

Rheological and phase behaviour of amphiphilic lipids

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RESUMEN

Comportamiento reológico y de fase de lípidos anfifílicos

En este capítulo se realiza una revisión de las distintas estructuras coloidales de asociación que pueden formar los lípidos anfifílicos en estado líquido-cristalino y de sus correspondientes propiedades de flujo en cizalla. Se describe la estructura y comportamiento reológico de cristales líquidos termotrópicos, con énfasis en los de tipo esméctico, fases gel, y cristales líquidos liotrópicos: nemáticos, laminares, laminares diluidos, dispersiones de laminares, hexagonales y cúbicos. Se hace hincapié en la importancia de una buena caracterización reológica y reo-óptica de cara a sus aplicaciones prácticas, desarrollo de formulaciones y como una técnica útil para determinar diagramas de fases y detectar cambios de estructura. Se ha usado una metodología histórica para analizar la evolución de la caracterización reológica e identificación de las diferentes estructuras líquido-cristalinas y estructuras afines. La interpretación de comportamientos de flujo viscoso no newtonianos, fenómenos tixotrópicos y antitixotrópicos y de las propiedades viscoelásticas lineales, determinadas con ensayos dinámicos y de fluencia, y no lineales, descritas mediante la diferencia de esfuerzos normales y ensayos de relajación del esfuerzo, se basa en la interrelación microestructura-comportamiento reológico. La naturaleza policristalina de los cristales líquidos resulta ser muy sensible a la cizalla, debido al cambio de tamaño y orientación de los dominios líquido-cristalinos mientras fluyen.

PALABRAS-CLAVE: Comportamiento de fase — Comportamiento reológico — Lípidos anfifílicos.

SUMMARY

Rheological and phase behaviour of amphiphilic lipids

This chapter reviews the different association structures which are likely to be formed by amphiphilic lipids in the liquid-crystalline state and their corresponding shear flow properties. The structure and rheological behaviour of thermotropic liquid crystals, emphasizing the properties of smectic mesophases, and those of lyotropic liquid crystals such as: nematic, lamellar, diluted lamellar, lamellar dispersions, hexagonal and cubic mesophases are described. The importance of a comprehensive rheological characterisation, including reo-optical techniques, is pointed out for their practical applications, development of formulations and as a useful technique to assist in the determination of phase diagrams. A historical approach has been used to discuss the evolving field of the rheology and structure identification of liquid crystals formed by amphiphilic lipids and surfactants. Non-Newtonian viscous shear flow, thixotropic and antithixotropic phenomena, linear viscoelastic

properties -described by dynamic and creep compliance experiments- and non-linear viscoelastic properties - described by the difference of normal stresses and stress relaxation tests are interpreted on the basis of a microstructure-rheology relationship. The polycrystalline nature of liquid crystals turns out to be rather sensitive to shear due to the change of both size and orientation of the liquid-crystalline monodomains under flow.

KEY-WORDS: Amphiphilic lipids — Phase behaviour — Rheological behaviour.

INTRODUCTION

Amphiphilic lipids contain a hydrophilic head and one or two hydrocarbon long tails in the same molecule. The former tends to dissolve in water or polar solvents, while the latter tends to do so in nonpolar solvents. As a consequence, they form association structures, above both a critical temperature and concentration, in order to reduce the free energy in the system to a minimum.

Depending on the chemical nature of the amphiphilic lipid, water concentration, temperature, and the concentration of additives such as different oils, inorganic salts, alcohols and sugar, different types of association structures (micelles, lyotropic liquid crystals -also called lyotropic mesophases-, gel phases) can exist in these systems. Such a fascinating variety of association structures leads to the occurrence of a wide range of rheological properties (Muñoz et al, 1989, 1991). In turn, this means that a tailor-made rheological response of an amphiphilic lipid system can be achieved by calculated changes in microstructure (Barnes, 1980). Conversely, rheology may assist in the determination of phase diagrams since it is sensitive not only to changes of association structures but also to variations of both composition and temperature within the realm of existence of a particular phase or mesophase (Rounds, 1994), (Dimitrova et al, 1995), (Kröger, 1996). This is due to the fact that the rheology of amphiphilic lipid systems is dependent on the physico-chemical interactions governing the association structure formed.

Even though some progress has been made in the theoretical calculation of phase diagrams (Evans and Wennerström, 1994), it cannot be denied that the actual determination of phase diagrams relies on experimental work. In fact, the increasing use of new or improved techniques has revealed significant errors in earlier phase diagrams, mainly studied by isoplethal instead of isothermal methods (Laughlin, 1990). Besides classical techniques such as direct observation, centrifugation, polarising microscopy textures, dilatometry, calorimetry and small-angle x-ray diffraction, Laughlin (1990) cited deuterium (or phosphorus) nuclear magnetic resonance, improvements in calorimetric methods and the «lyotrope gradient» principle, as recent techniques increasingly used for carrying out phase studies. Additionally, electron microscopy techniques, such as freeze-fracture electron microscopy or cryo-transmission electron microscopy, small-angle neutron scattering, light scattering, time-resolved fluorescence quenching along with refined rheological and rheo-optical techniques must also be taken into account.

A further type of association structures formed by amphiphilic lipids are thermotropic liquid crystals (also referred to as thermotropic mesophases), which are formed at temperatures embraced between those corresponding to the pure crystalline state and the actual melting point of the amphiphilic lipid. In this chapter, all the types of thermotropic mesophase structures will be covered for the sake of completeness, even though amphiphilic lipids basically form smectic mesophases.

Liquid crystals have interesting applications in different fields: in the detergent and related industries (Barnes, 1980), in the cosmetics industry (Comelles et al, 1994), in pharmacy, as vehicle or solubilization media of active principles, in biology, for membrane simulation, vesicles, extraction of peptides and proteins (Goldstein and Leibler, 1987), (Brown and Wolken, 1979), in the food industry (Krog et al, 1985), (Söderberg and Ljusberg-Wahren, 1990), (Larsson and Dejmek, 1990), (Kim and Baianu, 1991) in emulsion technology, as stabilisers since they may impart suitable rheological properties to the droplet interface and to the continuous phase (Pilpel and Rabbani, 1987), (Riego and Gómez Herrera, 1988) and so on.

Micelles will not be addressed in this review since they would require a full chapter for themselves. This work focuses on gel phases and on the different lyotropic liquid-crystalline structures formed by synthetic as well as biological amphiphiles, with emphasis on their rheology.

A historical approach is used to discuss the continually evolving field of the rheology of amphiphilic lipids. Readers who are not familiar with

rheological techniques are referred to some excellent books, such as the introductory-level volume by Barnes et al (1989), the more advanced books by Ferguson and Kemblowski (1991) and Macosko (1994) or the fundamental work by Ferry (1980).

CRYSTALLINE STATE

In the solid state amphiphilic lipids form crystalline structures which are currently studied by X-ray diffraction. Their molecules are packed in bilayers with the polar heads located on the external plane and with the hydrocarbon chains showing a parallel arrangement inside the bilayers. In fact, their packing properties are similar to those of fatty acid crystals.

Lipid molecules show polymorphic behaviour insofar as they exhibit different packing in the solid state with ageing time and present multiple melting phenomena. Polymorphism is associated with changes in the tilt of the molecules in the bilayers and possible of variations in hydrocarbon chain packing (Larsson, 1994).

LIQUID CRYSTALS AND THERMOTROPIC LIQUID CRYSTALS

Liquid Crystals

Liquid crystals, also called mesophases, may be considered as an intermediate state of matter between liquids and solids. While in the crystalline state the movement of molecules is practically restricted, liquids exhibit structures with short-range order and molecules can readily flow. Molecules in liquid crystals achieve some freedom of relative movement while still retaining a kind of long-range order. This results in structures in which molecules are frequently associated with a parallel or near-parallel arrangement.

Liquid crystals originate when a crystal is subjected to influences which loosen the hold of the molecules on one another due to either a rise of temperature in some cases or the addition of a solvent in others. The former mechanism leads to thermotropic liquid crystals and the latter to lyotropic liquid crystals, both of them exhibiting polymorphism.

