the wall of the Couette cell. At a threshold value of shear rate characteristic of each system, the bilayers break up and are transformed to vesicles, also called lamellar droplets, spherulites, liposomes, or «onions» (van de Pas, 1993; van der Linden, 1996). For shear rates higher than a critical value, a two-phase region exists in which extended bilayers are in equilibrium with vesicles. A single vesicle phase is reached by increasing shear rate, which can exhibit a high degree of positional ordering (Diat, 1995). For even higher shear rates the vesicles are finally transformed to a perfectly aligned lamellar phase that is supposed to be free of defects. More recently, other authors have investigated the presence of multilamellar vesicles (MLVs) in different surfactant systems (Weigel, 1996; Sierro, 1997). Escalante et al. (Escalante, 2000) have observed that the transition from a non-perturbed lamellar phase is irreversible and, for a given system, the characteristic parameter for the transformation process is the deformation applied. Partal et al. (Partal, 2001) have found that the transition to a vesicle phase occurs at a critical stress which increases with surfactant concentration. On the contrary, in some binary systems with a relatively high surfactant concentration, this transition to a MLV phase has not been observed (Franco, 1995; Nemeth, 1998; Laüger, 1995), probably due to an insufficient bending flexibility of the membranes (Vinches, 1994).

On the other hand, historically less attention has been paid to the linear viscoelastic behavior of lamellar liquid-crystalline phases and only in the last years the viscoelasticity of lamellar phases has been extensively studied. Kilpatrick et al. (Kilpatrick, 1994) have studied the linear viscoelastic properties of different lyotropic phases present in the Cesium n-Tetradecanoate/water system; Robles-Vásquez et al. (Robles-Vásquez, 1993) have investigated the linear viscoelastic response of aqueous systems containing a sodium sulfosuccinate as surfactant; and Dimitrova et al. (Dimitrova, 1995) have provided some linear viscoelastic data related to phase transitions among different liquid-crystalline structures in the phase diagram of a polyethoxylated alcohol containing 7 mol of ethylene oxide. Finally, Jager-Lezer et al. (Jager-Lezer, 1998, 1999) have studied the role of the chemical nature of the surface in contact with a lamellar mesophase to understand its rheological behavior. In this sense, previous studies (Cordobés, 1997) demonstrated that more elastic responses can be obtained by adding a linear chain hydrocarbon to a binary hexagonal system. Thus, development of a plateau region in the frequency dependence of the dynamic functions can be obtained as heptane concentration increases. All of these studies prove the complex behavior of lamellar phases in the linear viscoelastic regime. The present research is concerned with the viscous and linear viscoelastic behavior of the lamellar mesophase in both binary polyethoxylated alcohol/water systems and ternary systems, solubilizing a linear chain hydrocarbon. The phase diagram of polyethoxylated alcohol/water/heptane has been previously studied (Cordobés, 1997). This phase diagram shows a direct hexagonal liquid-crystalline region between 40 and 50% (w/w) surfactant and a lamellar liquid-crystalline region between 55 and 75% (w/w) solubilizing a maximum amount of heptane of 30% (w/w). The overall objective of this work was to study the effect that surfactant and heptane concentrations exert on transient and steady flows and linear viscoelastic response. In addition to this, the effect of shear on the non-perturbed lamellar phase structure was analyzed.

2. EXPERIMENTAL

A poly(ethylene glycol) nonylphenylether (NPFE-10) from Sigma (St. Louis, U.S.A.) was used as received. Lamellar liquid-crystalline systems were prepared by mixing this nonionic surfactant with distilled deionized water and n-heptane of analytical grade, obtained from Panreac (Barcelona, Spain). Surfactant concentration ranged from 60 to 75% (w/w) for binary systems and 50 to 75% (w/w) for ternary systems containing up to 30% (w/w) of heptane solubilized, inside of the zone of existence of the

lamellar structure in the phase diagram (Cordobés, 1997).

Three different types of rheological measurements were performed in this work:

- 1) Oscillatory tests were carried out in a control stress rheometer, RS-100 from Haake (Karlsruhe, Germany) with cone and plate geometry (60 mm, 4°). A transparent bell with saturated atmosphere was placed around the measuring device in order to prevent changes in composition due to heptane or water evaporation during measurement. All the samples had the same recent past history, and were left for 20 minutes in the sensor system before any measurement. Frequency sweep tests were carried out at constant stress inside the linear viscoelastic region in a frequency range of 10^{-2} - 10^2 rad/s. Previously, in order to obtain the linear viscoelastic range for the samples studied, strain sweeps at a constant frequency of 1 Hz were performed, and the values of the critical strain, γ_c , which delimit the linear viscoelastic region, were determined.
- 2) Steady-state flow measurements were performed in controlled-shear rate rheometers RV100/CV100 or RV100/CV20N, depending on the sample viscosity, from Haake (Karlsruhe, Germany), using a Mooney-Ewart geometry (ME15). Steady-state flow curves were obtained in a shear rate range of 0.1 - 300 s $^{-1}$.
- 3) Transient flow experiments were carried out in the above mentioned controlled-shear rate rheometers at different constant shear rates between 0.5 and 100 s $^{-1}$.

All rheological tests were performed at 25°C and 2 days after the sample was prepared. In previous studies, it was pointed out that rheological properties of samples was not influenced by time. At least two replicates of each test were done.

