The static and dynamic structure factor of polymer-like lecithin reverse micelles

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Abstract. — We report a detailed analysis of the static and dynamic structure factor of polymer-like lecithin reverse micelles. We previously demonstrated that one can directly apply the results from conformation space renormalization group theory for semi-dilute 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 [1]. The present study confirms these findings and shows that this approach can be extended to the \(Q\)- and \(c\)-dependence of the static \(S(Q)\) and dynamic \(S(Q, \tau)\) structure factor.

Introduction.

Surfactant systems in which giant worm-like micelles are formed have frequently been used as model systems for an experimental investigation of the static and dynamic properties of « equilibrium polymers », where the term equilibrium (or « living ») polymer is used for linear macromolecules that can break and recombine [2-9]. Therefore equilibrium polymers are transient structures with a relatively short live time \(\tau_b\), and they exhibit a wealth of interesting dynamic properties on time scales both long or short compared to \(\tau_b\). Due to the finite live time of the particles, the molecular weight distribution of equilibrium polymers such as micelles is not constant but in thermal equilibrium and thus depends strongly on surfactant concentration and temperature [2]. This is quite different from « classical » polymers such as polystyrene, where the molecular weight distribution is quenched after the preparation procedure.

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 cross-over concentration \(c^*\) 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, \((\partial \Pi / \partial c)^{-1}\), or the static correlation length, \(\xi_s\), directly obey the same simple universal scaling
laws as do classical polymers. 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, \( \xi_b \), which is measured on a time scale much shorter than \( \tau_b \), 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, \( D_s \), or the zero shear viscosity, \( \eta_s \), exhibit a behavior which is dramatically different from those found for classical polymers, and are not yet fully and quantitatively understood [2, 8, 10, 11].

One of the major difficulties in a quantitative understanding of the dynamic properties of equilibrium polymers comes from the explicit dependence of \( D_s \) or \( \eta_s \) on the molecular weight distribution. Since micelles have a concentration-dependent equilibrium molecular weight distribution \( n(N) \) with an average \( \bar{N} \) which is believed to follow a power law form \( \bar{N} \sim c^x \), this leads to an additional contribution to the \( c \)-dependence of \( D_s \) and \( \eta_s \) [2]. A quantitative interpretation of the experimental data would thus require an independent determination of \( x \), 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, i.e., from the static structure factor \( S(0) \). In classical polymer solutions \( \bar{N} \) can be obtained from a concentration dependence at low values of \( c \), i.e., in the virial regime. However, unambiguous information on \( \bar{N} \) 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 \( n(N) \) and \( S(0) \) very difficult, especially because simple virial expansions of \( S(0) \) are not valid anymore at the values of \( c/c^* \) which can be achieved for most model systems investigated so far.

We have recently shown that one can successfully attack this problem by directly applying the results from conformation space renormalization group theory for semi-dilute 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 [1]. When compared to scaling theory, renormalization group theory has the clear advantage that prefactors are derived for the power laws in the limit \( c \gg c^* \), and that the transition from the dilute to the semi-dilute regime is described as well. We have tested this approach using lecithin water-in-oil (w/o) microemulsions as a model system for equilibrium polymers. This system is quite unique in the sense that it shows a characteristic sphere-to-rod transition normally observed in aqueous solutions only. The addition of trace amounts of water to lecithin reverse micellar solutions induces one-dimensional growth and the formation of giant flexible cylindrical aggregates. For lecithin/cyclohexane solutions at a given surfactant concentration, the micellar size increases with increasing water to surfactant molar ratio, \( w_0 \), and reaches a plateau at \( w_0 \approx 14 \). At \( w_0 \approx 10 \), the resulting micellar particles are extremely large even at very low surfactant concentrations. Based on a systematic static light scattering study of lecithin/cyclohexane solutions, we were able to obtain detailed and quantitative information on both the micellar size distribution and the intermicellar interaction effects, i.e., on the weight average molecular weight, \( M_w \), and on the static structure factor, \( S(0) \).

Here we now extend our investigations to \( Q \neq 0 \) and present a detailed study of the static \( (S(Q)) \) and dynamic \( (S(Q, t)) \) structure factor as a function of the surfactant concentration using static (SLS) and dynamic (DLS) light scattering. We now use our new data as a further quantitative test of our previous findings, and we shall show that within this theoretical framework a self consistent interpretation of the SLS and DLS results is possible and that we
can obtain information on the micellar size, structure and intermicellar interactions over a wide range of concentrations.