Thermotropic Liquid Crystals

Thermotropic liquid crystals occur when some pure organic solids or mixtures of solids are heated and do not pass directly from the solid state to the liquid state but they form a semi-fluid phase that

shares some properties typical of solids and some others commonly found in liquids. Ordinary thermotropic liquid crystals are usually classified as nematic, cholesteric and smectic (Brown and Wolken, 1979). Additionally, a large number of polymorphic transitions can be detected with pure amphiphilic lipids between the crystalline and the liquid states (Winsor, 1974).

Nematic Liquid Crystals (N)

Nematic liquid crystals consist of an arrangement of parallel or nearly parallel elongated molecules, which are mobile in three directions (they do not form layers), due to the lack of a periodic arrangement, and can rotate about one axis. However, the mean distance between molecules is smaller than their diameter, thus resulting in the rotation not being free and in significant intermolecular interactions. This may give rise to complex flow properties, although nematic liquid crystals exhibit fluid-like properties and less viscosity than smectic liquid crystals. In fact, nematic liquid crystals possess the lowest structural order in thermotropic liquid crystals and they are transformed on heating to the isotropic liquid without undergoing a further mesophase transition. They are uniaxial from an optical point of view with the optic axis parallel to the mean direction of the long molecular axes, the so-called nematic director. However, they exhibit distinctive textures—mainly threadlike disclination lines associated with structural discontinuities in the material (Hartshorne, 1974) when observed under polarising microscopy.

Cholesteric Liquid Crystals (N*)

Cholesteric liquid crystals are sometime classified as a special type of nematic liquid crystals. As the name indicates, they were first detected with cholesteryl esters. The structure can be described as that of a nematic mesophase twisted about an axis perpendicular to the long axes of the molecules. While on a local scale the nematic and cholesteric structures are alike, on a large scale the cholesteric director follows a helical form. As a consequence of its structure, this mesophase exhibits a very strong optical activity. In general, the lack of long-range translational order is responsible for their fluid-like properties. However, the occurrence of highly viscous cholesteric liquid crystals with gel-like properties was reported to exist in cholesteryl nonanoate. These liquid crystals were also observed in those homologues which form strongly twisted cholesteric mesophases when upon cooling an isotropic liquid, an isotropic texture was first observed, before a birefringent texture appeared.

This behaviour was ascribed to the formation of a regular lattice of alignment singularities (Saupe, 1974).

Smectic Liquid Crystals

In smectic liquid crystals the elongated molecules are essentially parallel to one another, and are arranged in layers with the mean direction of the long axes of the molecules normal to the layers. This term is derived from the Greek «smectos», whose meaning is «like soap», and is used because alkyl carboxylates form mesophases of this type.

Smectic liquid crystals are fluid but far more viscous than nematic liquid crystals. Their fluidity is due to the flexibility of the layers and also to the fact that interlayer attractions are weak compared with the lateral intermolecular forces and, therefore the layers can slide over each other quite easily while still remaining essentially parallel. For this reason, they can exhibit different characteristic textures when observed under polarising microscopy, such as homeotropic, focal conic, «bâtonnets» and fan like textures. Smectic liquid crystals may be classified as structured or unstructured phases depending on the molecular order within a layer. A comprehensive study of polymorphism for this kind of liquid crystals was given by Demus et al (1983).

Idziak et al, (1994) used a Couette shear cell with concentric cylinders which are transparent to x-rays to determine the orientation of a smectic-A liquid crystal as a function of the shear rate. At low shear rates the orientation was not uniform but a heterogeneously mixed polydomain texture with layers randomly oriented parallel or normal to the flow direction. At high shear rates, a homogeneous orientation regime was observed where the layers oriented perpendicular, by no means parallel as could be expected, to the flow direction.

The occurrence of thermotropic mesophases in amphiphilic lipids is a consequence of a balance of the strong attraction between hydrophilic head groups and the weak attractive forces between hydrocarbon chains. Soaps are among the most well-known amphiphilic lipids that form thermotropic liquid crystals. Different structures (mainly ribbon, disc and lamellar phases) have been proposed to exist in these systems (Winsor, 1974), (Tiddy, 1980). Tamamushi (1974) reported that smectic liquid crystals, like the corresponding lyotropic lamellar mesophase, formed by ammonium salts of higher normal carboxylic acids exhibited non-Newtonian (pseudoplastic) rheological properties at intermediate shear rates and maximum values of apparent viscosity at the melting point of the liquid crystal. A further comparison between the rheology

of thermotropic and lyotropic liquid crystals can be made with the ternary system of ammonium laurate, n-octanol and water. The main conclusion was that the activation energy for viscous flow of the thermotropic liquid crystal turned out to be one order of magnitude higher than that of the lyotropic mesophase (Tamamushi et al, 1976). Different types of phospholipids and 2-monoglycerides of intermediate chain length form lamellar structures, where hydrocarbon chains exhibit a sort of fluid-like disorder due to the weakness of the van der Waals forces compared to the motion caused by thermal energy. This is compensated by attraction forces between polar heads, guaranteeing the continuous existence of the bilayer structure (Chapman, 1982), (Larsson, 1994).

GEL PHASES

Gel phases may be found when crystals of amphiphilic lipids are hydrated so that water reaches the hydrophilic region of the bilayer and the crystals swell, keeping the crystalline structure of the bilayer and the «all-trans» conformation of the chains (Larsson, 1994). The structure consists of alternating «solid-like» hydrocarbon bilayers and water layers. Dialkyl lipids like lecithin present a parallel arrangement of tails which are not inclined, while monoglycerides favour bilayers with a certain tilt. Furthermore, potassium stearate forms monolayers with interdigitating hydrocarbon tails (Tiddy, 1980), (Tiddy and Walsh, 1983). A good description of gel phases formed by soap/water systems was provided by Winsor (1974). Alternatively, this structure may occur when the lyotropic lamellar mesophase is cooled below the transition temperature to the crystalline state. This transition may be detected by a change in either the qualitative shape of the sample viscoelastic spectrum or the quantitative values of the viscoelastic functions, such as the storage modulus, the loss tangent, the instantaneous compliance, etc. Ekwall (1975) also claimed that a sort of gel phase may be produced when a stiff hydrocarbon skeleton, like that of cholesterol, is solubilized in a lyotropic mesophase.

While, in some cases, such as the tetradecylamine-water system (Larsson and Al-Mamun, 1974), gel phases are considered thermodynamically stable, in others the gel is metastable evolving to a mixture of water and hydrated crystals of the amphiphilic lipid, the so-called coagel. However, Laughlin (1990), (Laughlin et al, 1990) claimed that the gel «state» should not be regarded as a discrete phase, but it probably consists of colloiddally structured biphasic mixtures of an ordered phase (crystal hydrates) and a liquid phase.

The gel structure represents an intermediate state between a liquid crystal with its aggregates of unordered hydrocarbon tails in a semifluid state and the crystalline state with ordered chains (Brown and Wolken, 1979). It should be noted that saturated diacyl-phosphatidylcholines show an intermediate structure between the gel phase and the lamellar mesophase upon increasing temperature, the so-called rippled phase (Larsson, 1994).

LYOTROPIC LIQUID CRYSTALS

Lyotropic liquid crystals are formed when polar solvents like water or glycerine are added to amphiphilic lipids in certain composition ranges. Surfactants in dilute aqueous dispersions may assemble into a variety of micellar aggregates above both a critical concentration and temperature, exhibiting different geometrical shapes. These are controlled by geometrical constraints and by the interface curvature, which in turn are determined by intra-micellar forces occurring in different planes (Mitchell and Ninham, 1981). As surfactant concentration increases inter-micellar forces become progressively more important and may cause either a change in the critical packing parameter (Israelachvili, 1985) leading to a further shape transition or a disorder/order transition to the liquid crystalline state (Tiddy and Walsh, 1983). The role of entropic forces between amphiphilic surfaces has also been taken into account by Israelachvili and Wennerström (1996).

Structure of Lamellar Liquid Crystals (L_α)

The most common lyotropic liquid crystal has a lamellar structure. In the detergent industry, it is known as the neat soap phase. The molecular packing in the lamellar structure gives double layers with the water-insoluble tails together and the hydrophilic part of the molecule in the boundaries with water. The double layers pack parallel to one another and are separated from each other by a water layer. The hydrocarbon chains are to some extent disordered, exhibiting essentially fluid-like properties and being able to move in all directions. However, this ability is restricted by the interactions of hydrophilic groups with water.

