RHEOLOGY OF SURFACTANTS: WORMLIKE MICELLES AND LAMELLAR LIQUID CRYSTALLINE PHASES

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Contents

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 posses 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 non linear 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 (Israleachvili, 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, $(v/al) \approx 1$, 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 ($1/3 < v/al < 1/2$) than that of a spherical micelle ($v/al < 1/3$) 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

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)

$$F = k_{\mathrm{B}}T \sum_{N} c(N)\left[\ln c(N) + E / k_{\mathrm{B}}T\right] \tag{1}$$

where $k_{\mathrm{B}}T$ is the Boltzmann temperature and E accounts for the two end-caps energy per chain. The term $c \ln(c)$ 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 (ϕ). Minimization of Eq. (1) at fixed total volume fraction gives an exponential size distribution

$$c(N) \propto \exp\{-N / \overline{N}\}; \quad \overline{N} = \phi^{1/2} \exp\left[E / 2k_{\mathrm{B}}T\right] \tag{2}$$

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 $\overline{c}_{AS}$ and Z are modified as:

$$c_{AS}(t) = \overline{c}_{AS} + \Delta c_{AS}(t)$$

$$Z(t) = \overline{Z} + \Delta Z(t) \tag{3}$$

The time dependence of the total number of micelles Z can be established according to the following kinetic equation:

$$A_{(S-k)} + A_k \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_S$$
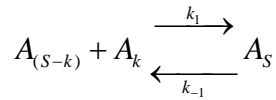
which is described as

$$-\frac{dZ}{dt} = k_1 c_{A(S-k)} c_{Ak} - k_{-1} c_{AS} \tag{4}$$

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,

$$k_1 c_{A(S-k)} c_{Ak} = k_{-1} c_{AS} \tag{5}$$

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):

$$\frac{d\Delta Z(t)}{dt} = -\frac{\theta}{\theta - 1} \beta \Delta Z(t) \tag{6}$$

where

$$\beta = \frac{\sum_{S,k} k_{-1}(s,k) \overline{c}_{AS}}{\overline{Z}} \tag{7}$$

$$\theta \propto \frac{N_w}{N} \tag{8}$$

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:

$$Z(t) = \overline{Z} \exp\left[-t/\tau_B\right] \tag{9}$$

where

$$\tau_B^{-1} = \frac{\theta \beta}{\theta - 1} \tag{10}$$

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_{-1} is independent of the position along the micelle where scission occurs. The average scission constant is:

$$\beta = \frac{\sum_s s\,\overline{c}_{AS}\,k_{-1}}{\overline{Z}} = Nk \qquad = Nk_B \tag{11}$$

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

$$\tau_B = \frac{1}{2Nk_B} \tag{12}$$

which is a result that agrees with the expression of the relaxation time reported by Cates (1988, 1990). τ_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 l an end can move by reptation during its lifetime τ_B obeys

$$D_C(\overline{L}) \approx \frac{\tau_B}{l^2} \tag{13}$$

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

$$\frac{\tau_{rep}}{\overline{L}^2} \approx \frac{\tau_B}{l^2} \tag{14}$$

The waiting time τ for the appearance of a new end within l is given by

$$\frac{\tau}{\overline{L}} = \frac{\tau_B}{l} \tag{15}$$

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

$$\tau = (\tau_B \tau_{rep})^{1/2} \tag{16}$$

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 (τ_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 τ_{rep}) and the kinetics of scission-recombination (with a characteristic time τ_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., $\varsigma \langle\langle 1$, the linear viscoelastic response at low and intermediate frequencies is Maxwellian with a single relaxation time $\left(\tau_B \tau_{rep}\right)^{1/2}$. 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 $\varsigma \approx 1$, 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.
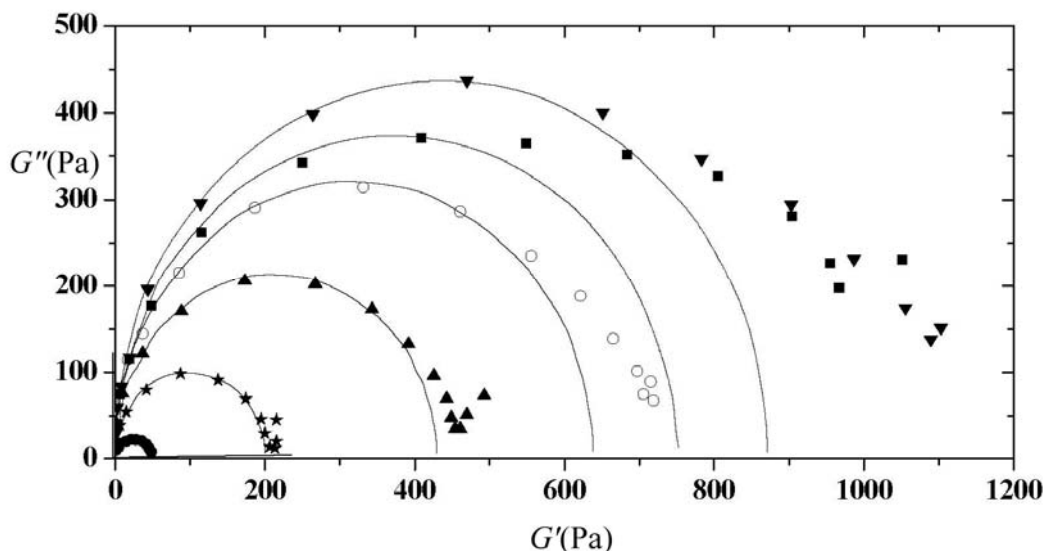

