Structure and Dynamics of Viscoelastic Surfactant Solutions – An Application of Concepts from Polymer Science

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Abstract. This article shows how additional information on the structure, phase behavior, and dynamics of polymer-like surfactant solutions can be obtained through concepts borrowed from polymer physics. Particular emphasis is given to the interpretation of static and dynamic light scattering and small-angle neutron scattering experiments.

Introduction

The physics of long flexible polymer chains has strongly been influenced by the discovery of the relationship between polymer statistics and phase-transition problems. The subsequent development of a number of universal scaling laws for static and dynamic properties of polymers by de Gennes and coworkers introduced new concepts and analogies to other branches of science. The progress made in the theoretical understanding of the static and dynamic properties of polymers was accompanied by the availability of new experimental techniques such as neutron scattering or dynamic light scattering, which provide powerful tools for the experimentalists [1][2].

However, while these recent developments have been beneficial for polymer science, they have remained quite unnoticed by many scientists working in other areas of chemistry, biochemistry, and biophysics. As a consequence, these modern trends in polymer physics have had e.g. only a minor impact on studies in the field of surfactant science, where self-assembling molecules form particles of colloidal size such as micelles, microemulsions, or vesicles. Their physical chemistry has been studied quite extensively, with major emphasis on stability requirements (i.e. characterization of two- and multicomponent phase diagrams) and structure, size, and shape of the aggregates. However, few attempts have been made in order to profit from recent advances in polymer theory and to gain additional insight into the physical chemistry of surfactant solutions by making analogies to polymers.

One notable exception can be found in the recently developed field of ‘equilibrium polymers’, where the term equilibrium (or ‘living’) polymer is used for linear macromolecules that can break and recombine [3]. Therefore, equilibrium polymers are transient structures with a relatively short lifetime $T_b$, and they exhibit a wealth of interesting dynamic properties on time scales both long or short compared to $T_b$. Typical examples of equilibrium polymers are micelles, where the formation of macromolecular structures is a result of a subtle balance of opposing forces which arise from weak van der
Waoles, hydrophobic, H-bonding, screened electrostatic and steric interactions between the individual surfactant monomers [4]. Due to the finite life time of the particles, the molecular-weight distribution of micelles is not constant but in thermal equilibrium and thus depends strongly on surfactant concentration and temperature [3]. This is quite different from 'classical' polymers such as polystyrene, where the monomers are covalently linked and the molecular-weight distribution is quenched after the preparation procedure. Several groups soon realized that surfactant systems in which giant worm-like micelles are formed can be used as ideal model systems for an experimental investigation of the static and dynamic properties of equilibrium polymers [3][5-11].

It is the aim of this article to show that additional and detailed information on the structure, dynamics, and phase behavior of micellar aggregates can be obtained by making analogies to polymer solutions and using modern polymer theory for an interpretation of data from scattering and rheological experiments. This will be illustrated with selected examples, where analogies are made to two different fields of polymer science: i) static conformation of individual polymer chains, and ii) formation of an entanglement network at moderate polymer concentrations and its static and dynamic properties.

**Lecithin Reverse Micelles – Phenomenological Observations and Phase Behavior**

Mixtures of surfactants, oil and water represent a prime example of molecularly organized systems, where the molecular interactions can lead to self-association of the surfactant molecules and the formation of a rich variety of different structures such as microemulsions and lyotropic mesophases. A schematic example of a typical phase diagram for a ‘model 3-component microemulsion’ is shown in Fig. 1. We see that, depending upon the composition of the system, a variety of different structures and phases are formed. We shall now look more carefully at the structures formed in the organic solvent-rich corner of the phase diagram, i.e. at the isotropic L₀-phase, where water-in-oil (w/o) microemulsions or so-called reverse micelles form.