Microstructural observations under shear in an optical shearing cell (Linkham Scientific Instruments, U.K.) equipped with polarizing microscopy completed the rheological study of the lamellar phase. Samples were collected in the shearing cell and then were submitted to the same transient shear history input in the controlled-shear rate rheometers.

3. RESULTS AND DISCUSSION

a) *Linear viscoelasticity.* As is well-known, the application of strains lower than the critical strain which delimits the linear viscoelastic region, γ_c , allows the study of the rheological behavior of the non-perturbed liquid-crystalline structure, while higher values produce structural modifications. The values of γ_c depend of the linear viscoelastic function selected for its determination. In this work, the storage and loss moduli were selected, and the

values of γ_c were calculated by the crossover between two lines: G' or G'' =constant (at low shear stresses) and G' or G'' = $f(\sigma^n)$ (at higher shear stresses). Figure 1A shows the evolution of the storage and loss moduli with the applied strain for selected lamellar systems (5% heptane), from the hexagonal liquid-crystalline phase (55% NPFE-10) up to the isotropic surfactant-rich phase (75% NPFE-10) boundaries. Figure 1 B shows the linear viscoelastic range for systems containing 60% NPFE-10 and different heptane content. As can be observed in Tables I and II, higher values of γ_c were obtained from the storage modulus except for the binary system. When higher strains were applied the evolution of both linear viscoelastic functions was clearly different. The values of G' let down continuously when strain increases, while the loss modulus shows an initial growth followed by a further decrease. However, this initial increase is a function of the frequency selected to perform the strain sweep. Thus, it has been verified that the loss modulus continuously decreases as the strain increases by applying a constant frequency of 10 Hz (Cordobés, 2000). This fact has been observed in others lamellar phases studied in the literature (Alfaro, 2000).

As previously demonstrated (Robles-Vásquez, 1993; Robles-Vásquez, 1994) and shown in Figures 1 and 2, lamellar liquid-crystalline phases are characterized by a small linear viscoelastic range. The values of the critical strain, γ_c , which produces a certain degree of destruction in the liquid crystalline structure, did not present a significant dependence with surfactant content, for a constant heptane concentration (Table I). On the other hand, this critical strain shows minimum values at intermediate

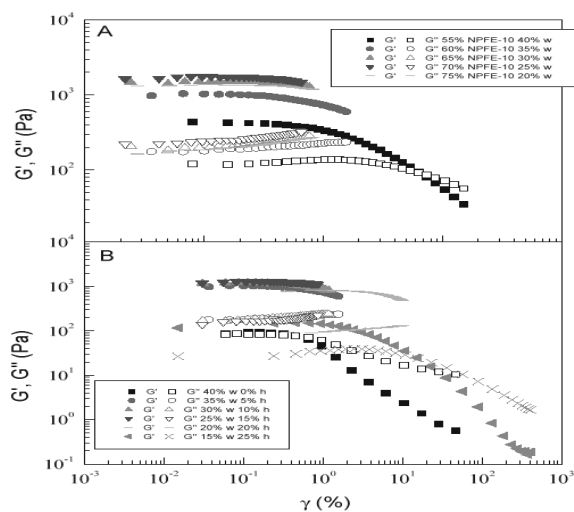


Figure 1
Strain sweep tests for systems containing 5% (w/w) heptane (A) and 60% (w/w) NPFE-10 (B).

Table I
Values of the critical strain which delimits the linear viscoelastic region for systems containing 5% (w/w) heptane.

%(w/w) surfactant	%(w/w) water	γ_c in G'	γ_c in G''
55	40	0.30±0.03	0.15±0.03
60	35	0.19±0.02	0.07±0.02
65	30	0.30±0.03	0.10±0.03
70	25	0.27±0.02	0.04±0.02
75	20	0.44±0.04	0.08±0.04

Table II
Values of the critical strain which delimits the linear viscoelastic region for systems containing 60% (w/w) surfactant

%(w/w) water	%(w/w) heptane	γ_c in G' (%)	γ_c in G'' (%)
40	0	0.29±0.03	0.42±0.03
35	5	0.19±0.02	0.07±0.02
30	10	0.14±0.03	0.07±0.03
25	15	0.30±0.04	0.23±0.04
20	20	0.35±0.03	0.09±0.03
15	25	1.11±0.05	0.20±0.05

heptane concentrations for fixed surfactant contents (Table II). These minimum values move to higher heptane content as NPFE-10 concentration decreases. Moreover, liquid-crystalline systems with

higher heptane concentrations show a more rapid decrease of the viscoelastic functions in the non-linear region, which can be attributed to a higher structural breakdown.

The linear viscoelastic properties of lamellar phases were determined by means of frequency sweeps inside the linear viscoelastic region. As can be observed in Figures 2 and 3, the frequency dependence of G' and G'' was always similar. Thus, almost constant values of G' and a clear minimum in G'' can be detected for most systems. This mechanical spectrum corresponds to the «plateau» region, which has been related to the formation of an elastic structural network due to the interactions between liquid-crystalline domains (Kilpatrick, 1994). Similar results have been found in the literature for systems with different types of surfactants and hydrocarbons (Alfaro, 2000; Jiménez, 2000; Nemeth, 1998). As can be observed, lamellar phases are characterized by higher values of storage modulus in a wide range of frequencies. Thus, only the system containing 50% (w/w) NPFE-10 and 5% (w/w)

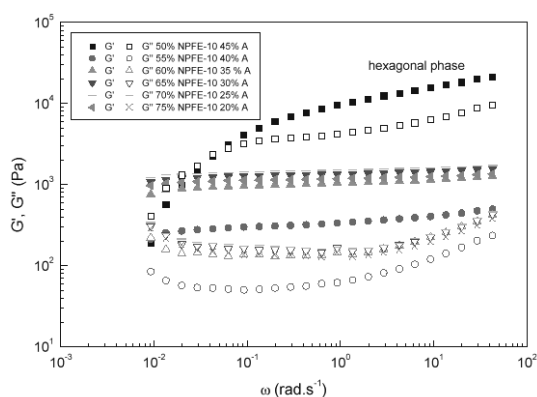


Figure 2
Evolution of storage and loss moduli as a function of frequency for systems containing 5% (w/w) heptane.