The structure of the lamellar bilayer can be determined by X-ray diffraction. The thickness of the water layer can vary from ~0.8nm to >10nm depending on the composition, while surfactant bilayer thicknesses are generally about 10-50% less than the length of two «all-trans» surfactant chains (Tiddy and Walsh, 1983). The thickness decreases with increasing temperature or water concentration; these changes of thickness may be attributed to the

folding of the hydrocarbon chains and/or the tilt of the molecules in the layers.

This mesophase looks slightly translucent, exhibiting semi-fluid properties with a weak-gel rheological consistency, which does not apparently change within its realm of existence. It is optically anisotropic when viewed through a microscope between crossed-polars, showing textures clearly different from those shown by the hexagonal mesophase. Lamellar liquid crystalline textures may be homeotropic or focal-conic (threadlike, mosaic or oily streaks patterns), (Rosevear, 1954), (James y Heathcock, 1981). While the former is likely to occur when a sample is gently sheared between the slide and cover-slip, the mosaic texture is enhanced either at high temperature or after extensive shearing (Franco et al, 1995). In fact, shear favours disclination defects in the microstructure following the flow direction (Gallegos et al, 1987a).

In practice, the whole microstructure is polycrystalline; i.e. it is formed by the combination of clusters of flexible bilayers, each of them characterized by a director which defines the main orientation of the so-called monodomain. In other words, the polydomain lamellar microstructure is formed by connected liquid crystalline monodomains with random orientation so that from a macroscopic point of view it looks disoriented and with structural defects (Barnes, 1980). The technique of freeze-fracture transmission electron microscopy provides clear pictures supporting the microstructure above described (Heusch and Kopp, 1987 and 1988), (Jousma et al, 1987).

The lamellar mesophase may be in equilibrium through two- and three- phase regions with almost all the other mesophases that occur in amphiphilic systems (Ekwall, 1975). In binary systems the theoretically expected sequence as water concentration decreases would be: micelles, lyotropic liquid crystals (nematic, cubic, direct hexagonal, bicontinuous cubic, lamellar, reversed bicontinuous cubic, reversed hexagonal), reversed micelles and crystalline surfactant or thermotropic liquid crystal. In practice, not all such possible transitions do occur in real systems.

Rheology of Lamellar Liquid Crystals (L_{α})

The pioneering studies on the rheology of lyotropic liquid crystals dealt with the flow properties of lamellar mesophases by determining upward and downward flow curves, which showed thixotropic and antithixotropic behaviours (Solyom and Ekwall, 1969). Tamamushi (1976) demonstrated the existence of viscoelasticity in ternary systems. Further manifestations of viscoelasticity were reported for a lecithin/water binary system after detecting normal stress differences under shear flow, measuring the

stress relaxation after steady flow and attempting to conduct small amplitude oscillatory shear experiments (Duke and Chapoy, 1976). Bohlin and Fontell (1978) proposed the theory of cooperative coordination number to explain the flow of the lamellar mesophase. They suggested that shearing was likely to create large strongly oriented domains and also claimed that shear stress followed a power-law relationship with shear rate in multi-step flow curves, and with time in stress relaxation tests. The exponent was the reciprocal of the cooperative coordination number, which was defined as the number of structural units interacting each other. An average value of 2 was proposed for the lamellar mesophase since it was modelled as flexible aqueous layers sandwiched between hydrocarbon bilayers. This theory was extended to fit oscillatory shear results of lamellar and hexagonal mesophases, although no evidence of linear viscoelastic behaviour was given (Bohlin, 1979). Unfortunately, the whole theory has been demonstrated that fail to explain the general rheology of lyotropic mesophases, at least as formulated by its authors.

The rheology of the lamellar mesophase formed by hen-egg lecithin and water was studied by Bourgoin and Shankland (1980). They proposed that pre-sheared samples exhibited a plastic behaviour, reaching a lowest shear rate of about $0.002s^{-1}$. They confirmed the predictions of Bohlin and Fontell (1978) that stress relaxation after steady shear consisted of two steps: a nearly instantaneous relaxation followed by slow stress decay. Again they could not conduct dynamic viscoelasticity measurements in the linear domain.

Hirsch et al (1982) studied the flow viscous properties of a lamellar mesophase formed in a quaternary anionic surfactant/alcohol/hydrocarbon/water or brine system. They reported shear thinning flow properties and maximum viscosities at intermediate hydrocarbon concentration within the lamellar region. They also observed a drop in viscosity with both temperature and NaCl concentration, which was less and less apparent with increasing shear rates. Eventually a high salt concentration led to the mesophase destabilization and the melting point of the liquid crystal was detected by a transition from shear thinning to Newtonian behaviour also confirmed by the lack of birefringent textures.

Muñoz et al (1988a), (1991) reported that the Ostwald-de Waele power law indexes of the lamellar mesophase formed by a polyoxyethylene fatty alcohol $C_{12-14}EO_8$ were hardly influenced by either concentration or temperature, although a steady drop in viscosity was always found as temperature approached the melting point of the liquid crystal. Oswald and Allain (1988) were the first to emphasise the role of structural defects in the

fluid rheology of lamellar mesophases. In fact, they attributed the appearance of a small peak in viscosity around the temperature locating the lamellar/isotropic transition to a marked increase in the density of dislocation loops. Paasch et al (1989) claimed that the lamellar mesophase of several nonionic surfactants C_xEO_y of low HLB exhibited yield stresses which were dependent on the mechanical pre-treatment of the samples.

A significant improvement in the rheological characterization of lyotropic liquid crystals have been observed in the nineties, due to the fact that high quality rheometers were manufactured at affordable prices and the use of combined structural and rheological techniques. The transient viscous flow of the lamellar mesophase was analysed by Gallegos et al (1991) and Franco et al (1995). They ascribed the stress decay with shear time not only to the orientation of liquid crystalline domains but also to their breakdown in smaller ones. Start-up at the inception of shear and flow interrupted experiments did not show structural recovery of the lamellar mesophase after reaching the steady-state response. Interesting undershoot phenomena occurring at concentrations and temperatures close to a phase transition were explained on the basis of mechanically induced defects, which in turn were favoured by thermodynamically stable structural defects. The existence of different kinds of defects in the lamellar microstructure had been previously studied by several authors (La Paz et al, 1984), (Allain, 1985).

McKay et al (1991) reported linear viscoelasticity results obtained by small amplitude oscillatory shear for the lamellar mesophase formed by a double tail anionic amphiphilic lipid at a composition located on the border with a dispersion region. This material turned out to be extremely sensitive to shear, hence only below a strain of 1% a non-destructive response was guaranteed and an instantaneous structural probe provided. Unfortunately, only was the frequency dependence of the storage modulus (G' , elastic component) given in their paper. No information was provided on the loss modulus (G'' , viscous component), preventing the linear viscoelastic behaviour of this material from being characterized. This work was completed and improved by (Robles-Vázquez et al, 1993) since the whole linear viscoelastic spectrum was given and interpreted on the basis of a weak-gel response, which implies a preponderance of the elastic component on the viscous one within the standard available experimental conditions. The occurrence of a clear minimum in elasticity at intermediate concentration was explained as the result of a balance between an increase in bilayer interactions, ionic strength (screening effects) and hydration forces as surfactant content rises. The viscous flow was described as

shear thinning, with viscosity being proportional to the reciprocal of shear rate. If this were the case, the shear stress would not depend on shear rate and therefore, this response should have been related to a manifestation of the sample elasticity. This can be confirmed upon analysing the results obtained later, in a wider shear rate range, by Alfaro (1997), who used and controlled rate rheometer, and Montalvo (1999), who used a controlled stress rheometer, for lamellar mesophases formed with nonionic and cationic surfactants, respectively. Both studies demonstrate that the shear rate dependence of stress followed a power-law relationship, after a critical shear rate value, exhibiting similar flow indexes (0.5 and 0.6, respectively) higher than the null values predicted by Robles-Vázquez et al (1993). These also checked that the Cox-Merz rule failed for the lamellar mesophase, as expected.