In contrast to aqueous micellar systems, reverse micelles at moderately high values of surfactant concentration c and molar ratio of water to surfactant w_o are generally believed to have a droplet-like structure, with a radius which depends primarily upon w_o and which is almost independent of surfactant concentration (see region L₀ in Fig. 1) [12]. It came thus as a surprise, when Scarsazzi and Luisi reported the formation of viscoelastic lecithin reverse micellar solutions at very low values of w_o and quite low surfactant volume fractions, i.e. under conditions where for droplet-like small structures, and in the absence of strong electrostatic effects, only weak intermicellar interactions should be present [13]. We subsequently investigated the structural and dynamic properties of these systems and found that the viscosity of reverse micellar solutions of soybean lecithin in a number of different organic solvents increases dramatically upon the addition of very small quantities of water [14][15]. In general, the zero shear viscosity η_s increases with increasing w_o and reaches a distinct maximum at a well defined w_o,max. The value of η_s at w_o,max depends strongly upon lecithin concentration, temperature and nature of the organic solvent used. The ratio of η_s/η_o, where η_o is the viscosity of the solvent, can be as high as 10⁶ at w_o,max. Upon further addition of water, η_s generally decreases and phase separation can be observed. The value of w_o,max seems to be quite independent of lecithin concentration, but it does depend to some extent upon the nature of the organic solvent used. Fig. 2 shows representative examples of the dependence of η_s on w_o for lecithin in isooctane and cyclohexane, respectively. It clearly illustrates how a simple addition of three molecules of water per molecule of lecithin to a liquid-like lecithin/isoctane solution causes the viscosity of the solution to increase to values as high as (8.3 ± 0.8)·10² Pa·s. We see from Fig. 2A, that the value of w_o,max is indeed independent of lecithin concentration, but that the absolute values of η_s at w_o,max strongly depend on the lecithin concentration. Fig. 2 also shows that lecithin/ cyclohexane solutions can incorporate a significantly larger amount of water, and that w_o,max is shifted to w_o,max = 12 for this system.

We were subsequently able to explain the unusual polymer-like properties of lecithin reverse micelles with a water-induced one-dimensional micellar growth into very long and flexible cylindrical reverse micelles, i.e., a characteristic
sphere-to-flexible cylinder transition normally observed in aqueous solutions only [15]. At high enough volume fractions \( \Phi \), these giant polymer-like reverse micelles would then be able to entangle and form a transient network similar to semidilute polymer solutions, which would explain at least qualitatively the tremendous increase in zero shear viscosity observed at higher values of \( w_o \) and \( \Phi \). An example for the location of the viscoelastic micellar phase in the ternary phase diagram and a schematic representation of the proposed simple model for the structural properties of lecithin reverse micelles is shown in Fig. 3. However, the hypothesis of a water-induced formation of flexible cylindrical micelles and the existence of entanglement networks was largely based on 'low-resolution' light scattering and rheological measurements and analogies to classical polymer theory. In the next chapter, we shall see how we can directly confirm this picture and verify the postulated analogy between the structural properties of polymer chains and lecithin reverse micelles using a combination of static light scattering and small-angle neutron scattering.

**Polymer-like Structure of Lecithin Reverse Micelles – Light and Neutron Scattering Studies**

To study the structure of lecithin reverse micelles in dilute solutions, we measured the time-averaged scattering intensity \( I(Q) \) as a function of the scattering vector \( Q \), whose magnitude is given by \( Q = (4\pi/\lambda) \cdot \sin(\theta/2) \), where \( \lambda \) is the wavelength of the incident light (or neutrons) in the medium and \( \theta \) is the scattering angle, over a wide range of \( Q \) values. In such a static scattering experiment, we can derive important information on the structure of the particles that scatter light or neutrons [16]. The basis for structural investigations with static (elastic) scattering experiments is schematically shown in Fig. 4A. The incident light or neutrons can be described as an incoming plane wave. The polymer can be divided into many subregions, which all act as small scattering centers. If the largest dimension of the polymer is small compared to the wavelength \( \lambda \), all subregions see the same incident field, and the amplitude of the scattered wave can be written as a simple sum of the contributions from the individual scattering centers. In this case, the scattering experiment yields information on the average particle mass only.