Materials and methods.

Soybean lecithin was obtained from Lucas Meyer (Epikuron 200) and used without further purification. Cyclohexane and iso-octane (spectroscopic grade) were purchased from Fluka. Samples were prepared as described previously [12, 13].

Static and dynamic light scattering measurements were performed at a temperature of 25.0 ± 0.1 °C. Approximately 1 ml of solution was transferred into the cylindrical scattering cell (10 mm inner diameter). The scattering cell was then sealed and centrifuged between 20 and 420 minutes at approximately 5000 g and 25 °C in order to remove dust particles from the scattering volume. Measurements were made with a Malvern 4700 PS/MW spectrometer, equipped with an argon ion laser (Coherent, Innova 200-10, λ₀ = 488 nm), a digital correlator (128 points) and a computer controlled and stepping motor driven variable angle detection system.

Static light scattering (SLS) experiments were performed at 37 different angles (15° < θ < 150°) for low concentrations and at 13 different angles (30° < θ < 150°) for high concentrations, and 90 individual measurements were taken and averaged for each angle. The data was then corrected for background (cell and solvent) scattering and converted into absolute scattering intensities ΔR(0) (i.e. «excess Rayleigh ratios») using toluene as a reference standard. The excess Rayleigh ratio of the sample was calculated using

\[
\Delta R(\theta) = \frac{\Delta \langle I(\theta) \rangle}{\langle I_{ref}(\theta) \rangle} \cdot R_{ref}(\theta) \cdot \left( \frac{n}{n_{ref}} \right)^2
\]

(1)

where \(\Delta \langle I(\theta) \rangle\) and \(\langle I_{ref}(\theta) \rangle\) are the average excess scattering intensity of the solution and the average scattering intensity of the reference solvent toluene, \(R_{ref}(\theta) = 39.6 \times 10^{-4} \text{ m}^{-1}\) is the Rayleigh ratio of toluene, and \(n\) and \(n_{ref}\) are the index of refraction of the solution and the reference solvent, respectively [14]. Plots of \(Kc/\Delta R(\theta)\) versus \(Q^2/3\) were extrapolated to \(Q = 0\) to give intercepts \(Kc/\Delta R(0)\), where \(K = 4\pi^2 n^2 (dn/dc)^2/(N_A \cdot \lambda_0^4)\), \(dn/dc\) is the refractive index increment (values of \(dn/dc\) for soybean lecithin in cyclohexane as a function of \(\omega_0\) are given in reference [12]), \(|Q| = (4\pi n/\lambda_0) \sin (\theta/2)\) is the scattering vector, and \(c\) is the concentration of surfactant plus water, respectively. The static correlation length \(\xi_s\) was determined from the intercept and slope of the plot \(Kc/\Delta R(\theta)\) versus \(Q^2/3\) using a Lorentzian scattering law of the form

\[
\frac{Kc}{\Delta R(\theta)} = \frac{1}{M_{app}} [1 + Q^2 \xi_s^2].
\]

(2)

For samples with high values of \(\omega_0\) and low values of \(c\), i.e., for very large micelles in dilute solutions where \(\xi_s\) is large, only the linear part of the data at low \(Q\) was included in the fit.

Dynamic light scattering (DLS) experiments were performed at 37 scattering angles (15° < θ < 150°) at low concentrations and 7 scattering angles (30° < θ < 150°) at high concentrations, and between 4 to 20 intensity autocorrelation functions were individually analysed using a second order cumulant analysis [15]. The results were then averaged for each value of \(Q\), and an apparent cooperative diffusion coefficient \(D_{app} = \lim_{Q \to 0} \langle \Gamma \rangle /Q^2\) was
determined. From $D_{app}$ a hydrodynamic correlation length $\xi_h$ was calculated using

$$\xi_h = \frac{k_B T}{6 \pi \eta_0 D_{app}}$$

(3)

where $\eta_0$ is the viscosity of the solvent [16].

Results and discussion.

