RHEOLOGY OF SURFACTANTS: WORMLIKE MICELLES AND LAMELLAR LIQUID CRYSTALLINE PHASES

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Summary

In this chapter, the rheology of a special class of complex fluids is analyzed and reviewed. In particular, attention is focused on the dynamic behavior of systems constituted by aqueous phases of surfactants, namely, micellar solutions and lamellar liquid crystalline phases. Surfactants are molecules that possess a polar head and a non-polar tail (i.e., amphiphiles). The polar head may be nonionic or it may possess a charge, in which case they are classified as anionic (negatively charged), cationic (positively charged) and zwitterionic or amphoteric. In ionic surfactants, the polar head is balanced
by the presence of counterions. In an aqueous environment, surfactants can form a variety of microstructures such as micelles, vesicles and liquid crystalline phases, the conformations of which can be modified by the action of an external flow. Micellar solutions and liquid crystalline lamellar phases are microstructured fluids with fascinating rheological properties that have been studied intensively both scientifically and technologically in recent years.

The chapter deals with the linear and nonlinear viscoelastic properties of wormlike, giant micellar systems and of surfactant-based lamellar liquid crystalline phases. The nonlinear properties of wormlike micellar solutions are given special attention, in particular, to such interesting phenomena like shear-banding and shear thickening. Stability analyses under steady shear and transient flows are also described. Regarding the rheology of lamellar mesophases, attention is given to the shear-induced transition from aligned layers to multi-lamellar vesicles (MLV).

The emphasis of this chapter is to provide with an introduction to the latest developments in these fields by describing the experimental advances and techniques and the theoretical understanding and interpretation of the phenomena involved. A state of the art and ample bibliography is provided at the end of the chapter for further study.

1. Introduction

Micellar solutions and liquid crystals belong to the class of systems known as complex fluids. Surfactants reversibly self-assemble in aqueous (and non polar) environments and, unlike ordinary molecular solutions, the size, shape and aggregation geometry of these aggregates can be modified by external influences such as temperature, pressure and flow. Surfactants in aqueous solutions self-associate to form microstructures including long wormlike micelles, liquid crystals, vesicles, etc. (Israelachvili, 1991). Above the critical micelle concentration (cmc), they form small spherical micelles. A change of shape and growth from spheroidal to elongated micelles can occur by modifying parameters such as surfactant concentration, temperature, counterion or ionic strength (Israelachvili, 1991). Often these changes can lead to the formation of giant wormlike micelles that can be microns long.

In the dilute solution regime, above the cmc, adding amphiphiles to a micellar solution may result in a spontaneous assembly of macroscopic bilayer sheets, when the preferred aggregation geometry is the planar bilayer, which is achieved when the surfactant packing parameter, \( \frac{v}{al} \approx 1 \), being \( v \) the chain volume, \( a \) the head-group area and \( l \) the chain length (Israelachvili, 1991). This process is in fact, a first-order transition from a dilute phase of isolated amphiphiles into a condensed 2-D bilayer phase. The phase behavior associated with micelles whose spontaneous aggregation geometry is a cylindrical 1-D phase, can be regarded as an intermediate packing geometry of a higher growth dimensionality \( (1/3 < \frac{v}{al} < 1/2) \) than that of a spherical micelle \( (\frac{v}{al} < 1/3) \) and lower than that of a planar bilayer.

Early molecular theories dealing with micelle formation considered first the lamellar structure (Debye, 1948; 1949) suggested by McBain (1913). Later, Halsey (1953)
amended the energy expression to consider cylinders and concluded that 1-D growth will be rods and not disks or bilayers. The process of minimization of the free energy of a micelle, which comprises the repulsive interactions between the head groups on the micelle surface and the attractive van der Waals interactions between the tails, provides with the necessary conditions for achieving the equilibrium size and the critical micelle concentration. However, with surfactants that have a large surfactant packing parameter, the preferred structure will be onion-like vesicles and not micelles. Lamellar structures at given concentrations form liquid crystalline phases exhibiting a complex rheological behavior. Attention to these systems is given in Section 3 of this chapter.