In a further paper Robles-Vázquez et al (1994) demonstrated that upon addition of NaCl, the elasticity of the anionic lamellar mesophase went down as shown by the corresponding drop in G' . This was related to an effective ionic screening of the double-layer repulsive forces among bilayers. They also attributed a decrease in G' with decane concentration to a sort of lubricating effect of this hydrocarbon inside the hydrophobic moiety of the bilayers.

Calahorra et al (1992) reported that, in binary sucrose stearate/water systems, the transition between a lamellar dispersion region and a monophasic lamellar liquid crystal region could be detected by a marked fall in the critical shear rate for the onset of shear thinning behaviour at low shear rate, a change in the shear thinning slope and in the concentration dependence of the Newtonian limiting viscosity at low shear rate. Additionally, the occurrence of a sharp fall in the first difference of normal stresses (a manifestation of non-linear viscoelasticity) after having reached a maximum on the border with the dispersion region (Figure 1) was also associated with a threshold concentration for the monophasic lamellar region (Calahorra, 1991), (Gallegos et al, 1994). Such maximum points to the formation of a dispersion structure with the highest density of shear-induced defects. A similar conclusion can be drawn upon analysing the results reported by Kilpatrick et al (1994) for a cesium soap. In this case the onset of the lamellar liquid crystalline region can be detected by a marked fall of G' with surfactant concentration after the appearance of a maximum.

Dimitrova et al (1995) demonstrated that maximum viscoelasticity was observed at intermediate composition within the realm of existence of the lamellar mesophase in a binary nonionic surfactant-water system. However, viscoelasticity steadily dropped with temperature, vanishing at the melting point.

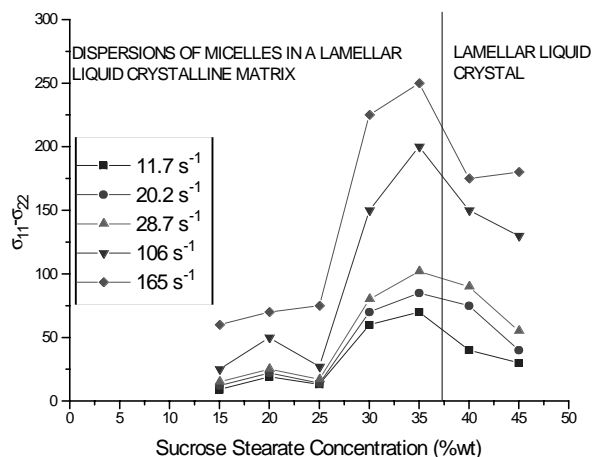


Figure 1

First difference of normal stresses, measured in a Haake Rotovisco RV20/CV20N rheometer at 50°C, against sucrose stearate concentration at different shear rates

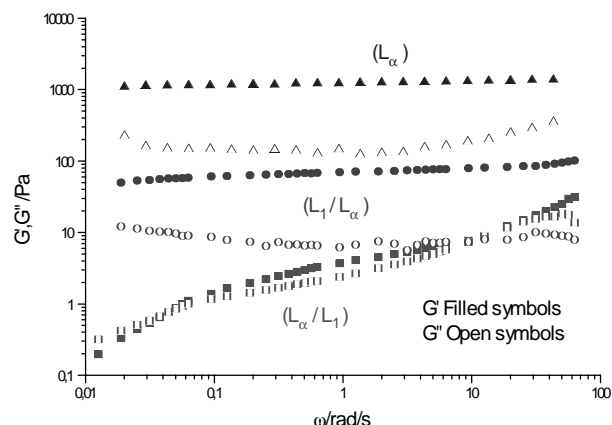


Figure 2

Viscoelastic or mechanical spectra (frequency dependence of the storage modulus, G' , and of the loss modulus, G'') of a lamellar liquid crystal, and two lamellar liquid crystal dispersions (L_α/L_1 : «micellar continuous») and (L_1/L_α : «liquid-crystalline continuous»). Measurements were conducted on a Haake Rheostress RS100 rheometer at 25°C

Increasing/decreasing flow curves determined by Soltero et al (1995a) on lamellar mesophases formed by an anionic and a cationic amphiphilic lipids, both of them with double-tail, may be interpreted assuming that metastable shear-induced structures are formed and eventually destroyed at high strain.

Viscosities of the lamellar mesophase formed in a ternary cationic surfactant/aromatic alcohol/water system were shown to increase with surfactant concentration, although this effect clearly vanished with increasing shear rates (Montalvo et al, 1996).

The rheology of different samples located within the lamellar region formed by a ternary nonionic surfactant/aromatic hydrocarbon/water system was studied by Alfaro (1997a). Small amplitude oscillatory shear (Figure 2), creep compliance and flow curve results indicated that the highest level of structure was shown by the lamellar mesophase at intermediate both mass surfactant/water ratio and hydrocarbon concentration; i.e. roughly around the centre of the realm of existence of the lamellar liquid crystal. This restricted zone was associated with optimum values of the critical packing parameter for the formation of bilayers (Alfaro et al, 1997b, 1998). The dynamic viscoelastic spectra were interpreted in the time domain by determining the corresponding linear relaxation spectra. The different values of the characteristic slope of the plateau zone have been related to different strength interactions within and among the lamellar monodomains (Alfaro et al, in press). In fact, the weak frequency dependence of the storage modulus and the low value of the characteristic

slope of the plateau relaxation zone may be related to the original theory of cooperative coordination number (Bohlin and Fontell, 1978). This is possible by assuming that the number of interacting structural units tends to infinite instead to 2, in agreement with the existence of a real microstructure consisting of a network formed by micron-sized close-packed liquid crystalline domains. A similar hypothesis has recently been proposed to model the linear viscoelasticity of food weak gels (Gabriele et al, 1999).

Stress relaxation results obtained in non-linear viscoelastic conditions were compared with the linear relaxation spectrum derived from dynamic viscoelasticity. In this way, the structural breakdown of the lamellar microstructure could be followed as strain was increased by calculating a damping function, which decreased with strain according to the model proposed by Soskey and Winter (1984). This damping function is useful for further modelling concerning constitutive equations (Alfaro 1997a).

The important role of the chemical nature of the surface in contact with a lamellar mesophase to understand its rheology was first outlined by Barnes (1980) but has been comprehensively studied by Jager-Lézer et al (1998, 1999). While «solid-like» viscoelastic results were obtained on classical stainless steels surfaces, non-linear viscoelasticity and a «fluid-like» viscous response were observed on quartz surfaces. These striking results, which were supported by small angle X-ray diffraction measurements, have been attributed to

a local alignment of lamellar layers parallel to the surfaces at short distances from the quartz plates, while in the bulk sample the layers are not perfectly oriented anymore. Alternatively, this phenomenon can be analysed as a sort of slip effect on the quartz surface. In any case, the relevance of this work can be better understood by considering the increasing popularity of rheometers, equipped with quartz sensor systems, to carry out parallel small-angle light scattering or small-angle neutron scattering measurements, as stated by Jager-Lézer et al (1998).

Structure and Rheology of Diluted Lamellar Mesophases: $L_{\alpha h}$, $L_{\alpha l}$, L_{α^+} , L_3

Lamellar liquid crystals can be swollen with water, although larger swellings are likely to be obtained upon addition of hydrocarbons or brine. This has been related to the occurrence of nonelectrostatic repulsive interactions between highly flexible bilayers, the so-called undulation interactions. These interactions due to thermal fluctuations are considered to be responsible for the formation of diluted lamellar mesophases (Bellocq, 1996). In fact, below 5%wt surfactant concentration, vesicles, diluted bilayers and sponge phases can be detected in complex phase diagrams and are raising a growing interest from both a theoretical and an applied point of view. Diluted lamellar mesophases are likely to appear in ternary systems of nonionic, sugar or zwitterionic surfactants, a cosurfactant and water (Hoffmann, 1994). They have also been reported to exist either in quaternary anionic surfactant, cosurfactant, NaCl and water or even in quinary systems (Bellocq, 1996). In addition, they are also formed in some binary systems containing double tail amphiphilic lipids, like didodecyldimethylammoniumbromide and water. Phospholipids in water can form either uni- or multilamellar vesicles, also called liposomes (Bóta et al, 1999). In fact, vesicles prepared from dipalmitoylphosphatidylcholine and water exhibit at least five different multilamellar structures in excess of water (Jørgensen, 1995). It is important to point out that phospholipids vesicles are considered as model systems for living cell membranes due to their similarities (Mouritsen et al, 1995). In addition, they have well-known applications in cosmetics but also in the food industry for microencapsulation of sensitive ingredients (Kim and Baianu, 1991).