Typical examples for the $Q$-dependence of the scattering intensity $I(Q)$ and the apparent diffusion coefficient $\langle I \rangle/Q^2$ as obtained from lecithin/cyclohexane reverse micellar solutions at $c < c^*$ and $c > c^*$ are given in figures 1 and 2 for $w_o = 14$ and $c = 5.11 \text{ mg/ml}$ and $c = 30.7 \text{ mg/ml}$, respectively. In the limit of $c \to 0$, $\xi_s$ corresponds to $R_g/\sqrt{3}$, where $R_g = \langle R_g^2 \rangle_z^{1/2}$ and $\langle R_g^2 \rangle_z$ is the $z$-average mean square radius of gyration of the particles. At $c < c^*$, scattering experiments at low $Q$ values thus primarily reflect the water- and concentration-induced growth and the giant size of the micellar aggregates. The resulting large static correlation length results in a very pronounced angular dependence of the intensity, and deviations from a simple Lorentzian scattering law (Eq. (2)) are clearly visible at higher values of $Q$. An analysis of the low $Q$ part of the intensity data shown in figure 1 for $c = 5.11 \text{ mg/ml}$ yields $\xi_s = 659 \text{ Å}$. This value of $\xi_s$ is much larger than the value of the persistence length $l_p = 110 \pm 30 \text{ Å}$ previously measured with small angle neutron scattering.

![Graph](image)

Fig. 1. — $I(Q)/I(0)$ as a function of $Q$ for lecithin/cyclohexane w/o microemulsions at $w_o = 14$ and $c = 5.11 \text{ mg/ml}$ (○) and $c = 30.7 \text{ mg/ml}$ (■). Also shown are theoretical curves for $\xi_s = 659 \text{ Å}$ and a Lorentzian scattering law $I(Q)/I(0) = 1/[1 + Q^2 \xi_s^2]$ (Eq. (2)) (dotted line), polydisperse worm-like chains with $l_p = 110 \text{ Å}$ (dashed line) or polydisperse semi-flexible chains with excluded volume interactions [19] (solid line). See text for details.
At $Q \cdot \xi \gg 1$, scattering experiments probe the interior of the micelles (or the « blob » if $c \gg c^*$) and the static light scattering experiment provides us thus with information on the chain conformation. For $Q \cdot \xi, \gg 1$ and $Q \cdot \ell_p \ll 1$, where $\ell_p$ is the persistence length, $I(Q)$ should reach an asymptotic power law of the form $I(Q) \sim Q^{-2}$ for Gaussian chains and $I(Q) \sim Q^{-5/3}$ for « perturbed » chains with excluded volume effects. However, the asymptotic limit can not be reached with light scattering for our system due to the restricted $Q$-range. Nevertheless we clearly see from figure 1 that the data at is in clear disagreement with the form factor for polydisperse (Gaussian) worm-like chains shown as the dashed line, but in quantitative agreement with theoretical calculations based on chain statistics appropriate for excluded volume effects (Fig. 1, solid line) [17-19].

Figure 2 shows the $Q$-dependence of $\langle \Gamma \rangle /Q^2$, where $\langle \Gamma \rangle$ is the first cumulant obtained from a second order cumulant analysis of the intensity autocorrelation function, for the same sample [20]. We find two characteristic regimes for the $Q$-dependence of $\langle \Gamma \rangle /Q^2$. At $Q \cdot \xi \ll 1$, the dynamics of concentration fluctuations examined by DLS are dominated by translational diffusion of the polymer coil in the dilute regime ($c < c^*$), and the relevant relaxation process for concentration fluctuations is diffusive, i.e., characterized by $\langle \Gamma(Q) \rangle \sim Q^2$. We can define an apparent diffusion coefficient $D_{\text{app}} = \lim_{Q \rightarrow 0} \langle \Gamma(Q) \rangle /Q^2$, from which we can then calculate a hydrodynamic correlation length $\xi_h$ using equation (3). For $c \rightarrow 0$, $\xi_h$ corresponds to the hydrodynamic radius $R_h$ of the polymer coil, which increases with increasing molecular weight according to a power law of the form $R_h \sim M^\nu$, where $\nu = 0.5$ for theta solvents and $\nu = 0.6$ for good solvents, respectively. However, it is important to point out that for polymers the experimentally observed excluded volume exponent is generally smaller than the theoretical prediction [21, 22]. For polydisperse solutions, $R_h = \langle 1/R_h \rangle^{-1}$. The dynamic light scattering experiments also confirms the water-induced formation of giant aggregates for $w_0 = 14$ and $c = 5.11 \text{ mg/ml}$. An extrapolation $Q \rightarrow 0$ leads to a value for the hydrodynamic correlation length of $\xi_h = 605 \text{ Å}$. At $Q \cdot \xi_h \ll 1$, the relatively weak $Q$-dependence primarily reflects the polydispersity of the samples.