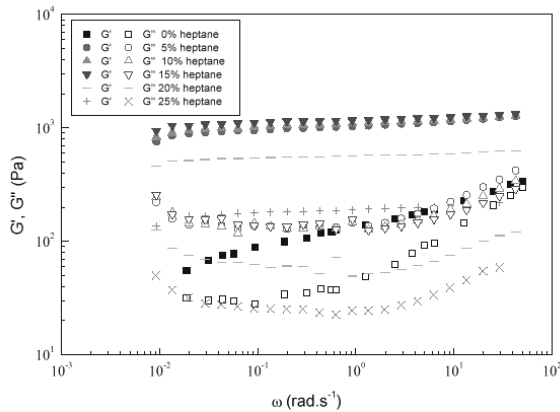


Figure 3
Evolution of storage and loss moduli as a function of frequency for systems containing 60% (w/w) surfactant.

heptane, located inside the hexagonal region in the phase diagram, showed a crossover point between both viscoelastic functions in the frequency range studied. Therefore, the dynamic oscillatory properties of hexagonal phases are characterized by the appearance of a terminal region at low frequencies (Cordobés, 1997), which was not detected in the lamellar systems.

As can be observed in Figure 2, an increase in surfactant concentration leads to an increase in the values of the linear viscoelastic functions up to a maximum value (i.e. 70% NPFE-10 for systems containing 5% heptane) and then decreases. This effect can be clearly observed in Table III in which the values of the plateau modulus, G_N^0 , calculated as the G' value for which the loss tangent was minimum (Cordobés, 1997), are shown. These maximum values were found at lower surfactant concentrations as heptane content increases, probably due to the proximity of the hexagonal phase boundaries (Cordobés, 2000). These results indicate a higher degree of development of the liquid-crystalline structure as a consequence of the solubilization of heptane (Kilpatrick, 1994). These maximum values of G_N^0 at intermediate surfactant content coincide with minimum values of loss tangent. On the other hand, the proximity to the phase transition is characterized by minimum values of the plateau modulus, which decrease by increasing the amount of heptane solubilized. This behavior can be related to a change in the texture of the lamellar phase when it is observed in the polarization microscope. Thus, Nemeth et al. (Nemeth, 1998) studying a non-ionic surfactant/water system, observed a typical texture of «Maltese Crosses» at surfactant concentrations previous to the maximum values in the viscoelastic functions. Afterwards, the oily streaked-type microstructure was observed. This change of texture indicates a change in the orientation of the domains

(Platz, 1995), which could be related with the deviation found in the trend of the storage modulus (see Table III). These observations are in good agreement with the findings of other authors (Dimitrova, 1995; Thadros, 1995).

Figure 3 shows the evolution of the storage and loss moduli as a function of frequency for a fixed NPFE-10 content and different heptane concentrations. As can be observed, initially, the higher the solubilization of heptane, the higher the values of the viscoelastic functions. This occurs in a heptane concentration of up to around 15%. Starting from this point, a decline occurs probably due to the proliferation of defects in the liquid-crystalline structure in the proximity of the phase transition that induces minor elastic properties. Moreover, the binary system shows a higher tendency to a crossover point between the

Table III
Values of the plateau modulus for lamellar systems

%(w/w) surfactant	%(w/w) heptane	G_N^0 (Pa)
50	25	55±5
	20	40±3.5
55	5	300±10
	10	550±10
	15	520±15
	20	380±
	25	120±5
	30	110±4
60	0	88±5
	5	1020±6
	10	1280±20
	15	950±15
	20	550±10
	25	185±5
65	0	570±10
	5	1350±20
	10	1270±15
	15	950±12
	20	400±8
70	0	670±9
	5	1520±18
	10	1350±15
75	0	800±6
	5	1200±12

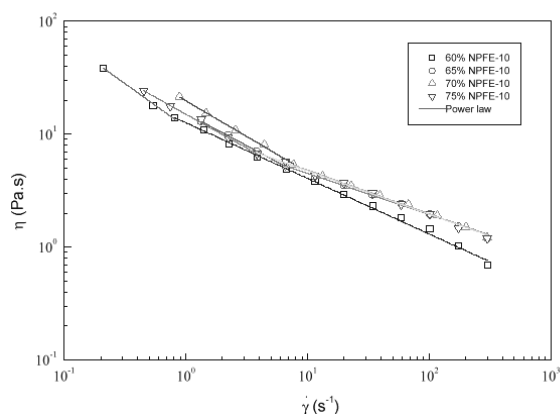


Figure 4
Steady-state flow curves for binary systems.