However, if the largest dimension of the particle is comparable or larger than \( \lambda \) (\( \lambda = 5000 \AA \) for light and \( \lambda = 10 \AA \) for neutrons), the situation becomes more complicated and the scattering experiment will yield additional information. In this case, the scattered waves from different regions in the particle can be out of phase (see Fig. 4A), and we must, therefore, take into account interference effects in the calculation of the total scattering amplitude. This can be done by calculating the pathlength differences for the light or neutrons scattered by all possible pairs of scattering centers within the particle, and comparing it with \( \lambda \). One can show that the optical path difference between two scattering centers separated by a distance vector \( \vec{r} \) is given by \( \Delta s = \vec{Q} \cdot \vec{r} \) [16]. The influence of the destructive intraparticle interference effects on the scattering intensity thus depends on the quantity \( Q \cdot r \), and interference effects are not important for \( Q \cdot r \ll 1 \). Therefore, \( 1/Q \) is often called...

**Fig. 2.** A) Zero shear viscosity \( \eta_s \) vs. added water to lecithin molar ratio, \( w_o \), for soybean lecithin in isooctane at \( \Phi = 0.144 \) (●) and \( \Phi = 0.036 \) (○), respectively, at 20.0°C. Also shown as dashed lines are the phase boundaries \( w_{o,cr} \) for phase separation into two macroscopically separated and optically clear phases (for details, see [15]). B) Zero shear viscosity \( \eta_s \) vs. \( w_o \) for soybean lecithin in cyclohexane at \( \Phi = 0.036 \) at 25.0°C. For details on the phase behavior, see [29].
the 'spatial resolution' of a scattering experiment, and the selection of the magnitude of the scattering vector \( Q \) determines the characteristic distances or length scales (length scale \( \sim 1/Q \)) which are being probed in a scattering experiment.

Taking into account the influence of intraparticle interference effects, we then see that the average scattering intensity \( I(Q) \) is proportional to \( S(Q) \), where \( S(Q) \) is the so-called static structure factor which results from a Fourier transform of the pair correlation functions \( g(r) \) of all the scattering elements of the particles [17]. The structural information obtained in a scattering experiment is thus indirect only, and we can only aim for a self-consistent data analysis and interpretation based on explicit structural models and assumptions for the intra- and intermolecular interaction effects.

Here, we can now directly profit from the enormous progress achieved in a theoretical understanding of the static structure factor observed in solutions of classical synthetic polymers. Based on the previously postulated model of flexible and polymer-like cylindrical reverse micelles, we can test whether the experimental data are indeed compatible with this model, and try to extract quantitative information on the composition dependence of the overall particle size, polydispersity, and flexibility of the micelles formed in lecithin w/o microemulsions. For flexible polymers, \( I(Q) \) has several distinct regimes which permit a quantitative study of the different length scales characterising overall dimension (radius of gyration, \( R_g \)), flexibility (persistence length, \( l_p \)), and local cylindrical cross-section (\( R \)) [17][18][19]. We can thus try to verify the postulated analogies between the structural properties of flexible polymer coils and lecithin reverse micelles using the predictions for \( I(Q) \) from polymer physics: For very low values of \( Q (1/Q < R_g) \), the scattered intensity \( I(Q) \) becomes insensitive to structural details and is dominated by the finite overall length of the particles, and we can determine the radius of gyration \( R_g \) of the particles. The low-\( Q \) regime will thus clearly reflect the water-induced aggregate growth postulated in our model. At intermediate \( Q (R < 1/Q < R_g) \), \( I(Q) \) becomes much more sensitive to the local aggregate structure, and polymer theory predicts for flexible polymer coils that \( I(Q) \) should decay with a power law of the form \( I(Q) \sim Q^{-x} \), where \( 1.7 \leq x \leq 2.0 \). At large values of \( Q \), \( I(Q) \) is controlled by distances over which polymers are rod-like rather than flexible, and for \( 1/Q \sim l_p \), we expect a crossover to an asymptotic \( Q^{-1} \)-depend-
ence for \( I(Q) \) which is typical for locally cylindrical structures. At still larger \( Q \) values, the finite cross-sectional radius of the polymer can be studied [7][18][19].