Diluted lamellar mesophases may exhibit different structures. The organization of the so-called $L_{\alpha h}$ phase is similar to classical concentrated lamellar liquid crystals since stacks of flexible open bilayers are formed. On the other hand, the $L_{\alpha l}$

phase consists of closed bilayers (vesicles), which may be unilamellar (Oberdisse et al, 1998) or multilamellar («onion-like» vesicles) exhibiting a wide size distribution (Bergmeier et al, 1997, 1998a, 1998b), (Marques et al, 1998). Neighbouring vesicles may be in closed contact, sharing part of the bilayer or even merging each other (Caria et al, 1998). Even though a fluorescence dye was used by Menger et al (1996) to differentiate some types of vesicles, the most important technique to obtain information on the microstructure of these phases is freeze fracture electron microscopy (Hoffmann, 1994). In ternary surfactant/alcohol/water systems, an increase in the cosurfactant concentration leads to a phase transition from vesicles ($L_{\alpha l}$) to flat flexible bilayers $L_{\alpha h}$ (Valiente, 1995).

Phase transitions between the $L_{\alpha l}$ and $L_{\alpha h}$ can be followed by changes in the rheology of these systems. Densely packed multilamellar vesicles are likely to exhibit strong viscoelastic properties with extremely long relaxation times due to a high level of interactions among them (Hoffmann and Ulbricht, 1997). However, in some cases, the occurrence of low-interacting vesicles results in fluid-like viscoelastic properties, although even in this case the $L_{\alpha l}$ phase exhibits both higher apparent viscosities and viscoelasticity than the $L_{\alpha h}$ phase (Hoffmann, 1994), (Montalvo, 1999).

The effect of shear on diluted lamellar mesophases has been extensively studied by Roux and coworkers. They propose three main states of orientation depending on the characteristic distance between membranes as well as the shear rate (Diat et al, 1993), (Roux et al, 1993) and (Roux, 1997). At very low shear rate the bilayers are mainly parallel to the flow with defects in the two other directions. At higher shear rate or for more diluted systems, the bilayers arrange themselves in an isotropic state consisting of closed-packed multilamellar vesicles, whose size can be controlled by the shear rate. In fact, the size decreases as the inverse of the square root of the shear rate. Panizza et al (1996) have shown that the plateau modulus rises as the vesicle size decreases and enhanced interactions among the polyhedral vesicles take place. A further increase in shear rate results in bilayers oriented again in parallel to the flow but with no defects remaining in the flow direction. The rheological results were supported by a combination of several techniques: polarising microscopy, birefringence measurements, light scattering and neutron scattering (Diat et al, 1993 and 1995). A similar mechanism seems also to work for semi-diluted lamellar mesophases as demonstrated by Laüger et al (1996), who conducted simultaneous rheo-small angle light scattering measurements for a defective lamellar mesophase of a ternary system containing 65% water.

A further diluted lamellar mesophase is located between the micellar phase and the diluted lamellar mesophase in complex systems, the so-called L_4 or L_{α^+} , which consists of unilamellar or multilamellar vesicles with only a few layers. Only does it show birefringence under flow and present fluid-like rheological properties if unilamellar vesicles are formed. However, high viscosity and viscoelasticity are observed when multilayers occur (Bellocq, 1996). Furthermore, Jonströmer and Strey (1992) reported that the L_4 membrane is more rigid than those of the other diluted lamellar mesophases.

Another diluted phase can be also found in complex systems as well in binary systems close to isotropic micellar solutions and swollen lamellar mesophases stabilized by undulation forces, the so-called sponge or L_3 phase (Mitchell et al, 1983), (Freysingas et al, 1996), (Wagner and Strey, 1999).

Koshinuma et al (1999) have recently reported a transition from the sponge phase to unilamellar vesicles above a critical temperature and a subsequent transition to multilamellar vesicles upon a further increase in temperature, in binary aqueous systems of two ionic phospholipids: the sodium salts of dilauryl- and dimyristoylphosphatidylglycerol.

L_3 consists of isotropic phases of randomly connected unentangled bilayers which separate two equivalent regions of solvents having a Gaussian curvature. In fact, the structure can be described as a molten bicontinuous cubic mesophase (Hoffmann, 1994), (Bergmeir et al, 1997) so that the average curvature at each point of the bilayer is zero since the two curvatures are considered to have the same magnitude an opposite signs. This phase exhibits no significant viscoelasticity and low Newtonian viscosities at low shear rates but above a critical shear rate a shear thinning response is usually observed and attributed to a shear-induced phase transition to a $L_{\alpha h}$ phase, whose bilayers orientate in the flow direction (Hoffmann et al, 1991), (Mahjoub et al, 1996), (Montalvo et al, 1998). The sponge phase has been theoretically modelled by Cates et al (1996).

Stable dispersions may be formed with diluted lamellar mesophases due to the viscoelasticity of at least one of the phases. Vesicles and extended bilayers coexist in $L_{\alpha}/L_{\alpha h}$ dispersions as proved by freeze-fracture electron microscopy (Hoffmann, 1994). In addition, the occurrence of stable dispersions of a diluted lamellar mesophase and an L_4 phase has been ascribed to the high viscosity of the latter (Bellocq, 1996). Not only are stable dispersions formed in diluted systems, but classical lamellar liquid crystals can also form highly stable dispersions displaying interesting rheological behaviours.

Structure and Rheology of Lamellar Liquid-Crystalline Dispersions

Lamellar liquid crystals can form stable dispersions in binary as well as in more complex systems out of the «diluted» regions. These dispersions may be «water-continuous» or «liquid-crystalline» continuous. Alexopoulos et al (1989) reported that lamellar liquid-crystalline-continuous dispersions of the double-tail anionic surfactant, sodium bis(2-ethyl-hexyl)sulfosuccinate (AOT) might exhibit antithixotropic properties, after conducting consecutive experiments in a capillary viscometer. The dynamic viscoelasticity of the same system was initially studied by McKay et al (1991), reaching the main following conclusions: a) the linear dynamic viscoelastic range was rather small; i.e. the whole microstructure turned out to be extremely sensitive to shearing forces, b) once these dispersions were gently sheared out of the linear region, a complete structural recovery could not be checked and c) the consequence of a train of increasing shear rates was to promote an increase in G' , which could have been interpreted as a first indication of a structural build-up process associated with a shear-induced microstructure transition. This was confirmed later by Valdés et al (1993) carrying out increasing and decreasing shear rate flow curve experiments for the same binary system.

The existence of a phase inversion in a binary sucrose stearate /water system, between a dispersion of lamellar liquid crystalline domains in a micellar continuous phase and a dispersion consisting of micelles suspended in a lamellar liquid crystalline matrix, was supported on both their distinctive rheological properties and polarising microscopy textures (Calahorra, 1991), (Calahorra et al, 1992) and (Gallegos et al, 1994). The critical concentration defining a transition from a system formed only by a micellar phase to a system consisting of a lamellar liquid crystalline dispersion in a micellar continuous phase was set up on the basis of the observation of spherulites polarising microscopy textures as well as of a dramatic inflexion point in the plot of the critical shear rate for the onset of shear thinning response against sucrose stearate concentration. A dramatic reduction in the linear dynamic viscoelastic range and the onset of measurable first difference of normal stresses pointed to the phase inversion (Figure 3).