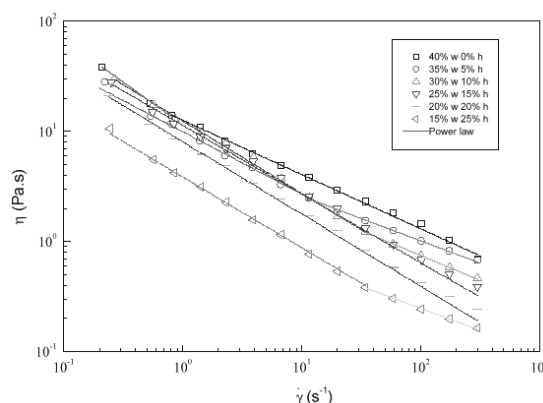


Figure 5
Steady-state flow curves for systems containing 60% (w/w) surfactant.

storage and loss moduli at low frequencies, lower development of the plateau region and higher values of the slope of G' vs. ω . The plateau modulus reaches a maximum value for a concentration of 10% of heptane indicative of a major development in the elastic network. These maximum values move to lower heptane content as NPFE-10 concentration increases (Table III).

b) *Viscous flow behavior.* The flow behavior of lamellar liquid-crystalline systems was determined in a range of shear rates comprized between 0.1 and 300 s^{-1} (Figures 5, 6 and 7). The flow properties are rather similar for all the systems studied, although for higher and intermediate values of shear rates, viscosity curves depend on composition. Up to 10 s^{-1} , the evolution of apparent viscosity as a function of shear rate is characteristic of a shear thinning fluid, showing, in general, a power-law decrease in viscosity. For higher values of shear rates, flow curves are greatly dependent on a composition showing shear thinning, Newtonian or even shear thickening behaviors. Thus, different regions of potential dependence of viscosity can be observed when shear rate is increased up to 300 s^{-1} . The experimental data can be fitted to a power law in each region, defined as:

where n is the flow index and k is the consistency in-

$$(1)$$

dex defined for each potential region.

Two different regions of potential decline of viscosity were found for binary systems (Figure 4), defined by flow indexes « n » and « m », respectively, « n » for values of shear rate lower than a critical shear rate, γ_1 , which delimits the change in the power law tendency, and « m » for values comprized between γ_1 and the maximum shear rate achieved. Similar values of « n » (around -0.6) were found for all

the binary systems studied, except for the system with the lowest content in surfactant (60% NPFE-10), which presents a value of « n » equal to -0.77 . This system is close to the hexagonal phase transition. In the second region of potential decrease, the same effect was found (see Table IV). This shear-thinning behavior has been related to the formation of ordered bylayer structures being aligned in the flow direction (Laun, 1992; Montalvo, 1998). Moreover, Meyer et al. (Meyer, 2000) found different flow regimes depending of shear rate for two lyotropic and thermotropic systems using a control stress rheometer. These authors propose that the first regime can be associated to the presence of «oily streaks» aligned in the flow direction and detected by polarizing microscopy as elongated objects. The second regime was characterized by the presence of a shear-induced onion state. In this case, the viscosity curves can be related to the existence of bylayer or «oily-streaks» structures aligned in the flow direction. The different values of flow indexes found can be explained on the basis of the resistance that the bylayers oppose to flow. It must be emphasized that values of « m » are always lower than « n » (Table IV), probably due to the higher shear-induced alignment of the bylayers in the flow direction achieved as shear rate increases. Moreover, the extension of the first region of potential decay of viscosity, defined by the values of γ_1 , is higher for the systems with the highest surfactant content. As a consequence, it can be deduced that systems with lower surfactant concentration and closer to the transition phase region, are more sensitive to the formation of structures induced by shear flow due to a higher amount of defects in the liquid-crystalline structure (Franco, 1995).

As previously mentioned, flow properties of lamellar liquid-crystalline systems are strongly dependent on shear rate and composition. Figure 5 shows the viscous flow curves of selected systems

Table IV
Values of the flow indexes for potential decrease of viscosity of binary systems

%(w/w) surfactant	%(w/w) water	n	m
60	40	-0.77	-0.50
65	35	-0.57	-0.36
70	30	-0.63	-0.38
75	25	-0.60	-0.38

as a function of heptane content. All the systems evaluated show the same flow behavior above mentioned. However, the number of potential decrease viscosity regions depends on the ability of the liquid-crystalline phase to solubilize heptane. Thus, systems with intermediate concentrations of hydrocarbone (15 and 20% (w/w)) present only a region of potential decrease. Both systems present the higher relative elastic properties for this surfactant concentration showing minimum values of the loss tangent. The rest of lamellar liquid-crystalline systems show the two regions of viscosity decrease.

A more complex behavior can be observed in Figure 6 for systems containing 50 and 55% (w/w) surfactant and maximum content of hydrocarbone solubilized. Three different regimes can be observed. First, a shear-thinning region, at low shear rates, where the sample behaves as a pseudoplastic fluid, characterized by the formation of ordered bilayers structures being aligned in the flow direction (Laun, 1992; Montalvo, 1998). In the second region, shear-thickening or Newtonian flow regimes can be observed, depending on the composition, when a critical shear rate, γ_1 , is reached. This could be explained on the basis that, at this point, some of the bilayers begin to close, resulting in the formation of vesicles. The transition between both flow regimes is taken to be an indication of microstructural changes. The third regime, above a critical shear rate, γ_2 , is characterized by another shear-thinning region. Escalante et al. (Escalante, 2000) related this shear-thinning behavior with the alignment of new multilamellar vesicles formed during shear. However, Roux et al. (Roux, 1994) identified the last regime with a Newtonian behavior, related to the rupture of the vesicles and the total alignment of the bilayers.