Figure 1. Cole-Cole plots at 30 °C for wormlike micellar solutions of CTAT as a function of surfactant concentration (in wt. %): (●) 5; (*)10; (▲) 15; (○) 20; (▼) 25; (■) 30 (Soltero et al.,1996).
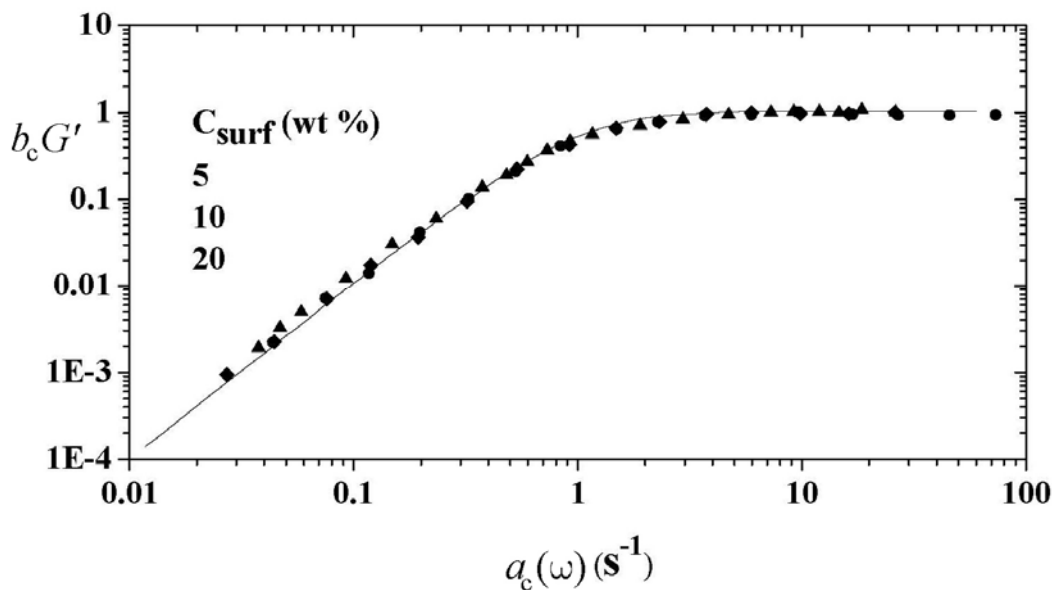

Figure 2. Time-concentration super-position master curves for G' at 30 °C for wormlike micellar solutions of CTAT as a function of surfactant concentration (in wt. %): (●) 5;

$(\blacktriangle)$ 10; (Λ) 20.

Shifting factors are $a_C = \tau_{rep}$ and $b_C = (\tau_{rep} / \eta_0)$. (Soltero et al., 1996).

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., $\omega\tau_B \ll 1$, all data follow closely the Maxwell asymptotic limit, $G''/G_0 \approx (G'/G_0)^{1/2}$. However, at high frequencies, i.e., $\omega\tau_B \gg 1$, 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 $b_C = (\tau_{rep} / \eta_0)$. 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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Bibliography

Acierno D, La Mantia F.P., Marrucci G, Titomanlio G. (1976) Nonlinear viscoelastic model with structure-dependent relaxation times. 2. Comparison with LD polyethylene transient stress results, J Non-Newton Fluid Mech 1,147–157.

Adam M., Delsanti M. (1985), Dynamical behavior of semidilute polymer solutions in a θ solvent: Quasi-elastic light scattering experiments, Macromolecules 18, 1760-1770.