Valdés et al (1993) also located the phase inversion point of lamellar liquid-crystalline dispersion of AOT thanks to the occurrence of a local minimum, preceded by a local maximum, in both the limiting dynamic viscosity at low frequency (which must coincide with the limiting Newtonian viscosity at low shear rate) and the relaxation time of the Maxwell model. These authors state that below the inversion

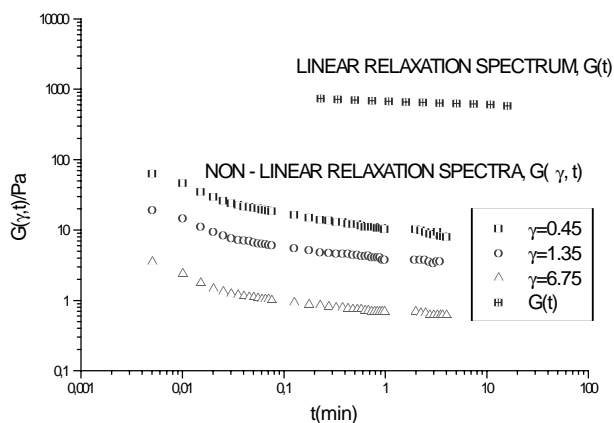


Figure 3

Linear and non-linear relaxation spectra of a lamellar liquid crystal. Measurements were conducted on a Haake Rheostress RS100 and a Haake Rotovisco RV100/CV100 at 25°C

point the viscoelastic spectra obtained were fluid-like, while above such critical point they changed to weak-gel-like.

Phase inversions between lamellar liquid crystalline stable dispersions have been also found in ternary systems. Take for instance, the nonionic surfactant/hydrocarbon/water system studied by Alfaro (1997). The transition between lamellar dispersions with an aqueous medium and those with a liquid crystalline continuous phase could be detected by their different textures under polarising microscopy along with changes in rheological properties (Alfaro et al, 1997c). While the former exhibited viscoelastic spectra typical of entangled polymeric solutions, the latter showed a weak-gel response but with lower values of the dynamic functions G' and G'' than in fully developed monophasic lamellar mesophases (Figure 2). These differences also arose in the corresponding relaxation spectra, where only the lamellar liquid crystalline dispersions consisting of vesicles embedded in an isotropic aqueous medium presented a pseudoterminal relaxation zone. The fact that the viscoelastic spectra of the liquid-crystalline-continuous phase only differed in the G' and G'' values has been proposed as a further probe that essentially the relevant microstructure must be the same as in the lamellar mesophase but with weaker interactions (Alfaro et al, in press). These dispersions also showed shear-induced structural build-up phenomena as demonstrated by their antithixotropy in increasing/decreasing flow curves and the comparison with the complex viscosity derived from small amplitude oscillatory shear experiments (Figure 4). In some cases, the viscosity of these dispersions may be even higher than that of

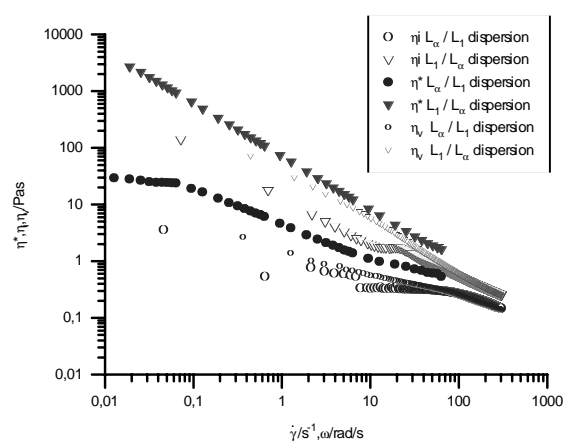


Figure 4

Complex viscosity (η^*), viscosity values derived from upward flow curves (η_i) and viscosity values derived from downward flow curves (η_v) of lamellar liquid-crystalline dispersions, plotted against oscillation frequency and shear rate, respectively. Measurements were conducted on a Haake Rheostress RS100 (oscillatory shear results) and on a Haake Rotovisco RV20/CV20N (flow curve results)

the lamellar mesophase, since while for the latter the effect of shear is to orient and break the liquid-crystalline domains (leading to a drop in viscosity), for the former the effect may be to favour a structure transition, to one probably dominated by densely-packed vesicles coexisting with extended bilayers.

Structure and Rheology of Lyotropic Nematic Liquid Crystals (N_D , N_C)

Nematic mesophases are formed by some surfactants in a small concentration range between normal micellar solutions and direct hexagonal or lamellar liquid crystals. They were discovered by Lawson and Flautt (1967) and have been detected in ternary or quaternary systems at higher surfactant concentration than diluted lamellar mesophases (Hoffmann, 1994), in binary systems containing fluorocarbon (Hoffmann, 1984) or polymer (Lüthmann et al, 1985) or nonionic surfactants (Lüthmann and Finkelmann, 1986).

These mesophases are classified as discotic nematic (N_D) or calamitic nematic (N_C). The structure of the former may consist of long flexible bilayers micelles exhibiting some degree of order more or less arranged in layers so that they are not restricted to stay in one fully developed extended lamellar structure. With respect to the structure of the latter, it is based on long rod micelles packed in a loose hexagonal array (Tiddy and Walsh, 1983). While N_D nematic liquid crystals may be considered precursors of the lamellar mesophase, (N_C) nematic liquid crystals seems to be precursors of the direct hexagonal mesophase. Not only may a change in

composition lead to a nematic/lamellar mesophase transition but also a change in temperature, as reported by Holmes and Charvolin (1984).

Nematic lyotropic liquid crystals can be detected by polarising microscopy since they exhibit similar textures to those typical of thermotropic nematic liquid crystals. They are not too viscous and can be oriented by strong magnetic fields in different time scales.

The transient flow properties of a calamitic nematic liquid crystal have been studied by Berret and Roux (1995). They observed damped oscillations of viscosity at low shear rate before reaching a steady state response. Such oscillations were related to tumbling instability of the nematic director as a consequence of a rearrangement (changes in size and orientation) of the liquid crystalline polydomain structure.

Hexagonal liquid crystals (H_1), (H_2)

Hexagonal liquid crystals were first reported as the «middle soap» phase in soap-water systems by McBain et al (1938). According to small angle X-ray diffraction, their structure consists of long rodlike (cylindrical) micelles lying parallel to each other in a hexagonal array. If the hydrophobic portions of the molecules are directed to the centre of the cylinders and the hydrophilic portions are located on the external surface of the cylinders, the direct hexagonal mesophase (H_1) is formed. Conversely, if the hydrophilic heads are oriented towards the centre of the cylinders with an aqueous solution filling the centre of the cylinders and the hydrophobic portions towards the outer surface of the cylinders, the reversed hexagonal mesophase (H_2) is formed (Ekwall, 1975). This mesophase is far more frequent in biological amphiphilic lipids than H_1 (Larsson, 1994). Hexagonal mesophases are the second most important type of lyotropic liquid crystals, after the lamellar mesophase, on account of the size of their realm of existence.

From a macroscopic point of view, both types of hexagonal liquid crystals look like quasi-transparent gels exhibiting high rheological consistency.

They exhibit focal-conic birefringent textures under polarising microscopy. Their main typical textures are described as fan-like, angular, «bâtonnets» at high temperature, and in the case of sheared samples, non-geometrical. It should be taken into account that as in the lamellar mesophase the microstructure is polycrystalline, with hexagonal monodomains separated by intervening grain boundaries (Kilpatrick et al, 1994).

Only a small number of papers on the rheology of the hexagonal mesophase have been published. Groves and Ahmad (1976) proposed that the rod-

like aggregates probably aligned in the flow direction along their long axis; otherwise the whole hexagonal microstructure would have to be distorted and even the cylinders destroyed in order to be able to flow. The theory of cooperative coordination number was used to explain dynamic viscoelastic and steady-state flow results of hexagonal liquid crystals, proposing an average number of six structural units interacting with each other (Bohlin and Fontell, 1979), (Bohlin, 1980). Unfortunately, this cooperative coordination number does not work for other hexagonal systems. Martínez Moreno et al (1984) reported that the hexagonal mesophases formed by two nonionic surfactants of high hydrophilic/lipophilic-balance, in their respective water binary systems, showed shear thinning properties with a yield stress. The fact that the yield stress was clearly sensitive to the recent previous thermal history of the samples was attributed to the occurrence of different initial orientations in the liquid crystal. In other words, these results seemed to indicate that a possible decrease in the density of structural defects as a consequence of the increasing/decreasing temperature cycle could lead to a fall in the yield stress. However, the lack of structural hysteresis phenomena should have been checked. Muñoz et al (1987) reported flow indexes higher than those predicted by the cooperative coordination number theory, which were not influenced essentially either by temperature or by composition within the realm of existence of the hexagonal liquid crystal in a polyoxyethylene fatty alcohol/water binary system. However, a steady decrease in differential viscosity with temperature was also observed.