Giant micelles resulting from the growth of cylindrical 1-D structures are equilibrium or “living polymers” as the micelle molecular weight fluctuates with time, as opposed to conventional polymers where their molecular weight is constant. These micelles can interact themselves to form rings or branched structures that lead to the formation of elastic networks with fascinating rheological properties. As is described in several sections of this chapter, the rheological behavior of these micelles can be dominated by the rate of reversible scission. Theoretical models aimed to interpreting measurements of rheological properties focus on the dynamic processes of micellar diffusion and the kinetics of micellar breakage and recombination to set the time scales for relaxation in entangled wormlike micellar solutions (Cates and Fielding in Kaler and Zana, 2007).

The flow properties of viscoelastic surfactant solutions include near-Maxwellian behavior in the linear regime and a drastic shear thinning in the non-linear regime. Section 2.1 deals with linear viscoelasticity and the kinetic process of fusion and scission reactions of micelles, together with the relevant relaxation mechanisms that govern the dynamics of these systems. In the strongly entangled region where the micellar solution is viscoelastic at rest, strong shear thinning is usually observed. This flow behavior is analyzed in Sections 2.2-2.4. A very interesting phenomenon consisting in that the solution becomes highly viscoelastic after a period of shearing occurs at low concentrations, where the quiescent solution is almost inviscid. These effects have been termed shear thickening and attention to them is given in Section 2.5.

Lastly, it is worth mentioning that viscoelastic surfactant solutions have generated not only scientific interest, but also they have been used in applications ranging from detergents, hydraulic fluids and slurry transport fluids; the oil and gas industry has also employed these fluids in well completion and stimulation applications (Wasan and Ginn, 1988). Since the micellar structure is dynamic and can be controlled by the local fluid environment, it can be destroyed upon exposure to hydrocarbon fluids or modified by adjusting the salinity. Either of these effects, in turn, modifies the solution viscosity. A review of the relevant scientific aspects and industrial applications of a class of viscoelastic surfactant solutions is provided elsewhere (book edited by Wasan and Ginn, 1988; Zana and Kaler, 2007).

In the following sections, a brief review and introduction into the rheological behaviors of giant micellar systems and of lamellar liquid crystalline phases are provided in this chapter. Recent developments on the most important manifestations of the dynamics of these systems are further examined in this chapter.

2. Wormlike Micellar Systems

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2.1. Linear Viscoelasticity

An important aspect in the rheological characterization of micellar solutions is the study of the relaxation process occurring after fast perturbations acting upon the solution. The relaxation in micellar solutions involves a fast and a slow process. Micellar systems are in dynamical equilibrium with free surfactant molecules in solution, in such a way that the surfactant molecule is exchanged between the micelles and the inter-micellar solution. This exchange process occurs simultaneously to that of breakage-recombination of the micelles. The time scale of the exchange process is much faster than that associated to the breakage-recombination dynamics. The latter process involving the kinetics of scission/fusion reactions has been treated by Kahlweit (1981), Cates (1987), and Turner and Cates (1990).

Wormlike micelles with an exponential distribution of length has been considered by Cates (1990), although it is well established that spherical micelles can coexist with elongated ones, and thus the distribution of micellar lengths can be bimodal (Eriksson, 1990). The exponential distribution is the result of mean field theory. In a system where there are no closed loops nor branch points, let us consider $c(N)$ the number density of aggregates of $N$ monomers. In this case the mean-field free energy density obeys (Cates, 1990)

$$ F = k_B T \sum_N c(N) \left[ \ln c(N) + E / k_B T \right] $$

where $k_B T$ is the Boltzmann temperature and $E$ accounts for the two end-caps energy per chain. The term $\ln(c)$ comes from the entropy of mixing of micelles of different lengths or sizes. These are the terms sensitive to the micellar size distribution $c(N)$, while all other contributions reside in the reference free energy $F_0(\phi)$, which depends only on the total volume fraction ($\phi$). Minimization of Eq. (1) at fixed total volume fraction gives an exponential size distribution

$$ c(N) \propto \exp\left\{ -N / \bar{N} \right\}; \quad \bar{N} = \phi^{1/2} \exp\left[ E / 2k_B T \right] $$

The micellar length distribution can be described in terms of either the number density $c_{AS}(t)$ of aggregate $A_s$, which is a function of $s$ (the aggregation number) or of the moments of the distribution. In the latter, the zero-order moment is the total number $Z(t)$ of aggregates and this moment is not affected by the exchange reaction. In the time scale of the scission-fusion process, the change of $Z$ with time can be observed, since it is the slower time scale where the kinetics imposes relations between $c_{AS}$ and $Z$.