![Fig. 2. — $\langle \Gamma(Q) \rangle /Q^2$ as a function of $Q$ for lecithin/cyclohexane w/0 microemulsions at $w_0 = 14$ and $c = 5.11 \text{ mg/ml}$ (O) and $c = 30.7 \text{ mg/ml}$ (●).](image-url)
For $Q \cdot \xi \gg 1$ we primarily see the internal motion of the polymer chains. The dynamic structure factor is then characterized by a decay rate $\langle \Gamma(Q) \rangle \sim Q^3$ in the so-called Zimm model. As shown in figure 1b, for $Q \cdot \xi_h \gg 0.6$ we do observe a very pronounced $Q$-dependence, and the plot of $\langle \Gamma \rangle/Q^2$ versus $Q$ appears to be linear. This indicates that $\langle \Gamma \rangle \sim Q^3$, in agreement with the predictions for the contribution of internal chain dynamics to the intensity autocorrelation function [22]. A similar behavior has already been observed for aqueous ionic micellar solutions [6].

At higher concentrations $c \gg c^*$, $\xi_s$ and $\xi_h$ do not depend on the individual micellar size anymore, but are related to the « mesh size » of the entanglement network which decreases strongly with increasing concentration. Under these conditions, $I(Q)$ is now well described by equation (2) over the entire $Q$-range accessible in our experiments ($4.8 \times 10^{-4}$ Å$^{-1} \leq Q \leq 3.5 \times 10^{-3}$ Å$^{-1}$), and $\langle \Gamma \rangle/Q^2$ is almost independent of $Q$ over a much wider range of $Q$-values as expected for an entanglement network. An example for the scattering data obtained for $c \gg c^*$ is shown in figures 1 and 2 for $w_0 = 14$ and $c = 30.7$ mg/ml. For this sample we now find $\xi_s = 210$ Å and $\xi_h = 230$ Å, which can be compared to $\xi_s = 659$ and $\xi_h = 605$ for $w_0 = 14.0$ and $c = 5.11$ mg/ml.

The results from the SLS and DLS measurements are summarized in figures 3a and b, where $\xi_s$ and $\xi_h$ are plotted as a function of $w_0$ and $c$. We see that the data at low concentrations primarily reflect the strong water-induced micellar growth and the concentration dependence of the micellar size distribution. At $w_0 \gg 10$, the water-induced micellar growth is particularly pronounced, and the resulting microemulsion particles are extremely large even at very low values of $c$. Both $\xi_s$ and $\xi_h$ then reach a maximum at $c = c^*$ and decrease at higher values of $c$ with a power law of the form $\xi \sim c^{-x}$, where $x = 0.65 \pm 0.05$ for $\xi_h$ and $x = 0.7 \pm 0.1$ for $\xi_s$ [12]. For $c \gg c^*$, both $\xi_s$ and $\xi_h$ become independent of $w_0$.

We can now try to use the data shown in figure 3 for a quantitative test of our previous attempt to characterize the dependence of $M_w$ on $c$ and $w_0$, which was based on the application of conformation space renormalization group theory for semi-dilute polymer solutions to static light scattering data from lecithin-cyclohexane solutions [1]. The basis for this analysis was the connection between the scattered intensity and the osmotic compressibility. In the limit of $Q \to 0$, $(\partial H/\partial c)^{-1}$ is related to the static structure factor $S(Q)$ by the relation [23].

$$S(0) = \frac{N_A}{M} k_B T \left( \frac{\partial H}{\partial c} \right)^{-1}$$  \hspace{1cm} (4)

which together with equation (2) yields

$$\frac{\Delta R(0)}{Kc} = M_w S(0) = M_{app}$$  \hspace{1cm} (5)