In the second regime, for 55% NPFE-10, an increase in viscosity was observed in the system containing 25% (w/w) heptane. This increase was not found for a higher amount of heptane (30%), in which a Newtonian zone can be detected. The same increase in viscosity can be observed for systems containing 30% heptane but only 55% NPFE-10 A

similar behavior has been found in a quaternary system of the anionic sodium dodecylsulfate (SDS), pentanol, dodecane, and brine (Roux, 1994). These authors observed that a transition for a lamellar to a vesicle phase could be discontinuous, when a jump in the viscosity is produced ($\Delta\eta \neq 0$), or continuous, when a Newtonian region is observed ($\Delta\eta = 0$). In this case, an increase in viscosity values takes place in systems with low values of the surfactant/water ratio, which can be related to a higher appearance of shear-induced vesicles.

Figure 6 also provides information on the possible reversibility of structural changes occurring in the system. The effect of an upward/downward shear rate program for 30 minutes can be observed in Figure 6. Thus, shear rate was increased up to 300 s^{-1} for 5 min, this maximum shear rate was maintained for 10 min and then was decreased for 15 min. The system with lower surfactant/water ratio (50% NPFE-10, 30% heptane) clearly shows irreversibility, as the significant higher values of viscosity obtained by reducing shear rate indicates (solid symbols) in comparison to those observed by increasing shear rate (open symbols). This is due to the fact that the vesicles formed are stable in time

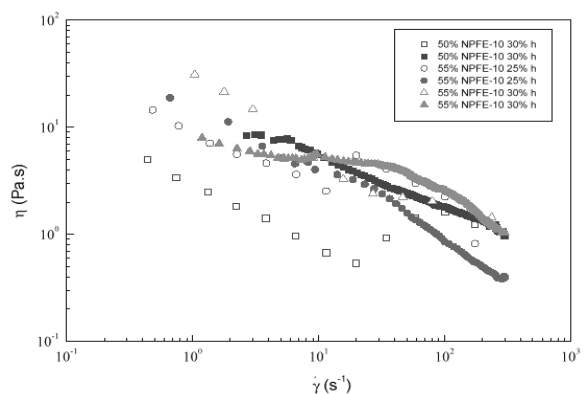


Figure 6
 Steady-state flow curves for selected systems containing maximum heptane content. Solid symbols correspond to flow curves obtained after an upward/downward shear rate program.

and the values of viscosity of the vesicle phase are higher than that of the lamellar phase of stacked bylayers (Escalante, 2000). However, this behavior changes by increasing the surfactant/water ratio. Thus, the system with higher surfactant/water ratio (55% NPFE-10, 30% heptane) showed a decrease in viscosity values, probably due to the total alignment of the bylayers in the flow direction and, consequently, the destruction of the vesicles formed during the upward shear rate ramp, as suggested by Partal et al., (Partal, 2001). The system with 55% NPFE-10 and 25% heptane presents intermediate characteristics of the two different behaviors previously described.

c) *Shear-induced structural observations.* As previously shown, shear flow causes an important effect on the structural modifications of lamellar liquid-crystalline phases. In this section shear-induced structural changes are studied by means of combined rheological and polarizing microscopy observations. As previously described (Franco, 1995), the evolution of transient viscosity for similar systems consists of an initial growth of viscosity (stress overshoot), due to the viscoelasticity of the liquid-crystalline phase, followed by a decrease in viscosity down to an equilibrium or steady-state value (Figure 7). These results can be explained by the partial alignment of the lamellar bylayers in the direction of the flow field, and finally, total alignment of the bylayers occurs, and consequently, an equilibrium viscosity is reached. However, for systems sheared at intermediate values of shear rate (between 2 and 10 s^{-1}) a slight increase in viscosity (stress undershoot) takes place related to the development of mechanically induced defects in the structure of the lamellar phase (Franco, 1995; Partal, 2001). As can be observed, this slight increase in viscosity starts at lower times as shear rate increases and disappears for the highest values of shear rate (100 s^{-1}).

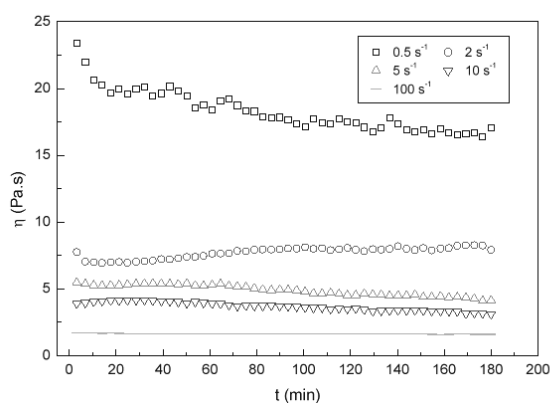


Figure 7

Transient tests for a binary system containing 70% (w/w) surfactant.