Alexopoulos A.H., Puig J.E., Franses E.I. (1979). Phase continuity and surface properties of AOT/water liquid crystal dispersions. J. Colloid Interf. Sci. 128:26-34.

Angelov B., Angelova A., Ollivon M., Bourgaux C., Campitelli A. (2003). Diamond-type lipid cubic phase with large water channel, J. Am. Chem. Soc. 125 (24), 7188-7189.

Aradian A., Cates M.E. (2005). Instability and spatiotemporal chaos in a shear thickening fluid model. Europhys. Lett. 70 (3), 397-403.

Auernhammer G.K., Brand H.R., Pleiner H. (2002) Shear-induced instabilities in layered liquids _Phys. Rev. E. 66, 061707.

Bandyopadhyay R, Sood A. K. (2001). Chaotic dynamics in shear-thickening surfactant solutions,

Europhys. Lett. 56 (3), 447-453.

Barentin C., Liu A. J. (2001). Shear thickening in dilute solutions of wormlike micelles. Euro Phys. Lett. 55 (3), 432-438.

Bautista F., de Santos J.M., Puig J.E., Manero O. (1999) Understanding thixotropic and antithixotropic behavior of viscoelastic micellar solutions and liquid crystalline dispersions. I. The model. Jour. Non-Newt. Fluid Mech. 80 93-113.

Bautista F., Pérez-López J.H., García J.P., Puig J.E., Manero O. (2007) Stability analysis of shear-banding flow with the BMP model, Jour. Non-Newt. Fluid Mech. 144, 160-169.

Bautista F., Soltero J.F.A., Macias E.R., Puig J.E., Manero O. (2002) Irreversible thermodynamics approach and modeling of shear-banding flow of wormlike micelles. J. Phys. Chem. B. 106 (50), 13018-13026.

Bautista F., Soltero J.F.A., Pérez-López J.H., Puig J. E., Manero O. (2000). On the shear banding flow of elongated micellar solutions. J. Non-Newt. Fluid Mech. 94, 57-66.

Bergenholtz J., Wagner N.J. (1996). Formation of AOT/brine multilamellar vesicles, Langmuir 12, 3122-3126.

Berret J. F., Porte G. (1999). Metastable versus unstable transients at the onset of a shear induced phase transition, Phys. Rev. E 60, 4268-4271.

Berret J.F. (2006) In Molecular Gels. Materials with self-assembled fibrillar networks, R.G. Weiss, and P. Terech (Eds.), Springer, Secaucus.

Berret J.F., Gámez-Corrales R., Lerouge S., Decruppe J.P. (2000). Shear-thickening transition in surfactant solutions: New experimental features from rheology and flow birefringence. Eur. Phys. J. E. 2 (4), 343-350.

Berret J.F., Gamez-Corrales R., Séréro Y., Molino F, Lindner P. (2001). Shear-induced micellar growth in dilute surfactant solutions. Europhys. Lett. 54 (5), 605-611.

Berret J.F., Lerouge S., Decruppe J.P. (2002). Kinetics of the shear thickening transition observed in dilute surfactant solutions investigated by flow birefringence. Langmuir 18 (20), 7279-7286.

Boltenhagen P., Hu Y., Mathys E.F., Pine D. J. (1997). Inhomogeneous structure formation and shear-thickening in worm-like micellar solutions. Eurphys. Lett. 38 (5), 389-394.

Brochard F., de Gennes P.G. (1977). Dynamical scaling for polymers in theta solvents, Macromolecules 10, 1157-1161.

Buhler E., Munch J.-P. Candau, S.J. (1995). Dynamical properties of wormlike micelles: a light scattering study, J. Phys. II, 5, 765-904

Candau S. J., Hirsch E., Zana R. (1984). New aspects of the behavior of cetyltrimethylammonium bromide micelles: light scattering and viscometric studies, J. Phys. France 45, 1263-1270.

Cates M. E. (1987), Reptation of living polymers: dynamics of entangled polymers in the presence of reversible chain-scission reactions. Macromolecules 20, 2289. [One of the first theoretical discussions on the rheology of giant micelles].

Cates M. E. (1988). Dynamics of living polymers and flexible surfactant micelles: scaling laws for dilution, J. Phys. France 49, 1593-1600.

Cates M. E. (1990). Non- linear viscoelasticity of wormlike micelles (and other reversible breakable polymers), J. Phys. Chem. 94, 371.

Cates M. E. and Turner M.S. (1990). Flow-induced gelation of rodlike micelles. Europhys. Lett. 11 (7), 681-686.