The hexagonal mesophase exhibits time-dependent flow properties as demonstrated by start-up experiments at the inception of shear (Gallegos et al, 1987b). Upon imposing a constant shear rate, the shear stress grew for a short but measurable time, until a peak value was reached, then it dropped until the steady state was achieved. Gallegos et al (1988a) related the time dependent response and stress relaxation results to the viscoelasticity of the hexagonal liquid crystal. These authors fitted the shear stress decay with shearing time to a series of two first-order kinetic functions. Both kinetic constants were found to increase with shear rate in the composition range associated with the maximum thermal stability of the liquid crystal. The peak shear stresses depended on shear rate according to the Casson equation and the corresponding yield stress increased linearly with surfactant concentration, although a significant deviation was observed at high surfactant concentration near the border of the hexagonal region. This work was improved later by comparing the transient response with the predictions of the

Leslie-Ericksen theory developed for polymeric liquid crystals. The situation in surfactant hexagonal mesophases turned out to be more complex than in some polymeric liquid crystals, with strains corresponding to peak viscosities clearly dependent on shear rate. Furthermore, the quick partial recovery of the peak viscosities after stress relaxation indicated that the transient flow response was due to both the orientation of long rod-like micelles and some breakdown of the polydomain liquid crystalline structure (Gallegos et al, 1990).

In quaternary systems containing anionic and nonionic surfactants, inorganic salt and water, the effect of increasing the concentration of anionic surfactant was to decrease both the viscosity and the yield stress of the hexagonal mesophase (Gallegos et al, 1988b), (Muñoz et al, 1989). The same effect was observed upon raising the inorganic salt concentration (Muñoz et al, 1988b).

The influence of composition and temperature on the linear dynamic viscoelasticity of hexagonal liquid crystals was first reported by Muñoz et al (1990). As these measurements were conducted within the linear domain, the microstructure was not irreversibly destroyed during the experiment and, therefore, the results obtained were a sort of fingerprint of the hexagonal liquid crystalline structure. The straight lines obtained in a Cole-Cole diagram were related to a gel-like behaviour, the elastic component being independent of water concentration but decreasing with temperature. A power law relationship was used to fit the frequency dependence of the complex viscosity with an exponent ranging from -0.84 to -0.73 as temperature increased. In any case, these exponents gave an indication of the strong network formed by the hexagonal liquid crystal. Additionally, the lack of a true yield stress in this kind of mesophase and the failure of the Cox-Merz rule were confirmed for the first time in hexagonal liquid crystals.

Small amplitude oscillatory shear experiments conducted on a hexagonal liquid crystal sample of a cationic surfactant at a composition close to the micellar transition yielded fluid-like viscoelastic behaviour (Soltero et al, 1994), fitting the Hess model, which had been previously used for micellar solutions (Thurn et al, 1985). Low values of both the elastic and viscous components were obtained, probably due to the high measurement temperature chosen and also to the proximity of the micellar region. An increasing temperature ramp conducted at higher surfactant concentration at a composition well within the hexagonal mesophase region, demonstrated that the elastic and viscous components reached maximum values at exactly the same critical temperature. Above this temperature a marked steady drop in the viscoelastic functions

without any discontinuity at the melting point was observed (Soltero et al, 1995b). Kilpatrick et al (1994) confirmed the gel-like properties of the hexagonal mesophase by determining the mechanical spectrum of a water/*n*-tetradecanoate system at roughly room temperature. The existence of a true yield stress was proposed despite the fall in the elastic component as frequency decreased.

Simultaneous rheological and small angle light scattering measurements were carried out by Richtering et al (1994 a and b) to demonstrate that the hexagonal mesophase exhibits two orientations under shear; first perpendicular at short shearing time and eventually parallel to the flow direction at long shearing time. The same effect was observed upon aligning the hexagonal liquid crystal by large amplitude oscillatory shear. This resulted in a progressive decrease in both the elastic and viscous components when the initial polydomain microstructure was modified to achieve first a perpendicular orientation and later an in-flow orientation (Linemann et al, 1995).

As far as the influence of composition and temperature on the rheology of hexagonal liquid crystals is concerned, Dimitrova et al (1995) showed for a binary nonionic surfactant/water system, that the maximum values of both the elastic and viscous components were obtained at intermediate water concentration, where the structure of the mesophase was better developed. On the other hand, the elastic component steadily dropped with temperature within the hexagonal region, while the viscous one remained essentially constant up to a critical temperature at which the liquid crystal melted. This temperature correlated well with that derived from DSC measurements, confirming the validity of both techniques.

Mechanical and relaxation spectra (using the Generalized Maxwell model), along with creep compliance tests have been used by Cordobés et al (1996, 1997) to illustrate the influence of the solubilization of a saturated hydrocarbon in the hexagonal mesophase formed by a nonionic surfactant in water. The addition of hydrocarbon yielded a wider plateau region, which was even larger as temperature went down. They found viscoelastic properties typical of entangled polymeric solutions in the semi-diluted regime, probably due to the fact that the temperature chosen was roughly close to the melting point of the hexagonal mesophase as can be predicted upon observing the binary phase diagram (Franco et al, 1995). A further conclusion drawn from this work was that no true yield stress existed but a high limiting Newtonian viscosity at low shear, whose dependence on temperature was fitted to an Arrhenius-like equation. A limiting Newtonian viscosity has also been obtained by Montalvo

(1999) at low shear for hexagonal samples in a ternary cationic surfactant/ aromatic alcohol/water system. In fact, the flow curves determined by an increasing ramp of shear stress fitted the Cross model. From the model parameters it is possible to predict the shear thinning index flow, which showed lower values than those expected by the theory of cooperative coordination number. In fact, these results would account for an average number of interacting structural units always higher than 6, the original figure proposed by Bohlin and Fontell (1979). This may be considered as a further indication of the polydomain microstructure of liquid crystals.

Structure and Rheology of Cubic Liquid Crystals: (I_1), (I_2), (V_1), (V_2)

All cubic liquid crystals share the properties of being optically isotropic and exhibiting such a high viscosity that they have been described as clear stiff gels (Ekwall, 1975). If the cubic mesophase is in equilibrium with the direct hexagonal liquid crystal region at «high» water concentration, it is called I_1 mesophase. On the other hand, if it appears in equilibrium with the reversed micellar phase (L_2), it is called I_2 mesophase (Winsor 1974), (Tiddy and Walsh, 1983). The microstructure consists of close-packed giant direct (I_1) or reversed (I_2) spherical micelles arranged in a cubic pattern. A second type of cubic mesophases consists of a bicontinuous microstructure with an infinite periodical minimal surface (IPMS) of balanced curvature so that every point on the surface can be described as a saddle-point (Larsson et al, 1980). This surface divides the majority solvent into two interpenetrating but unconnected labyrinths as in the sponge phase. Three possible microstructures, defined by a particular type of IPMS, have been proposed for this kind of cubic mesophases: the so-called P, D and G surfaces (Larsson, 1994). The P-surface may be described as a system of tubes oriented in space so that they fuse at regular distances and the volume of solvent inside the tubes is equivalent to the volume outside. In the D-surface the tubes must be fused alternatively in a tetrahedral geometry and finally, in the G (gyroid)-surface the channel system is arranged in a complex helical pattern. A deeper and longer discussion on these structures, including clear illustrations, has been provided by Larsson (1994).

This cubic liquid crystal is referred to as the viscous isotropic cubic mesophase or bicontinuous cubic mesophase. V_1 and V_2 stand for these mesophases depending on their location on phase diagrams. V_1 usually appears between the direct hexagonal and the lamellar mesophase, while V_2

arises between the lamellar and the reversed hexagonal liquid crystal or in equilibrium with the isotropic liquid solution L_2 (Mitchell et al, 1983).