After a perturbation, the equilibrium values $\bar{c}_{AS}$ and $Z$ are modified as:

$$ c_{AS}(t) = \bar{c}_{AS} + \Delta c_{AS}(t) $$
The time dependence of the total number of micelles \( Z \) can be established according to the following kinetic equation:

\[ Z(t) = \bar{Z} + \Delta Z(t) \quad (3) \]

\[ A_{(s-k)} + A_k \xrightarrow{k_{s-k}} A_{S} \]

which is described as

\[ -\frac{dZ}{dt} = k_{1}c_{A(s-k)}c_{Ak} - k_{-1}c_{AS} \quad (4) \]

In Eq. (4), the first term of the right-hand side represents the fusion reaction of the micelles and the second term represents the scission reaction per unit time. \( k_{1} \) and \( k_{-1} \) are the fusion and scission rate constants, respectively. In equilibrium,

\[ k_{1}c_{A(s-k)}c_{Ak} = k_{-1}c_{AS} \quad (5) \]

According to the first order perturbations (3) and summing the right-hand side terms of Eq. (4) over all values of \( s \) and \( k \) leads to (Zana et al, 2007):

\[ \frac{d\Delta Z(t)}{dt} = -\frac{\theta}{\theta - 1} \beta \Delta Z(t) \quad (6) \]

where

\[ \beta = \sum_{s,k} \frac{k_{-1}(s,k)\bar{c}_{AS}}{\bar{Z}} \quad (7) \]

\[ \theta \propto \frac{N_w}{N} \quad (8) \]

\( N \) and \( N_w \) are the average aggregation number and the weight-average aggregation number, respectively. Equation (8) accounts for the polydispersity of the micellar size. According to the solution of Eq. (6), after a perturbation, the value of \( Z \) varies as:

\[ Z(t) = \bar{Z} \exp\left[-t/\tau_B\right] \quad (9) \]

where

\[ \tau_B^{-1} = \frac{\theta\beta}{\theta - 1} \quad (10) \]

This result shows that the slow relaxation process is mono-exponential because it is
associated to a single moment of the size distribution, namely, the relaxation of $Z$ controls the slow relaxation process. The other moments of the distribution correspond to the kinetics of the exchange process and have one or many fast relaxation times.

For giant micelles, the length distribution obeys an exponential law and the polydispersity is equal to 2. The scission rate constant $k_\text{sc}$ is independent of the position along the micelle where scission occurs. The average scission constant is:

$$\beta = \frac{\sum s c_s k_\text{sc}}{Z} = Nk = Nk_B$$  \hspace{1cm} (11)

Here $k_B$ stands for the breakage rate constant per unit length. Eq. (10) becomes:

$$\tau_B = \frac{1}{2Nk_B}$$  \hspace{1cm} (12)

which is a result that agrees with the expression of the relaxation time reported by Cates (1988, 1990). $\tau_B$ is defined as the mean breakage time for a micelle, or the lifetime of a chain before breaking, and of an end before recombination. In terms of the tube theory (Doi and Edwards, 1986), in the regime where the scission-recombination process occurs, the original chain ends do not survive long enough for ordinary reptation to occur; instead, each tube segment has to wait for a break to occur close enough to it, that the new chain end can pass through the given tube segment before disappearing again. The distance an end can move by reptation during its lifetime $\tau_B$ obeys

$$D_c(\bar{L}) \approx \frac{\tau_B}{l^2}$$  \hspace{1cm} (13)

where $D_c$ is the curvilinear diffusion coefficient. Since the one-dimensional diffusion process is similar to that of unbreakable polymers (except for the scission-recombination), we have

$$\frac{\tau_\text{rep}}{L^2} \approx \frac{\tau_B}{l^2}$$  \hspace{1cm} (14)

The waiting time $\tau$ for the appearance of a new end within $l$ is given by

$$\tau = \frac{\tau_B}{L}$$  \hspace{1cm} (15)