Cates M. E., Candeau S. J. (2001), Ring-driven shear thickening in wormlike micelles? Europhys. Lett. 55, 887-893.

Cates M.E., Head D.A., Adjari A. (2002) Rheological chaos in a scalar shear-thickening model. Phys.

Rev. E. 66 (2), 025202.

Chandrasekhar, S. (1992). Liquid Crystals. Cambridge University Press. Cambridge, England.

Coppola L., Muzzalupo R., Ranieri G. A., Terenzi M. (1995). Characterization of the lamellar phase aerosol OT/water system by NMR diffusion measurements, Langmuir 11, 1116.

Debye P. (1947), Molecular-weight determination by light scattering J. Phys. Colloid Chem. 51, 18-32.

Diat O., Roux F., Nallet F. (1993a). Effect of shear on a lyotropic lamellar phase, J. Phys. II France 3, 1427-1452.

Diat O., Roux F., Nallet F. (1993b). Lamellar phase under shear: SANS measurements, J. Phys. IV France 3, 193-204.

Diat O., Roux F., Nallet F. (1995). Layering effect in a sheared lyotropic lamellar phase, Phys. Rev. E 51, 3296-3299.

Dixon, P.K., Pine, D.J. and Wu, X.I. (1992). Mode selection in the dynamics of sheared polymer solutions, Phys. Rev. Lett. 68, 2239-2242.

Doi M. and Edwards S.F. (1986). The Theory of Polymer Dynamics, Clarendon Press, Oxford.

Eriksson J. C. and Ljunggren S. (1990). Model calculations on the transitions between surfactant aggregates of different shapes, Langmuir 6, 895.

Escalante J. I., Hoffmann H. (2000) The lamellar-to-vesicle phase transition by shear experiments. J. Phys Condens. Matter 12 A483–A489.

Escalante J. I., Soltero J. F. A., Bautista F., Puig J. E., Manero O. (2006), Time-dependent rheological behavior of liquid crystalline dispersions, Advances Structural Materials II, Mat. Sci. Forum Vol. 509, 177-186, Trans. Tech. Pub, Switzerland.

Escalante J.I., Macias E.R., Bautista F., Perez-Lopez J.H., Soltero J.F.A., Puig J.E., Manero O. (2003). Shear-banded flow and transient rheology of cationic wormlike micellar solutions. Langmuir 19, 6620-6626.

Fielding S.M., Olmsted P. D. (2003b). Early stages in the unified model of shear-induced demixing and mechanical of shear banding instabilities, Phys. Rev. Lett. 90, 2245011-2245014.

Fielding S. M. (2005). Linear instability of planar shear banded flow, Phys. Rev. Lett. 95, 13, 134501.

Fielding S. M., Olmsted P. D. (2006). Nonlinear dynamics of an interface between shear bands, Phys. Rev. Lett. 96,10, 104502.

Fielding S. M., Olmsted P.D. (2004). Spatiotemporal oscillations and rheochaos in a simple model of shear banding, Phys. Rev. Lett. 92, 084502.

Fielding S.M., Olmsted P. D. (2003a). Kinetics of the shear banding instability in startup flows, Phys. Rev. E 68, 3, 036313.

Franco J.M., Muñoz J., Gallegos C. (1995). Transient and steady flow of a lamellar liquid-crystalline surfactant/water system, Langmuir 11, 669-673.

Fredrickson A.G. (1970). A model for the thixotropy of suspensions, AICHE J 16, 436–438.

Fritz G., Wagner N.J., Kaler E.W. (2003). Formation of multilamellar vesicles by oscillatory shear, Langmuir 19, 8709-8714.

Goldzal A., Jamieson A. M., Mann A. J., Polak J.,Rosenblatt J. (1996). Rheology, optical microscopy and electron microscopy of cationic surfactant gels, J. Colloid Interface Sci 180, 261-268

Goveas J. L, Pine D.J. (1999). A phenomenological model for shear-thickening in wormlike micelle solutions, Europhys. Lett. 48 (6), 706-712.

Grand C., Arrault J., Cates M.E. (1997). Slow transients and metastability in wormlike micelle rheology. J. Phys. II (France) 6, 1081-1086.

Halsey, Jr. J.D. (1953) On the Structure of Micelles, J. Phys. Chem. 57, 87.

Hartmann V., Cressely R. (1997). Influence of sodium salycilate on the rheological behaviour of an aqueous CTAB solution. Colloids Surfaces A 121 (2-3), 151-162.