$S(0)$ for polymers can be written as a function of a reduced concentration

$$X = a (c/c^*) \sim c A_2 M_w,$$

where $a$ is a constant and $A_2$ is the (weight-average) osmotic second virial coefficient [24]. An explicit functional form for $S(0) = f(X)$ has for example been calculated by Ohta et al. using the renormalization group method, and good agreement between theory and light scattering data was found for classical polymers with different values of $M_w$ for an extended range of concentrations $10^{-2} < X < 10^2$, where $X$ is given for polydisperse polymers by [25]:

$$X = \frac{A_2 c M_w}{\frac{9}{16} \ln \frac{M_w}{M_n}}$$  \hspace{1cm} (6)
Fig. 3. — $\xi_s(A)$ and $\xi_h(B)$ as a function of the concentration $c$ of the dispersed phase for lecithin/cyclohexane w/o microemulsions at different values of $w_o$. The dashed lines connect points with equal values of $w_o$ and are drawn as a guide to the eye only. The solid line corresponds to a power law of the form $\xi \sim c^{-x}$, where $x = 0.7$ for $\xi_s$ and $x = 0.65$ for $\xi_h$, respectively: (△): $w_o = 6.0$; (□): $w_o = 8.0$; (○): $w_o = 12.0$; (●): $w_o = 14.0$.

A major problem in a direct application of polymer theory to our systems comes from the concentration and $w_o$ dependence of the micellar size distribution. Since both $A_2$ and $c^*$ thus depend on $w_o$ and $c$, we incorporated a power law of the form

$$M_w = B_1 \cdot c^x$$

(7)
for the $c$-dependence of the average particle size and a scaling law of the form $R_g \sim M^\alpha$ in the relations for $A_2$, given by

$$A_2 \approx 4 \pi^{3/2} N_A \frac{(R_g^2)^{3/2}}{M_w^2} \Psi$$

(8)

and $c^*$, which can be approximated by

$$c^* \approx \frac{3M}{4\pi N_A R_g^3}.$$  

(9)

This leads to $A_2 \sim c^{\alpha (3 \nu - 2)}$, and the reduced concentration $X$ is then given by

$$X = 2.10 B_1^{(3 \nu - 1)} B_2 \exp[\alpha (3 \nu - 1) + 1]$$

(10)

Equations (7) and (10) allowed us to explicitly take into account the «equilibrium polymer» features in the renormalization group treatment [1].

We were then able to construct a universal curve $(M_w/R)(\partial H/\partial c)$ versus a reduced concentration $X \sim c/c^*$ from the experimentally determined values of the osmotic compressibility if a power law of the form of equation (7) was used for the $c$-dependence of the average particle size [1]. While the exponents $\nu = 0.57 \pm 0.03$ and $\alpha = 1.2 \pm 0.3$ and the parameter $B_2 = (0.8 \pm 0.3) \times 10^{-6}$ cm$^3$ mol$^{-1}$ g$^{-3} \nu$ were found to be independent of $w_0$, the values of $B_1$ which are summarized again in Table I reflect the pronounced water-induced micellar growth [1]. From theoretical calculations using mean field models, $\alpha$ varies between $\alpha = 1/2$ based either on law of mass-action or Flory-Huggins lattice model calculations, and $\alpha = 0.6$ when using a scaling theory approach for semi-dilute solutions [2]. Therefore $\alpha = 1.2$ appears to be very large when compared to the theoretical predictions from mean field models and scaling arguments. However, preliminary results from Kerr effect measurements [26] with lecithin/cyclohexane w/o microemulsions also indicate a power law dependence of the particle size on concentration with an exponent which is of the same order as obtained in the previous light scattering study.

Table I.— $w_0$-dependence of constant $B_1(w_0)$ in relation $M_w = B_1 \cdot c^\alpha$ determined from SLS experiments (from Ref. [1]).