This gives a mean stress relaxation time in the scission-recombination regime as,

$$\tau = (\tau_B \tau_\text{rep})^{1/2}$$  \hspace{1cm} (16)
Linear viscoelastic data of wormlike micelles show in numerous cases that the relaxation spectrum is very narrow and that the system is Maxwellian (Shikata, 1987; Cates, 1987; Candau, 1984). For example, data obtained from a wealth of surfactants indicate that the system indeed obeys the relations of linear viscoelastic behavior with a single relaxation time from low to moderate frequencies. At high enough frequencies, however, the system is not strictly Maxwellian, since data depart from the single relaxation dynamics at a given characteristic frequency. Theoretical models herein have identified this departing frequency as the inverse of a characteristic time ($\tau_b$) that signals the onset for the micelles breaking process, where the scission-recombination kinetics occurs.

Dynamic light scattering studies (Buhler, 1995; Nemoto, 1995) have also dealt with the viscoelastic behavior of wormlike micelles. This technique measures the lifetime of concentration fluctuations, which are coupled to the viscoelasticity of the system. The spectrum resolves two modes of relaxation: slow and fast modes. The slower relaxation process has a characteristic time that depends on concentration, temperature and ionic strength in the same manner as the terminal time of stress relaxation measured by rheometry.

The transient nature of the wormlike micellar dynamics and the role of reversible scission have been invoked to explain the fact that the plateau region of the relaxation spectrum is similar to that of entangled polymers, and that the terminal region is characterized by a very narrow relaxation spectrum despite the high polydispersity of the micelles size (Lobl et al., 1984). Shikata et al. (1988) explained the concentration dependence of the plateau modulus ($G_0 \propto C^2$) by invoking that the elasticity of the plateau region results from the formation of entanglements described as a second order reaction between two molecular strands. The relaxation time in the terminal region would be determined by the kinetics of the entanglements, in such a way that the scission process takes place at the entanglement junctions. The scission step is a zero-order reaction and corresponds to bond interchange in the Cates model. As described above, the terminal relaxation time would result from the interplay of the dynamics of polymer diffusion (with characteristic time $\tau_{rep}$) and the kinetics of scission-recombination (with a characteristic time $\tau_b$). Therefore, the ratio $\zeta = \tau_b / \tau_{rep}$ determines the broadness of the relaxation spectrum. When the kinetic process controls the relaxation, i.e., $\zeta \ll 1$, the linear viscoelastic response at low and intermediate frequencies is Maxwellian with a single relaxation time ($\tau_b \tau_{rep}^{1/2}$). This regime is usually termed fast breaking regime. In this case the lifetime of the micelle is short and the frequency of scission is then proportional to the average micelle length $<L>$, which is given by $\tau_b^{-1} \propto <L>$. When the micelle lifetime is long $\zeta \approx 1$, deviations from a single relaxation process are observed and the broadness of the spectrum corresponds to that of reptation of the wormlike micelle over its whole length as in classical polymers. An exponential distribution of sizes yields a stretched exponential relaxation modulus. This regime is termed slow breaking regime.
At very high frequencies, corrections to Maxwell behavior have been introduced to describe relaxation at shorter time scales, when the diffusive process is no longer reptation but Rouse motion (Turner & Cates, 1991). The crossover to this time scale is reflected in the frequency domain by a minimum in the loss modulus. At this frequency, the inverse of the loss tangent $G'/G''$ is proportional to the ratio $<L>/l_e$, where $l_e$ is the entanglement length.

Figure 1. Cole-Cole plots at 30 °C for wormlike micellar solutions of CTAT as a function of surfactant concentration (in wt. %): (●) 5; (*) 10; (▲) 15; (○) 20; (▼) 25; (■) 30 (Soltero et al., 1996).

Figure 2. Time-concentration super-position master curves for $G'$ at 30 °C for wormlike micellar solutions of CTAT as a function of surfactant concentration (in wt. %): (●) 5;
Figure 1 shows Cole-Cole plots (i.e., the loss, $G''$, versus the storage, $G''$, moduli) of cetyltrimethylammonium tosilate (CTAT) solutions at 30 °C as a function of concentration. The size of the osculating circle increases with surfactant concentration, indicating an increase in the shear modulus. At low frequencies, i.e., $\omega \tau_b << 1$, all data follow closely the Maxwell asymptotic limit, $G''/G_0 \approx (G'/G_0)^{1/2}$. However, at high frequencies, i.e., $\omega \tau_b >> 1$, deviations from the osculating circle are observed, and for samples with low and intermediate concentrations, $G'$ goes through a minimum and then increases at higher frequencies. This upturn is related to the Rouse motion.