Hartmann V., Cressely R. (1997). Simple salt effects on the characteristics of the shear thickening exhibited by an aqueous micellar solution of CTAB/NaSal. Europhys. Lett. 40 (6), 691-696.

Hartmann V., Cressely R. (1998). Occurrence of shear thickening in aqueous micellar solutions of CTAB with some added organic counterions. Colloid Polym. Sci. 276 (2), 169-175.

Hartmann, V.; Cressely, R. (1997). Shear thickening of an aqueous micellar solution of cetyltrimethylammonium bromide and sodium tosylate. J. Phys. II France , 7 (8), 1087-1098.

Helfand E., Fredrickson G.H. (1989), Large fluctuations in polymer solutions under shear, Phys. Rev.Lett.62, 2468-2472.

Herle V., Fischer, P., Windhab E.J. (2005). Stress-driven shear bands and the effect of confinement on their structures. A rheological, flow visualization and rheo-SALS study. Langmuir 21 (20), 9051-9057.

Hernandez Acosta S., González Alvarez A., Manero O., Mendez-Sanchez A.F., Pérez-González J., De Vargas, L. (1999) Capillary rheometry of micellar aqueous solutions. J. Non-Newtonian Fluid Mech. 85, 229-247.

Herve P., Roux D., Bellocq A.M., Nallet F., Gulik-Krzywicki T. (1993). Dilute and concentrated phases of vesicles at thermal equilibrium, J. Phys. II France 3, 1255-1270.

Hoffmann H., Thunig C., Schmiedel P., Munkert U. (1994). Surfactant systems with charged multilamellar vesicles and their rheological properties. Langmuir 10, 3972-3981.

Hu Y.T., Boltenhagen P., Mathys E., Pine D.J. (1988). Shear thickening in low-concentration solutions of wormlike micelles. II. Slip, fracture, and stability of the shear induced phase. J. Rheol 42 (5), 1209-1229.

Hu Y.T., Boltenhagen P., Pine D. J. (1988). Shear thickening in low-concentration solutions of wormlike micelles. I. Direct visualization of transient behavior and phase transitions. J. Rheol 42 (5), 1185-1208.

Israelachvili J. N., Intermolecular and Surface Forces, Academic Press, New York (1992). [This is an important book dealing with the study of interactions among microstructures].

Jönsson B., Lindman B., Holmberg K., Kronberg B. (1998) Surfactants and Polymers in Aqueous Solution. John Wiley & Sons. Chichester, England.

Jou D., Casas-Vazquez J., Criado-Sancho, M. (2000). Thermodynamics of Fluids under Flow. Springer. Berlin.

Kadoma I.A., van Egmond J.W. (1997), Shear-enhanced orientation and concentration fluctuations in wormlike micelles: effect of salt , Langmuir 13, 4551-4561.

Kahlweit M. (1981). Physics of Amphiphiles: Micelles, Vesicles and Microemulsions, Degiorgio V., Corti M., eds., North Holland, Amsterdam.

Lauger J., Weigel R., Berger K., Hiltrop W., Richtering W. (1996), Rheo-small-angle light scattering investigation of shear-induced structural changes in a lyotropic lamellar phase, J. Colloid Int. Sci. 181, 521-529.

Lee J.Y., Magda J.J., Hu H., Larson R.G. (2002). Cone angle effects, radial pressure profile, and second normal stress difference for shear-thickening wormlike micelle. J. Rheol. 46 (1), 195-208.

Lerouge S., Decruppe J.P., Humbert C. (1998). Shear banding in a micellar solution under transient flow. Phys. Rev. Lett. 81 (24) 5457-5460.

Lin Z. Q., Zakin J. L., Zheng Y., Davis H. T., Scriven L. E., Talmon Y. (2001). Comparison of the effects of dimethyl and dichloro benzoate counterions on drag reduction, rheological behavior,and microstructures of a cationic surfactant. J. Rheol. 45 (4), 963-981.

Lobl M., Thurn H., Hoffmann H. (1984) Ber. Bunsenges. Phys. Chem. 88, 1102.

Lukaschek M., Müller S., Hasenhindt A., Grabowski D.A., Schmidt C. (1996). Lamellar lyomesophases under shear as studied by deuterium nuclear magnetic resonance. Colloid Polym. Sci. 274, 1, 1-7

Macías E.R., Bautista F., Soltero J.F.A., Puig J.E., Attané P., Manero O. (2003). On the shear thickening flow of dilute CTAT worm-like micellar solutions. J. Rheol. 47 (3), 643-658.