Fig. 5 shows that these different regimes can indeed be observed for lecithin reverse micelles [20]. We for example clearly see the dramatic micellar growth induced by the addition of only 0.5 molecules of water per lecithin molecule at low \( Q \), whereas the flexibility and local packing remains unchanged. The results from our scattering experiments do permit us thus to study individual structural properties such as overall size, flexibility or local packing of the reverse micelles in solution, and we can directly and quantitatively confirm the postulated model of polymer-like flexible aggregates.

Micellar Growth, Intermicellar Interactions, and Transient Network Formation

It has previously been shown for a number of aqueous surfactant solutions that it is possible to find conditions where the micelles grow dramatically with increasing surfactant concentration into giant and flexible rodlike aggregates. These worm-like micelles can then entangle and form a transient network above a crossover concentration \( \Phi^\star \) with static properties that are comparable to those of semidilute solutions of flexible polymers. It was demonstrated that scaling theory for polymers could successfully be applied to these semidilute solutions, and that a number of experimentally accessible quantities such as the osmotic compressibility \( (\partial P/\partial \Phi)^{-1} \), the static correlation length \( \xi \), directly obey the same simple universal scaling laws as do classical polymers [3]. However, it was also clearly shown that the understanding of the concentration dependence of dynamic properties was much more complicated due to the transient nature of the aggregates. It was found that dynamic quantities such as the hydrodynamic correlation length \( \xi_h \), which is measured on a time scale much shorter than \( \tau_m \), again closely follow the behavior of classical polymers. However, dynamic properties on long characteristic time scales such as the micellar long-time self diffusion coefficient \( D_0 \) or the zero shear viscosity \( \eta \) exhibit a behavior which is dramatically different from those found for classical polymers, and are not yet fully and quantitatively understood [3][10][21][22].

One of the major difficulties in a quantitative understanding of the static and dynamic properties of equilibrium polymers comes from the explicit dependence of \( D_0 \) or \( \eta \) on the molecular-weight distribution. Since micelles have a concentration-dependent equilibrium molecular weight distribution \( n(M) \) with an average \( M_w \), which is believed to follow a power law form \( M_w \sim \Phi^{a} \), this leads to an additional contribution to the \( \Phi \)-dependence of \( D_0 \) and \( \eta \) [3]. A quantitative interpretation of the experimental data would thus require an independent determination of \( a \), which is difficult to achieve. Experimental techniques for molecular-weight determinations in polymer solutions such as light scattering or osmotic pressure measurements always contain contributions both from the molecular-weight distribution as well as from intermolecular interaction effects. Therefore, unambiguous information on \( M_w \) is much more difficult to obtain for equilibrium polymers, since most systems form giant worm-like micelles even at concentrations close to the critical micelle concentration, the cmc. This makes a deconvolution of contributions from the size distribution and intermicellar interactions very difficult.

We can for example use dynamic light scattering (DLS) in order to illustrate the different effects encountered in experiments with equilibrium polymers. The basis for a dynamic (or quasielastic) light scattering experiment is schematically shown in Fig. 4B. The continuous fluctuations in the number of molecules per volume element due to Brownian motion result in fluctuations in the light-scattering intensity with time, which are superimposed on a background of scattering (i.e., \( <I(Q)> \) measured in the time-averaged static light scattering experiment) which arises from the fact that at any instant the particle concentration is likely to be different in the different volume elements (see Fig. 4B). For dilute particle suspensions, the kinetics of these intensity fluctuations will depend on the size (diffusion coefficient) of the particles: small and rapidly diffusing particles will produce rapid fluctuations, and large and slowly moving particles will cause slow fluctuations in the scattering intensity. At higher particle concentrations, we also have to