Time-concentration superposition is shown in Figure 2 for the storage modulus ($G'$) for CTAT wormlike micellar solutions. The shifting factors used are $a_c = \tau_{rep}$ and $b_c = (\tau_{rep}/\eta_b)$. Similar plots were reported elsewhere for micellar solutions made of a mixture of tetradecylpyridinium salicylate and tetradecyltrimethylammonium salicylate in presence of sodium bromide (Thurn et al, 1985).

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Biographical Sketches

Octavio Manero was born in Mexico City, the 20th of July, 1952. He received his BSc degree in Chemical Engineering from the Faculty of Chemistry of the National Autonomous University of Mexico (UNAM) in 1975 and the MSc degree in Chemical Engineering at the same institution in 1977. In 1980 he received his PhD degree in Applied Mathematics, Rheology, from the University of Wales. Research areas include Rheology, Non-Newtonian Fluid Mechanics, Transport Phenomena and Polymer Science and Engineering.

Work Experience.

Research Fellow at the Department of Chemical Engineering of the California Institute of Technology, from 1981 to 1983. In 1983 he was appointed professor at the Rheology and Mechanics of Materials Department, which belongs to the Materials Research Institute of UNAM, and he lectures at the Faculty of Chemistry and Faculty of Sciences of UNAM. He has been visiting professor in various universities (University of New York at Buffalo in 1988, University of Wales in 1990, and University of Grenoble in 1994, Metropolitan University in Mexico City in 1995 and University of Guadalajara). He was also visiting professor at Schlumberger Cambridge Research in 2000-2001. Associate Member of the University of Wales Institute of non-Newtonian Fluid Mechanics. Member of the Mexican Academy of Sciences and Mexican Academy of Engineering.
Recent publications.


Fernando Bautista Rico was born in Mexico City the 31st of May, 1961. He studied Chemistry and Physics at the National Autonomous University of Mexico (UNAM), receiving his BSc Degree with honors in 1982. At 1999 he obtained his PhD degree from the Universidad de Guadalajara. In his doctoral thesis Bautista showed how a simple model can describe the very complex rheological behavior of micellar solutions.

Work Experience:

He worked in the pharmaceutical industry. After graduating in 1982, he worked in the Faculty of Sciences at the University of Guadalajara. His actual appointment is professor at the Department of Sciences of the same University. He is member of various scientific societies (Society of Rheology, Mexican Physics Society). He has worked with professors Octavio Manero and Jorge E. Puig to develop the thermodynamic bases of the rheological behavior of complex fluids. Currently, his areas of research include electrorheology, hydrogels and bioproceses.

Recent publications.


Jorge E. Puig was born in Mexicali, B.C., México, the 10th of October, 1951. He received his BSc degree in Chemical Engineering from the Faculty of Chemical Sciences of the University of Guadalajara in 1973 and his PhD degree in Chemical Engineering from the University of Minnesota in 1982. His advisors were Professors L. E. Scriven and H. T. Davis. Research areas include Rheology, Surfactant and Colloid Science, and Polymer Science and Engineering.

Work Experience.

Research Fellow at the Department of Chemical Engineering and Materials Science of the University of Minnesota from 1976 to 1983. Researcher at the Mexican Institute of Petroleum from 1983 to 1984. In 1984 he was hired as a professor by the Faculty of Chemicals Science of the University of Guadalajara. In 1989 he was appointed Dean of the School of Chemical Science and in 1993, Head of the Department of Chemical Engineering at the same University. He has been visiting professor at the University of Delaware in 1991, National University of the South (Argentina) in 1996, University of Vasque Country (Spain) in 1998, and University of Barcelone in 2004. He is a member of the Mexican Academy of Science (1983) and of the Academy of Engineering (2003). He has served in several scientific committees and he has been a member of the Government Committee of the Council of Science and Technology of Mexico.

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