Macías E.R., González A., Manero O., González-Nuñez R, Soltero J.F.A., Attané P. (2001). Flow regimes of dilute surfactant solutiuons. J. Non-Newtonian Fluid Mech.101 (1-3), 149-171.

Manero O., Bautista F., Soltero J.F.A., Puig J. E. (2002). Dynamics of wormlike micelles: the Cox-Merz rule. Jour. Non-Newt. Fluid Mech.106, 1-15.

Manero O., Pérez-López J.H., Escalante J.I., Puig J.E., Bautista F. (2007). A thermodynamic approach to rheology of complex fluids: The generalized BMP model, Jour. Non-Newt. Fluid Mech. 146, 22-29.

Manero O., Rodríguez R. F. (1999). Thermodynamic description of coupled flow and diffusion in a viscoelastic binary mixture. Jour. Non-Equil. Thermodyn. 24, 177.

Marín-Santibañez B.M., Pérez-González J., de Vargas L., Rodríguez-González F., Huelsz G. (2006). Rheometry - PIV of shear-thickening wormlike micelles. Langmuir 22 (9), 4015-4026.

Marlow S.W., Olmsted P.D. (2002) The effect of shear flow on the Helfrich interaction in lyotropic lamellar systems. Eur. Phys. J. E 8, 485-497.

McBain J. W. (1950) Colloid Science, Health Co., San Francisco.

McKay K.W., Miller W. G., Puig J. E., Franses E. I. (1991). Steady and dynamic shear rheology of dispersions of lyotropic liquid crystals, Jour. Dispersion Sci. Tech. 12 (1), 37-58.

Milner S.T. (1991). Hydrodynamics of semidilute polymer solutions, Phys. Rev.Lett. 66, 1477-1480.

Milner S.T. (1993). Dynamical theory of concentrated fluctuations in polymer solutions, Phys. Rev. E 48, 3674-3691.

Montalvo G., Valiente M., Khan A. (2007). Shear-induced topology changes in liquid crystals of the soybean lecithin/DDAB/water system, Langmuir 23, 10518-10524.

Muller A. J., Torres M.F., Sáez A.E. (2004) Effect of flow field on the rheological behavior of aqueous cetyltrimethylammonium p-toluenesulfonate solutions. Langmuir 20 (10), 3838-3841.

Myska J., Lin Z. Q., Stepanek P., Zakin J. L. (2001). Influence of salts on dynamic properties of drag-reducing surfactants. J. Non-Newtonian Fluid Mech. 97 (2-3), 251-266.

Nakano M., Teshigawara T., Sugita A., Leesajakul W., Taniguchi A., Kamo T., Matsuoka H., Handa T. (2002). Dispersions of liquid crystalline phases of the monoolein/oleic acid/Pluronic F127 system. Langmuir 18, 9283-9288.

Oda R., Panizza P., Schmutz M., Lequeux F. (1997). Direct evidence of the shear-induced structure of wormlike micelles: gemini surfactant 12-2-12.Langmuir 13 (24), 6407-6412.

Oelschlaeger C., Waton G., Buhler E., Candau S.J., Cates M.E. (2002). Rheological and light scattering studies of cationic fluorocarbon surfactant solutions of low ionic strength. Langmuir 18 (8), 3076-3085.

Olmsted P. D., Lu C.-Y. (1999), Phase separation of rigid-rod suspensions in shear flow, Phys. Rev. E 60, 4397-4415.

Olmsted P.D., Radulescu O., Lu C.-Y.D., Johnson-Segalman model with a diffusion term in cylindrical Couette flow, J. Rheol. 44, 257-275.

Panizza P., Roux D., Vuillaume V., Lu C.-Y.D., Cates M.E. (1996), Viscoelasticity of the onion phase, Langmuir 12, 248-252.

Partal P., Kowalski A.J., Machin D., Kiratzis N., Berni M.G., Lawrence C.J. (2001). Rheology and microstructural transitions in the lamellar phase of a cationic surfactant, Langmuir 17, 1331-1337.

Pearson J.R.A. (1994) Flow curves with a maximum. J. Rheol. 38 (2), 309-331.

Petrov P. G., Ahir S. V., Terentjev E. M. (2002). Rheology at the phase transition boundary: 1. lamellar L-phase of AOT surfactant solution, Langmuir 18, 9133-1121-9139.

Picard G., Ajdari A., Bocquet L., Lequeux F. (2002) Simple model for heterogeneous flows of yield

stress fluids. Phys. Rev. E. 66, 051501.

Pignon F., Magnin A., Piau J.M. (1998). Thixotropic behavior of clay dispersions: Combinations of scattering and rheometric techniques. J Rheol 42, 1349–1373.