Figure 8 shows the evolution of the lamellar textures during a transient test at two-selected shear rates. Initially, applying a shear rate of 2 s^{-1} (Figure 8A), the characteristic mosaic texture of the non-oriented lamellar phase is detected. The proliferation of elongated structural units in the flow direction is observed later on. As can be observed, some typical «Maltesian crosses» are always present in the sheared lamellar matrix. The presence of «Maltesian crosses» has been related to the existence of shear-induced structures in lamellar phases such as onions, vesicles or spherulites (Partal, 2001; Goldszal, 1995). However, the appearance of these new structures is not generalized. As can be observed in Figure 8A, at intermediate times an incipient oily streak texture appears, and finally a total alignment of the bylayers occurs. Optical micrographs obtained when the lamellar phase is sheared at 10 s^{-1} show the same sequence of liquid-crystalline textures (Figure 8B). However, in this case, the mosaic texture was clearly followed by the «oily streaks» texture at intermediate times and, finally, the total alignment of this texture was again observed. As can be seen in Figure 9, the shear rate exerts an important influence on the texture of the lamellar phase. Thus, the different textures observed at the end of the experiments are rather similar to un-presheared samples when low values of shear rate were applied (i.e. 0.5 s^{-1}), in spite of the alignments of the lamellar units. On the contrary, an increase in shear rate promotes the development of the oily streaked texture and finally, for higher values of shear rates (i.e. 100 s^{-1}), the total alignment of the lamellar crystal is obtained (Figure 9).

As can be observed in Figure 10, the transient flow behavior of a lamellar ternary system with a relatively high heptane concentration (30% (w/w)) is quite different to that previously described for binary systems. Thus, an initial increase in viscosity with time, followed by a slight decrease of viscosity was always observed. Nevertheless, a stress undershoot was not detected in any case. This transient shear

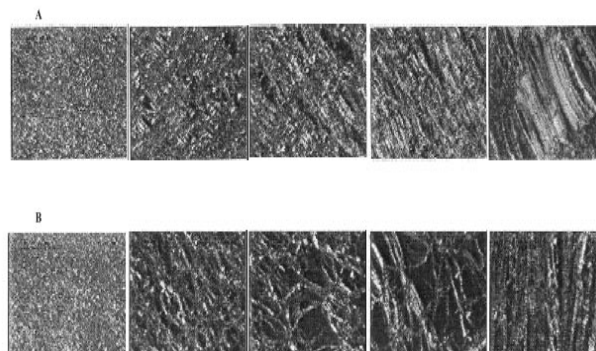


Figure 8

Evolution of lamellar textures with time for a binary system (70% (w/w) surfactant) at different shear rates (A: 2 s^{-1} , B: 10 s^{-1}).

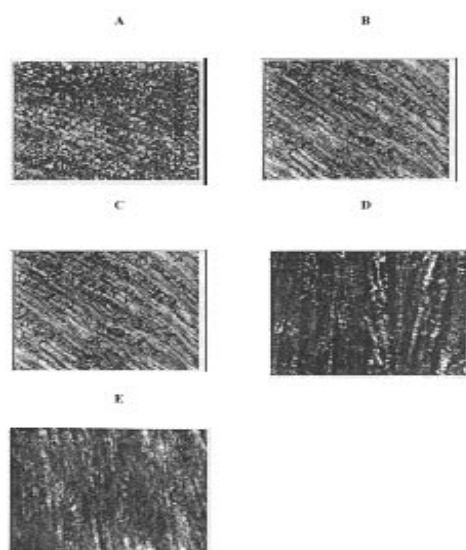


Figure 9

Lamellar textures observed at the end of transient experiments for a binary system (70% (w/w) surfactant). A: un-presheared sample, B: sheared at 0.5 s^{-1} , C: sheared at 5 s^{-1} , D: sheared at 10 s^{-1} , E: sheared at 100 s^{-1} .

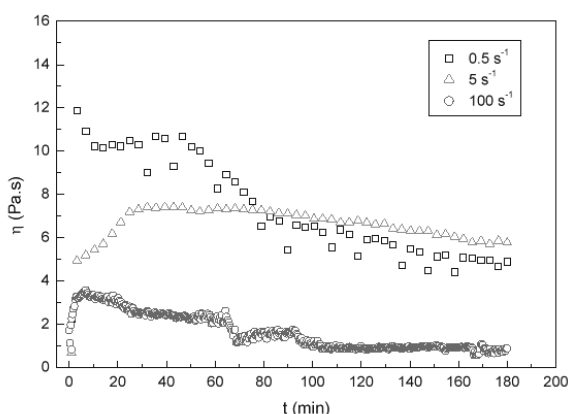


Figure 10

Transient tests for a ternary system containing 50% (w/w) surfactant and 30% (w/w) heptane.

flow causes microstructural changes in the liquid-crystalline phase, which have been related in the literature to the gradual development of vesicles or «onions» in the lamellar matrix (Roux, 1994; Escalante, 2000). The presence of these new structures has been detected using several techniques, being microscopy (polarizing and electron microscopy) the most widely used. The structural changes are reflected in the optical micrographs shown in Figure 11. The textures detected at relatively high shear rates, i.e. 40 s^{-1} , in concordance with others found in the literature (Diat, 1993; Meyer, 2000; Müller, 1999), seem to indicate the presence of close-packed monodisperse spherulites showing a homogenous granular texture. Furthermore, the texture of the system sheared at

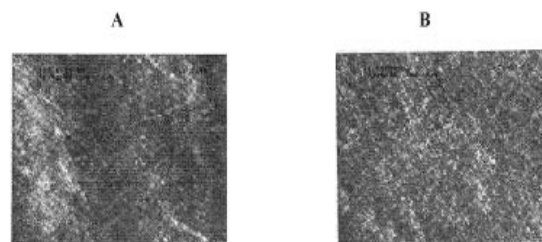


Figure 11

Lamellar textures observed at different shear rates (A) 40 s^{-1} and (B) 100 s^{-1} for a ternary system (50% (w/w) surfactant and 30% (w/w) heptane).