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**Fig. 5.** Plot of scattering intensity \( I(Q) \) vs. scattering vector \( Q \) for solutions of soybean lecithin in deuterated isooctane \((w_0 = 2.0 \text{ and } w_0 = 2.5) \) at \( \Phi = 0.0036 \). Data shown are obtained from light and neutron scattering experiments. Also indicated are the regimes/length scales where a different characteristic \( Q \) dependence can be observed (see text for details).
take interparticle interactions into account [16].

To understand the results obtained in measurements with polymerlike micellar solutions, we can first look at the existing knowledge from polymer theory, which is based on DLS experiments with synthetic polymers. At \( Q \cdot R_g << 1 \), the dynamics of concentration fluctuations examined by DLS are dominated by translational diffusion of the polymer coils in the dilute regime \((\Phi < \Phi^*)\), and we can determine a hydrodynamic correlation length \( \xi_h \). For low volume fractions \( \Phi \to 0 \), \( \xi_h \) corresponds to the hydrodynamic radius \( R_h \) of the polymer coil (i.e., a measure of the size of the polymer), which increases with increasing molecular weight according to a power law of the form \( R_h \sim M^v \), where \( v = 0.5 \) for theta solvents and \( v = 0.6 \) for good solvents, respectively. At higher concentrations \( \Phi \gg \Phi^* \), \( \xi_h \) does not depend on the individual micellar size anymore, but is related to the 'mesh size' of the entanglement network which decreases strongly with increasing concentration [23-25].

Typical results for the concentration and \( w_o \) dependence of the hydrodynamic correlation length \( \xi_h \) are obtained with DLS experiments with lecithin/cyclohexane solutions are shown in Fig. 6 (For details, see [25]). At low volume fractions \( \Phi \lesssim 6 \cdot 10^{-3} \), we observe a very pronounced increase of \( \xi_h \) with increasing \( w_o \) which primarily reflects the strong water-induced micellar growth from relatively small reverse micelles with \( \xi_h = 30 \) \( \text{Å} \) at \( w_o = 2.0 \) to giant polymer-like particles with \( \xi_h = 400-700 \) \( \text{Å} \) at \( w_o \geq 6.0 \). At these low values of \( \Phi \), we also see that \( \xi_h \) increases with increasing concentration, which indicates a concentration dependence of the micellar size distribution as predicted by the theoretical models for surfactant self-assembly. However, the concentration-dependent micellar growth is only visible at low values of \( \Phi \) and \( w_o \) and becomes increasingly masked by intermicellar interactions as the solution approaches the overlap threshold \( \Phi^* \). At volume fractions \( \Phi \gtrsim 6 \cdot 10^{-3} \), \( \xi_h \) first reaches a maximum and becomes more and more independent of \( w_o \). At even higher values of \( \Phi \), \( \xi_h \) decreases with increasing \( \Phi \), and the \( \Phi \) dependence can now be described by a power law of the form \( \xi_h \sim \Phi^{s} \), where \( s = 0.65 \pm 0.05 \) for all values of \( w_o \). The crossover to the power law dependence provides us with an estimate of \( \Phi^* \) as a function of \( w_o \), and we see from Fig. 6 that \( \Phi^* \) decreases with increasing \( w_o \). This is again in agreement with polymer theory, since \( \Phi^* \) should be proportional to \( L^{-1/2} \), where the contour length \( L \) is thought to increase with increasing \( w_o \) [15].