Porte G., Berret J. F., Harden J.L. (1997). Inhomogeneous flows of complex fluids: mechanical instability versus nonequilibrium phase transitions, J. Phys. II (France), 7, 459-472.

Proztl B., Springer J. (1997). Light scattering studies on shear induced structures of micelles. J. Colloid Interface Sci.190 (2), 327-333.

Puig J. E., Bautista F., Soltero J. F. A., Manero O., in Zana R., Kaler E. W. (2007). Giant Micelles. Properties and Applications. Surfactant Science Series, Vol. 140. CRC Press. Taylor & Francis, Boca Raton, FL., USA.

Quemada D. (1999) Rheological modeling of complex fluids. IV. Thixotropic and ''thixoelastic'' behavior. Start-up and stress relaxation, creep test and hysteresis cycles, Eur Phys J Appl Phys 5,1191–1207.

Ramsay J.D.F., Lidner P. (1993). Small-angle neutron scattering investigations of the structure of thixotropic dispersions of smectite clay colloids. J Chem Soc-Faraday Trans. 89, 4207–4214.

Rehage H., Hoffmann H. (1982). Shear induced phase transitions in highly dilute aqueous detergent solutions. Rheol. Acta 21 (4-5), 561-563.

Rincon E., Chavez A.E., Herrera R., Manero O. (2005) Rheological modeling of complex fluids: a transient network model with microstates. J. Non-Newtonian Fluid Mech. 131, 64-77.

Robles-Vásquez O., Corona-Galván S., Soltero J.F.A., Puig J. E., Tripodi S.B., Vallés E., Manero O. (1993). Rheology of lyotropic liquid crystals, J Colloid Interface Sci. 160, 65-71.

Rodriguez-Abreu C., Garcia-Roman M., Kunieda H. (2004). Rheology and dynamics of micellar cubic phases and related emulsions, Langmuir 20, 5235-5240.

Salmon J.-B., Colin A., Roux D. (2002). Dynamic behavior of a complex fluid near an out-of-equilibrium transition: approaching simple rheological chaos, Phys. Rev. E 66, 031505-1.

Salmon J.-B., Manneville S., Colin A. (2003a). Shear banding in a lyotropic lamellar phase. I. Time-average velocity profiles, Phys. Rev. E 68, 051503.

Salmon J.-B., Manneville S., Colin A. (2003b). Shear banding in a lyotropic lamellar phase. II. Temporal fluctuations, Phys. Rev. E 68, 051504.

Schmitt V., Marques C.M., Lequeux F. (1995). Shear-induced phase separation of complex fluids: the role of the flow-concentration coupling, Phys. Rev E 52, 4009-4915.

Shikata T., Hirata H., Kotaka T. (1987), Micelle formation of detergent molecules in aqueous media: viscoelastic properties of aqueous cetyltrimethylammonium bromide solutions. Langmuir 3, 1081-1086.

Soltero J.F.A., Bautista F., Puig J.E., Manero O. (1999) Rheology of cetyltrimethylammonium p-toluenesulfonate-water system.3. Nonlinear viscoelasticity. Langmuir 15, 1604-1612.

Soltero J.F.A., Robles-Vásquez O., Puig J. E., Manero O. (1995). Note: Thixotropic-antithixotropic behavior of surfactant-based lamellar liquid, J Rheol. 39, 235

Thurn H., Lobl M., Hoffmann H. (1985) Viscoelastic detergent solutions. A quantitative comparison between theory and experiment, J. Phys. Chem. 89, 517.

Truong M.T., Walker L.M. (2000). Controlling the shear-induced structural transition of rodlike micelles using nonionic polymers. Langmuir 16 (21), 7991-7998.

Turner M.S. and Cates M. E. (1991), Linear viscoelasticity of living polymers: A quantitative probe of chemical relaxation times, Langmuir 7, 1590-1594.

Valdés M., Manero O., Soltero J.F.A., Puig J. E. (1993). Rheology of lyotropic liquid crystals of aerosol OT, J Colloid Interface Sci 160, 59-64.

Versluis P., van de Pas J.C., Mellema J. (1997). Microstructure and rheology of lamellar liquid crystalline

phases, Langmuir 13, 5733-5738.

Versluis P., van de Pas J.C., Mellema J. (2001). Influence of salt concentration and surfactant concentration on the microstructure and rheology of lamellar liquid crystalline phases, Langmuir 17, 4825-4835.

Wang S. Q. (1991). Growth and dynamic polymers (micelles) in shear flow, Macromolecules 24, 3004-3409.