100 s^{-1} becomes more regular, which can be related to lower characteristic sizes of the structural units (Müller, 1999).

Rheological data and microscopy images used in this study seem to confirm the existence of vesicles in the lamellar shear-induced texture of systems formed by a non-ionic surfactant and a relatively higher content of a linear hydrocarbure, but do not provide information about vesicles formation. In order to obtain information about this process, techniques such as small angle light and neutron scattering should be used. Several authors have reported different mechanisms for shear induced vesicle formation depending on factors such as surfactant structure and concentration but also on their initial shear induced morphology (Richtering, 2001). Therefore, a more detailed investigation of this process is necessary.

4. REFERENCES

- Alfaro, M.C., Guerrero, A. and Muñoz, J. (2000) Dynamic Viscoelasticity and Flow Behavior of a Polyoxyethylene Glycol Nonylphenyl Ether/toluene/water System. *Langmuir*, **16**, 4711-4719.
- Barnes, H.A. (1980). Detergents in *Rheometry Industrial Applications*, p.33-110, K. Walters (Ed.), John Wiley&Sons, New York.
- Comelles, F., Caelles, J., Pascual, A. and Sánchez Leal, J. «18th International I.F.S.C.C. Congress», Venice, 1994.
- Cordobés, F. and Gallegos, C. (2000) Viscoelasticidad lineal de la fase líquido-cristalina laminar de un sistema tensioactivo no iónico/hidrocarburo/agua. *Grasas y Aceites*, **53**, 167-172.
- Cordobés, F., Muñoz, J. and Gallegos, C. (1997) Linear Viscoelasticity of the Direct Hexagonal Liquid Crystalline Phase for a Heptane/Nonionic Surfactant/Water System. *J. Colloid Interface Sci.*, **187**, 401-417.
- Diat, O., Roux, D. and Nallet, F. (1995) Layering effect in a sheared lyotropic lamellar phase. *Phys. Rev. E*, **51**, 3296-3299.
- Diat, O., Roux, D. y Nallet, F. (1993) Effect of shear on a lyotropic lamellar phase. *J. Phys. II France*, **3**, 1427-1452.
- Dimitrova, G.T., Thadros, Th.F. and Luckman, P.F. (1995) Investigations of the phase changes of nonionic surfactants using microscopy, differential calorimetry, and rheology. 1. Synperonic A7, a C₁₃/C₁₅ alcohol with 7 mol of ethylene oxide. *Langmuir*, **11**, 1101-1111.