<table>
<thead>
<tr>
<th>$w_0$</th>
<th>$B_1$ [g$^{1-\alpha}$/mol$^{1-\alpha}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>$4.5 \times 10^4$</td>
</tr>
<tr>
<td>6.0</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>8.0</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>12.0</td>
<td>$7.6 \times 10^6$</td>
</tr>
<tr>
<td>14.0</td>
<td>$1.0 \times 10^7$</td>
</tr>
</tbody>
</table>

We thus have a complete description of the $w_0$- and $c$-dependence of $M_w$ and $X$. In a next step we can now use this information and test if a self-consistent interpretation of the SLS and DLS results is possible within this theoretical framework. The theoretical basis for this is the dependence of $\xi_R/R_{g,0}$ on the overlap parameter $X$ for polymers in good solvents, where
$R_{g,o}$ is the radius of gyration which the polymer would have in the limit $c \to 0$, which can be written as

$$\xi_s/R_{g,o} = F_s(X).$$  \hspace{1cm} (11)$$

An explicit functional for $F(X)$ has been calculated with renormalization group methods by Nakanishi and Ohta [27]. Experimentally, one does indeed find a universal curve for $\xi_s/R_{g,o}$ versus $X$ for synthetic polymers, which shows no systematic dependence on the molecular weight or the solvent. However, while the theoretical $F_{s,RG}(X)$ based on the renormalization group theory calculations by Nakanishi and Ohta reproduces the correct shape of the experimental master curve, the calculated prefactor is clearly too low [21]. Instead of using the theoretical form of $F_{s,RG}(X)$ for our purposes only, we have also extracted the experimentally observed $F_{s,exp}(X)$ from reference [21]. Both $F_{s,RG}(X)$ and $F_{s,exp}(X)$ are reproduced in figure 4a.

We can now see if we are able to construct such a master curve from the data shown in figure 3a. Therefore we need to calculate $R_{g,o}(w_0, c)$ for all values of $w_0$ and $c$ investigated. This can be done as follows: we can calculate $M_w(w_0, c)$ and $X(w_0, c)$ for all samples investigated in the current study without any adjustable parameter using the results from the previous renormalization group analysis summarized above (Eqs. (7, 10) and Tab. I). From $M_w(w_0, c)$, we can then calculate the weight average contour length $L_w(w_0, c)$. This can also be done without any adjustable parameters since we know the local packing and the mass per unit length $M_w$ of the micelles from previous SANS measurements [12, 28, 29]. In a next step we can then determine the ideal single coil values of $R_{g,o}(L_w(w_0, c), \ell_p)$ from equation (12) [17, 30, 31]

$$\langle R_g(L)^2 \rangle = \frac{(2 \ell_p)^2 \left( \frac{L}{2 \ell_p} \right)^{1+\varepsilon}}{6 + 5 \varepsilon + \varepsilon^2}$$  \hspace{1cm} (12)

where $\varepsilon = 0.176$, and (13)

$$R_{g,o} = \left[ \int_0^\infty G(L, 0) \cdot \langle R_g(L)^2 \rangle \ dL \right]^{1/2}$$  \hspace{1cm} (13)

and using $\ell_p = 110 \text{ Å}$ [28] and a Schulz-Flory distribution for the size distribution $n(L)$. The intensity distribution function for a given value of $L$ at $Q \to 0$, $G(L, 0)$, as used in equation (13) is described by equation (14), [32]

$$G(L, 0) = \frac{n(L) \cdot L^2}{\int_0^\infty n(L) \cdot L^2 \ dL}$$  \hspace{1cm} (14)

The choice of the size distribution is both supported by previous light and neutron scattering experiments in dilute solutions [12] as well as based on theoretical grounds, since it matches the predictions of the micellar growth model, i.e., $n(M) \sim \exp(-M/M_w)$ and $M_w/M_n \approx 2$, where $M_n$ is the number-average molecular weight [2].