Wasan D.T., Ginn, M. E., Shah D.O. (1988). Surfactants in Chemical/Process Engineering, Surf. Sci. Series, Vol. 28, M. Dekker, New York.

Weber V., Schosseler F. (2002). Shear-thickening in salt-free aqueous solutions of a gemini cationic surfactant: a study by small angle light scattering. Langmuir 18 (25), 9705-9712.

Wheeler E.K., Izu P. and Fuller G.G. (1996). Structure and rheology of wormlike micelles, Rheol. Acta 35, 139-149.

Wu X.L., Pine D.J. and Dixon P.K. (1991), Enhanced concentration fluctuations in polymer solutions under shear flow, Phys. Rev. Lett. 66, 2408-2411.

Wunderlich A.M., Brunn P.O. (1989). The complex rheological behavior of an aqueous cationic surfactant solution investigated in a Couette-type viscometer. Colloid Polym. Sci. 267 (7), 627-636.

Wunderlich I., Hoffmann H., Rehage H. (1987). Flow birefringence and rheological measurements on shear induced micellar structures, Rheologica Acta 26 (6), 532-542.

Zana R., Kaler E. W. (2007). Giant Micelles. Properties and Applications. Surfactant Science Series, Vol. 140. CRC Press. Taylor & Francis, Boca Raton, FL., USA. [This book presents recent research on wormlike micelles].

ZilmanA.G., Granek R. (1999) Undulation instability of lamellar phases under shear: A mechanism for onion formation? , Eur. Phys. J. E 11, 593-608.

Zipfel J., Beghausen J., Lidner P., Richtering W. (1999b). Shear-induced structures in lamellar phases of amphiphilic block copolymers, J. Phys. Chem. Chem. Phys. 1, 3905-3910.

Zipfel J., Berghausen J., Lindner P., Richtering W. (1999c). Influence of shear on lyotropic lamellar phases with different membrane defects, J. Phys. Chem. B 103, 2841-2849.

Zipfel J., Lidner P., Tsianou M., Alexandritis P., Richtering W. (1999a). Shear-induced formation of multilamellar vesicles ("onions') in block co-polymers, Langmuir 15, 2599-2602.

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.

1.-Book Chapter**.**   Puig, J.E., Bautista, F., Soltero, J.F.A., Manero, O., "Non-Linear Rheology of Giant Micelles" in "Giant Micelles: Properties and Applications", Zana, R. & Kaler, E.W. (eds.) Taylor and Francis, New York (2007).

2.- J. Castillo-Tejas, A. Rojas-Morales, F. López-Medina, J.F.J. Alvarado, F. Bautista, O. Manero, "Flow of linear molecules through a 4:1:4 contraction-expansion using non-equilibrium molecular dynamics: extensional rheology and pressure drop". Journal of non-Newtonian Fluid Mechanics, 161 (2009) 48.

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 bioprocesses.

Recent publications.

1.- "A thermodynamic approach to rheology of complex fluids: the generalized BMP model", Bautista F., J. P. García, J.H. Pérez, J. E. Puig and O. Manero, Journal Non Newtonian Fluid Mech. 146, 1-3 (2007) 22-29

2.- López L. C., Orozco E. Cruz L.E., Gonzalez A., Bautista F, "Synthesis and Characterization of Acrylamide/Acrylic Acid Hydrogels Crosslinked using a novel Diacrylate of Glycerol to Produce Multistructured Materials", Journal of Polymer Science: Part A: Polymer Chemistry, 46, 8 (2008) 2667-2679

3.- Mendoza LD, Rabelero M, Escalante JI, , Bautista F and Puig JE, "Rheological behavior of surfactant-based precursors of silica mesoporous materials". Journal of Colloid and Interface Science, 320, 1 (2008) 290-297

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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.

*Recent publications***.**

1.- Synthesis and Characterization of Composites of DBSA-doped Polyaniline and Polystyrene-Based Ionomers", T. Del Castillo-Castro, M.M. Castillo-Ortega, I. Villareal, F. Brown, H. Grijalva, M. Pérez-

Tello, S.M. Nuño-Donlucas and J.E. Puig, Composites Part A – Applied Sci. & Manufacturing **38(2)**, 634-645 (2007).

2.- Rheological Behavior of Surfactant-based Precursors of Silica Mesoporous Materials", L. D. Yañez, M. Rabelero, J.I. Escalante, A. González-Álvarez, F. Bautista and J.E. Puig, J. Colloid and Interface Science 320, 290-297 (2008). ISSN: 0021-9797.