- Engström, S. (1990) *Lipid Technol.*, **2**, 42-45.
- Escalante, J.I., Gradzielski, M., Hoffmann, H. and Mortensen, K. (2000) Shear-induced transition of originally undisturbed lamellar phase to vesicle phase. *Langmuir*, **16**, 8653-8663.
- Franco, J.M., Muñoz, J. and Gallegos, C. (1995). Transient and steady flow of a lamellar liquid crystalline surfactant/water system. *Langmuir*, **11**, 669-673.
- Friberg, S.E. (1990). Applications of amphiphilic association structures. *Adv. Colloid Interface Sci.*, **32**, 167-182.
- Gallegos, C., Muñoz, J. y Flores, V. (1987) Estudio reológico de diagramas de fases de sistemas alcohol graso polietoxilado/agua I. *Jorn. Com. Esp. Deterg.*, **18**, 357-373.
- Goldszal, A., Jamieson, A.M., Mann, J.A., Polak, J. and Rosenblatt, C. (1995) Rheology, optical microscopy, and electron microscopy of cationic surfactant gels. *J. Colloid Interface Sci.*, **180**, 261-268.
- Jager-Lézer, N., Feutelais, Y., Doucet, J., Tranchat, J.F., Alard, V., Baszkin, A. and Grossiord, J.L. (1999) Influence of the chemical nature of various geometries on the rheological behaviour of a lamellar lyotropic phase. *J. Rheol.*, **43**, 1067-1081.
- Jager-Lézer, N., Tranchat, J.F., Alard, V., Doucet, J. and Grossiord, J.L. (1998) rheological behaviour of a lamellar lyotropic phase as a function of the substrate nature. *J. Rheol.*, **42**, 417-432.
- Jiménez, I., Montalvo, G. and Rodenas, E. (2000) Study of 1,2-Octanediol as cosurfactant of sodium dodecyl sulfate. *Langmuir*, **16**, 8604-8610.
- Kilpatrick, P.K., Khan, S.A., Tayal, A. y Blackburn, J.C. (1994). Rheological study of polycrystalline lyotropic mesophases in the cesium *n*-tetradecanoate/water system in *Structure and Flow in Surfactants Solutions*, p.229-238, C.A. Herb y R.K. Prud'homme, (Eds.), A.C.S. Symposium Series 578, Washington D.C..
- Laüger, J., Linemann, R., Richtering, W. and Lindner, P. (1995) Sfera orientation of a lamellar lyotropic liquid crystal. *Rheol. Acta*, **34**, 132-136.
- Laüger, J., Weigel, R., Berger, K., Hiltrop, K. y Richtering, W. (1996) Rheo-small-angle-light scattering investigation of shear induced structural changes in a lyotropic lamellar phase. *J. Colloid Interface Sci.*, **181**, 521-529.
- Laun, H.M., Bung, R., Hess, S., Loose, W., Hess, O., Hank, K., Hädicke, E., Hingmann, R., Schmidt F. and Lindner, P. (1992) Rheological and small angle neutron scattering investigation of shear-induced particle structures of concentrated polymer dispersions submitted to plane Poiseuille and Couette flow. *J. Rheol.*, **36**, 743-787.
- Lockwood, F.E., Benchaita, M.T. y Friberg, S.E. (1987) Study of lyotropic liquid crystals in viscometric flow and elastohydrodynamic contact. *Asle Transactions*, **30**, 539-548.
- Meyer, C., Asnacios, S., Bourgaux, C. and Kleman, M. (2000) Rheology of lyotropic and thermotropic lamellar phases. *Rheol Acta*, **39**, 223-233.
- Mitchell, J.D., Tiddy, G.J.T., Waring, L., Bostock, T. and Mcdonald, M.P. (1983) *J. Chem. Soc. Faraday Trans.*, **79**, 975-991.
- Montalvo, G., Rodenas, E. and Valiente, M. (1998) Phase and rheological behaviour of the dodecyltetraethylene glycol/benzyl alcohol/water system at low surfactant and alcohol concentration. *J. Colloid Interface Sci.*, **202**, 232-237.
- Moros, J.E., Cordobés, F., Gallegos, C. and Franco, J.M. (2001). Linear viscoelasticity of concentrated polyethylene glycol tert-octylphenyl ether solutions. *J. Dispersion Sci. Technol.*, **22**, 409-420.
- Muller, S., Börschig, C., Gronski, W. and Schmidt, C. (1999) Shear-Induced states of orientation of the lamellar phase of C₁₂E₄/water. *Langmuir*, **15**, 7558-7564.
- Müller-Goyman, C.C. (1987) *Acta Pharm. Technol.*, **33**, 126-130.
- Muñoz, J., Gallegos, C. y Flores, V. (1991) Structure and rheology in surfactant systems. *Tenside Surf. Det.*, **28** (3), 204-207.
- Németh, Z., Halász, L., Pálincas, J., Bóta, A. and Horányi, T. (1998) Rheological behaviour of a lamellar liquid crystalline surfactant-water system. *Colloids Surfaces A*, **145**, 107-119.
- Paasch, S., Schambil, F., Schuwer, M.J. (1989) The rheological properties of lamellar lyotropic liquid crystals. *Langmuir*, **5**, 1344-1346.
- Partal, P., Kowalski, A.J., Machin, D., Kiratzis, N., Berni, M.G. and Lawrence, C.J. (2001) Rheology and microstructural transitions in the lamellar phase of a cationic surfactant. *Langmuir*, **17**, 1331-1337.
- Pilpel, N. and Rabbani, M.E. (1987) Formation of liquid crystals in sunflower oil in water emulsions. *J. Colloid Interface Sci.*, **119**, 550-558.
- Platz, G., Polike, J., Thunig, C., Hoffmann, H., Nickel, D. and von Rybinski, W. (1995) Phase behaviour, lyotropic phases, and flow properties of alkyl glycosides in aqueous solutions. *Langmuir*, **11**, 4250-4255.
- Richtering, W. (2001) Rheology and shear induced structures in surfactant solutions. *Curr. Opin. Colloid Interface Sci.*, **6**, 446-450.
- Riego, M.B. and Gómez-Herrera, C. (1988) Química física interfacial de emulsionantes alimentarios. Parte II. Mecanismos de estabilización de emulsiones. Emulsiones en alimentos elaborados. *Grasas y Aceites*, **39**, 44-111.
- Robles-Vásquez, O., Corona-Galván, S., Soltero, J.F.A., Puig, J.E., Tripodi, S.B., Vallés, E. and Manero, O. (1993) Rheology of lyotropic liquid crystals of Aerosol OT. *J. Colloid Interface Sci.*, **160**, 65-71.
- Robles-Vásquez, O., Soltero, J.F.A., Puig, J.E. and Manero, O. (1994) Rheology of lyotropic liquid crystals of aerosol OT. III. Effect of salt and hydrocarbons. *J. Colloid Interface Sci.*, **163**, 432-436.
- Roux, D., Nallet, F. and Diat, O. Relation between rheology and microstructure of lyotropic lamellar phases in *Structure and Flow in Surfactants Solutions*, p. 300-305, C.A. Herb and R.K. Prudhomme (Eds.), American Chemical Society, Washington D.C., 1994.
- Sierro, P. and Roux, D. (1997) Structure of a lyotropic lamellar phase under shear. *Phys. Rev. Lett.*, **78**, 1496-1499.
- Thadros, Th.F., Dimitrova, G.T., Luckman, P. Ftaelman, M.C. and Loll, P. (1995) *Euro Cosmetics*, **3**, 17.
- Tiddy, G.J.T. (1980) Surfactant-water liquid crystal phases. *Phys. Reports*, 1-46.
- van de Pas, J.C. (1993). Ph.D. Thesis, Rijksuniversiteit Groningen, Groningen, The Netherlands.
- van der Linden, E., Hogersvorst, W.T. and Lekkerker, H.N.W. (1996) Relation between the size of lamellar droplets in onion phases and their effective surface tension. *Langmuir*, **12**, 3127-3130.
- Vinches, C., Coulon, C. and Roux, D. (1994) The symmetrical-asymmetrical transition of the sponge phase. 1. Effect of the salinity. *J. Phys. II*, **4**, 1165-1193.
- Weigel, R., Laüger, J., Richtering, W. and Lindner, P. (1996) Anisotropic small angle light and neutron scattering from a lyotropic lamellar phase under shear. *J Phys II*, **6**, 529-542.