The viscous isotropic mesophase can be considered as a natural intermediate stage in the progressive transition from the direct hexagonal to the lamellar mesophase or from the latter to the reversed hexagonal liquid crystal (Luzzati et al, 1968), (Hyde and Fogden, 1998). A further model has been proposed recently, suggesting that the lamellar mesophase progressively shifts to the hexagonal mesophase by means of symmetrical ruptures along a plane perpendicular to the lamellar bilayer through lamellar mesophases of different symmetry (Bourgoyne et al, 1995), (Mettout et al, 1997), (Holmes, 1998). Obviously, these intermediate mesophases are defective liquid crystals, which may be metastable and likely to yield complex rheological behaviour.

The number of papers published on the rheology of cubic liquid crystal is scarce although a growing interest can be observed in recent years. Bohlin et al (1985) followed a temperature-induced transition from a cubic to a reversed hexagonal mesophase in a sunflower oil monoglyceride-water system by conducting a temperature ramp in small amplitude oscillatory shear. A dramatic change in the complex modulus value and in the loss tangent (a viscoelastic function which provides information about the relative importance of the viscous and elastic components) was observed when their values levelled off at the onset of a well developed cubic or reversed hexagonal mesophase. However, the exact transition temperature could not be derived from the rheological results obtained, probably due to the high rate of temperature increase used.

Start-up at the inception of shear and stress relaxation after steady shear experiments revealed that the I_1 mesophase, studied in a nonionic surfactant-water system, was clearly more viscoelastic than the direct hexagonal mesophase (Muñoz et al, 1987). The same authors studied the flow behaviour and proposed a Herschel-Bulkley equation to describe the shear thinning properties of the I_1 mesophase above an apparent yield stress, which dropped sharply with temperature. Furthermore, the transition to a direct hexagonal mesophase upon adding a small amount of anionic surfactant was rheologically detected by a marked increase in the flow index (Muñoz et al, 1988). This indicated that the I_1 mesophase was more shear thinning than the H_1 ; i.e. the former did undergo a sharper fall in viscosity with shear rate than the latter, as was also demonstrated for the binary nonionic surfactant-water system (Muñoz et al, 1991).

Warr and Chen reported a plastic behaviour for a bicontinuous cubic mesophase formed in double-

tail cationic surfactant/hydrocarbons/water systems. The yield stress was found to increase with the surfactant/water ratio and was related to the disruption of the local curvature and interfacial area of the bilayer, which eventually leads to the bilayer destruction. Time-dependent measurements carried out at constant shear stress showed that an elapsed time of about 500 seconds was required to achieve steady-state results, explaining the occurrence of hysteresis loops in continuous flow curves.

Different viscoelastic behaviours have been reported for a simple cubic (I_1') and a body centered cubic (I_1'') mesophase occurring in a branched nonionic surfactant-water system (Linemann et al, 1995). The latter exhibited typical properties of strong gels, with a broad linear viscoelastic range and a frequency independent elastic component, which in turn is always substantially higher than the viscous component. The same behaviour was reported by Gradzielski et al for a standard I_1 mesophase (Gradzielski et al, 1995). As for the flow properties, shear melting behaviour related to the typical response of colloidal crystals, was observed in creep compliance tests. In fact, the onset of flow was suddenly achieved above a critical strain with an abrupt increase in shear rate (Linemann et al, 1995). Interestingly, the I_1' mesophase exhibited a preponderance of the viscous over the elastic component at low frequency, even though the plateau modulus is of the same order of magnitude as that of I_1'' (Richtering et al, 1994b). In any case, it is quite clear that the relaxation mechanisms were dramatically different in both cubic mesophases, being faster for the former than for the latter. In fact, the longest relaxation time (locating the onset of the terminal relaxation zone) could be readily calculated even at low temperature, demonstrating that the different viscoelastic behaviour was only due to the change of microstructure.

Bicontinuous cubic liquid crystals have been reported to exhibit a viscoelastic spectrum similar to that described above for the I_1' mesophase (Radiman et al, 1994), (Montalvo et al, 1996). Their viscoelastic spectrum fit the Maxwell model, with a single relaxation time, or the Generalized Maxwell model with only two relaxation times.

OUTLOOK

This chapter has covered a part of amphiphilic lipid science that the authors are familiar with in order to review the amazing variety of well-established colloidal structures they can form with emphasis on their correspondingly wide range of rheological behaviours.

Nowadays, the occurrence of different association structures in biological and synthetic amphiphilic

lipids is well documented. Excellent reviews on phase diagrams can be found in a broad range of scientific journals and books. In any case, the increasing use of refined techniques foresees the detection of new phases and the redefinition of earlier phase diagrams. Conversely, the rheology of these systems has received less attention, despite its importance from a theoretical as well as from an applied point of view. Although many papers have been published on the rheology of amphiphilic lipid systems in scientific journals and in chapters of more general books, most of them focus on the rheology of micellar solutions. To the authors' knowledge, this is the first review that comprehensively covers the rheology of gels and liquid crystals formed by these systems.

The increasing use of high quality rheometers and a better understanding of viscoelastic phenomena, along with significant refinements in the analysis of results have yielded a quantitative understanding of some underlying phenomena related to the shear flow of amphiphilic lipid systems. However, further advances in experimental rheometry, as well as in the development of both phenomenological and structural models can be predicted. The latter will benefit from a wide range of physico-chemical techniques, which are increasingly providing information on association structures, coupled with high-tech rheometers. In any case, improvements in theoretical modelling must rely on well-defined reproducible experiments.

Authors involved in this kind of studies should give all the experimental details needed to reproduce their measurements. Indeed, due to the polydomain microstructure of liquid crystals, special caution must be taken with the recent thermo-mechanical history of the sample to be characterized since it is well known that viscoelastic materials show fading memory phenomena. For this reason, it is advisable to properly determine an equilibration time before conducting any rheological measurement in order to check that the sample equilibrium structure has been recovered after being loaded into the sensor system. For similar reasons, increasing and decreasing temperature ramps should be carried out at a suitable rate, checking that linear viscoelastic conditions are guaranteed within the whole temperature range and, otherwise non-equilibrium structures are likely to be characterized. The study of possible wall-depletion phenomena, especially when sensors are made of certain materials, deserves special attention mainly in rheo-optical studies.

In order to understand the effect of shear flow on these association structures, more measurements of steady state viscosities and normal stresses would be welcome instead of conducting standard shear rate or shear stress ramps (as in flow curves). Only these steady state functions can be related to the new

equilibrium shear induced microstructure. We must take into account, for instance, that a viscosity value calculated from a flow curve, at an intermediate shear rate, is likely to be biased by previous shear rates applied in the ramp. However, for highly viscoelastic samples, we should be aware that the determination of steady state values at low shear rates is extremely time consuming and it may also be a challenge from an experimental point of view. In contrast to this drawback, steady state measurements may demonstrate that of yield stress in these association structures does not occur at all, since a large limiting Newtonian viscosity is likely to be reached, or at least a clear trend may be observed, at low shear rate. Yield stress can be considered as an engineering reality but it does not have any scientific meaning since it is a clear manifestation of strong viscoelasticity. In fact, it is a time-dependent parameter as demonstrated in the enlightening papers by Barnes and Walters (1985) and by Cheng (1986).

Additionally, pressure-driven capillary rheometers should be used to obtain information at the high shear rates involved in processing conditions. Apart from shear strain, extensional viscosities may be worth measuring since new insights into structure-rheology relationships may be achieved.

We propose rheometry as a useful tool to detect and follow phase reactions involving non-equilibrium phenomena, which are sometimes misinterpreted as equilibrium phase transitions (Laughlin, 1990). Advanced rheokinetics facilities can be found in modern rheometers which also offer useful experimental procedures. Take for instance, multiwave options, parallel superposition of oscillatory and steady shear measurements and measurements of dichroism and birefringence under flow. These new techniques, along with other rheo-optical experiments will be successfully applied in the research of the rheology of association structures formed by amphiphilic lipids.

Finally, we would like to emphasize that the development of research on structure-rheology relationships in amphiphilic lipid systems will increasingly benefit in near future from the enhancement of highly interacting multidisciplinary «polydomain» networks cooperatively formed by specialists in the different fields involved in this subject, namely: chemical, material and mechanical engineers, physical chemists, condensed matter physicists, biophysicists, food, polymer and pharmaceutical scientists.

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