It is thus clear that we only have a very small concentration regime where we can obtain the composition dependence of the micellar size distribution in a straightforward way, and this is certainly not enough in order to determine the exponent \( s \) in the micellar growth law \( \xi_h \sim \Phi^s \) with sufficient accuracy. However, we have recently been able to show that one can success-

Fig. 6. The hydrodynamic correlation length, \( \xi_h \) as a function of volume fraction, \( \Phi \), and water to lecithin molar ratio, \( w_o \). Data sets for \( \Phi = \) const. (path 1 in Fig. 3) and \( w_o = \) const. (path 2) are connected by dashed and solid lines, respectively. The surface marked as \( \Phi^* \) indicates the crossover from the dilute to the semidilute regime.
fully attack this problem by directly applying the results from conformation space renormalization group theory for semidilute polymer solutions to equilibrium polymers such as worm-like micelles or microemulsions, if one takes into account the fact that their size distribution is concentration-dependent [26][27]. Based on the postulated analogy between polymer-like micelles and classical polymers, it was thus possible to go well beyond a simple confirmation of scaling laws. The theoretical treatment did provide us with explicit information on the concentration dependence of both the micellar size distribution and the intermicellar interaction effects. Moreover, we were able to obtain detailed information on the so-called static and dynamic structure factor of polymer-like lecithin reverse micelles, which contains essentially all the important static and dynamic information on the structural properties of these systems.

Conclusions

The above presented data demonstrate the usefulness of an application of polymer theory to complex surfactant solutions. We have seen that it was possible to develop a model for the micellar structure and test it successfully by making analogies to dilute and semidilute polymer solutions. The results from neutron-scattering experiments with lecithin w/o microemulsions did permit us to directly study individual structural properties of the reverse micelles present in these solutions, and we could confirm the postulated model of flexible rodlike aggregates. Furthermore, our dynamic and static light-scattering measurements showed that lecithin reverse micellar solutions at higher surfactant concentrations, where intermicellar interactions dominate, have properties which exhibit the same universal scaling laws as previously found for polymers. Moreover, using the results from renormalization group theory for semidilute polymer solutions, we could even extract quantitative information on the concentration dependence of the micellar size distribution.

However, these examples also show the limits of such an approach, and the importance of a constant re-evaluation of the applicability and validity of such concepts. This is particularly obvious when comparing Fig. 2, 5, and 6. The results from scattering experiments, which characterize solution properties on a very short time scale, are in perfect agreement with polymer theory. They indicate that the micellar size increases first dramatically with increasing \( w_o \) before it reaches a plateau at high values of \( w_o \). However, a quite different behavior is seen when performing rheological experiments, which characterize solution properties on a long time scale. The data shown in Fig. 2 is at first in agreement with the strong increase of the micellar size with increasing \( w_o \), but then reaches a maximum and decreases steeply at still higher values of \( w_o \). This shows the limits of a straightforward application of polymer theory to surfactant solutions and indicates that the finite lifetime and the availability of other relaxation mechanisms in these systems must be taken into account. The ‘equilibrium polymer model’, which represents a first attempt to include the dynamic nature of micellar aggregates in a theoretical description of these solutions, shows how concepts from polymer science can be modified and extended to other systems [3][14][21].

Although not discussed explicitly in this article, such an interdisciplinary approach is of course not restricted to viscoelastic micellar solutions, but could be considered more generally in a variety of colloidal systems. Another well-documented example can be found in the use of inorganic colloids as precursors for ceramic materials, where Schafer has demonstrated how one can use polymer theory and fractal analysis in conjunction with kinetic growth models and small-angle scattering techniques to characterize the structure of these precursor solutions and to eventually tailor the properties of the resulting ceramic materials [28].

Colloid and surfactant sciences appear to undergo a ‘renaissance’ due to the increasing interest in using ultrafine particles for a wide variety of applications in materials science, pharmacy or biotechnology. It is thus my belief that an interdisciplinary approach, in which modern theoretical concepts are borrowed from scientific disciplines such as polymer physics or fractal geometry and included in the traditional theoretical treatment of colloids, can be very helpful for a variety of basic and applied research programs in scientific fields as diverse as biophysics or materials science.

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