We now have the theoretical values of $R_{g,o}(w_0, c)$ for all values of $w_0$ and $c$ investigated, and we can obtain the corresponding ratios of $\xi_s/R_{g,o}$ for all the measured values of $\xi_s(w_0, c)$ shown in figure 3a. These ratios are plotted as a function of $X(w_0, c)$ in figure 4a, and we see at once that the different individual data sets in figure 3a which exhibit a very
pronounced $w_0$ and $c$ dependence collapse onto a single "universal" master curve. Our values of $\xi_s/R_{g,0}$ closely follow the function $F_{\text{s, exp}}(X)$ previously found for synthetic polymers except for the lowest values of $X$, where the polymer data also exhibits the largest scatter. Figure 4a
shows that we can not only interpret the measured osmotic compressibility with a combination of \( S(0) \) given by renormalization group theory and a \( c \)- and \( w_0 \)-dependent micellar size distribution, as successfully demonstrated previously [1], but that this approach can be extended to a quantitative description of the full scattering curve \( I(Q) \). It demonstrates that the \( Q \)-dependence of \( S(Q) \) measured for polymer-like lecithin reverse micelles is fully consistent with the behavior of synthetic polymers. It is important to point out that, once we have calculated the set of constants \( B_1(w_0) \) and \( B_2 \), the construction of the plot of \( \xi_v(w_0, c)R_{g,\circ}(w_0, c) \) versus \( X(w_0, c) \) is performed with no adjustable parameters, and that we are thus able to predict the \( Q \)-dependence of \( I(Q) \) on absolute scale.

In a next step we can now test if the same approach can be applied to the dynamic structure factor also. Renormalization group treatment for dynamic properties such as \( \xi_v \) has not been performed as extensively as for static properties such as \( \xi_v \) or \( (\partial \Pi/\partial c)^{-1} \), but there are calculations available such as the one by Shiwa which predicts that

\[
\xi_v/R_{h,\circ} = F_h(X)
\]

where \( R_{h,\circ} \) is the hydrodynamic radius of the polymer coil in the limit \( c \to 0 \) [33]. While earlier measurements by Wiltzius et al. [34] did suggest that a plot of \( \xi_v/R_{h,\circ} \) versus \( X \) does not yield a universal curve and that \( k_D \cdot c \) should be used instead, where \( k_D \) is defined by \( D_{\text{app}} = D_{c,\circ} \cdot (1 + k_D \cdot c + \cdots) \), a careful analysis of the large data set available for polystyrene as the most widely examined (semi)-flexible polymer showed that plotting \( \xi_v/R_{h,\circ} \) versus \( X \) does indeed yield a universal curve [21]. However, the calculated prefactor is again too small, and we have thus plotted in figure 4b the theoretical curve \( F_{h,\text{RGT}}(X) \) from renormalization group theory as well as the experimentally observed master curve \( F_{h,\text{exp}}(X) \) which we extracted from the data given in reference [21].

A major difficulty in the construction of an experimental master curve using the DLS data from lecithin/cyclohexane solutions in figure 3b arises due to the lack of an appropriate theoretical relation \( R_{h,\circ}(L) = f(L, \ell_p) \) for semi-flexible chains with excluded volume effects (analogous to equation (12) for \( R_{g,\circ} \)) and the experimental observation that \( R_h \) reaches the asymptotic regime \( (R_h \sim M^\nu, \nu = 0.588) \) much more slowly than \( R_g \). We have therefore used an empirical approach \( R_{h,\circ} = C_{\ell_p} \cdot M^{0.55} \) as found for synthetic polymers in good solvents [21, 35], in which we write

\[
R_{h,\circ}(L, \ell_p) = R_{h,\text{wc}}(L, \ell_p) \cdot \left( \frac{L}{2 \ell_p} \right)^{0.05}
\]

where \( R_{h,\text{wc}} \) is the hydrodynamic radius of a worm-like chain with contour length \( L \) and persistence length \( \ell_p \) as given by equations (49-52) in reference [36]. The additional term \( (L/2 \ell_p)^{0.05} \) represents an « ad hoc » correction for the influence of excluded volume effects on the molecular weight dependence of \( R_h \sim M^\nu \) and changes the scaling exponent \( \nu = 0.5 \) of (Gaussian) worm-like chains to \( \nu = 0.55 \) found experimentally for synthetic polymers in good solvents.

Using equation (16), we can now calculate the ideal single coil values \( R_{h,\circ}(w_0, c) \) from equations (14) and (17)

\[
R_{h,\circ} = \left[ \int_0^\infty \frac{1}{R_h(L, \ell_p)} G(L, 0) \, dL \right]^{-1}
\]

and calculate the corresponding ratios of \( \xi_v/R_{h,\circ} \) for values of \( w_0 \) and \( c \) investigated analogous to the procedure for the static correlation length described above. The plot of
$\xi_h(w_0, c) R_{h,o}(w_0, c)$ versus $X(w_0, c)$ is shown in figure 4B, and we see that all individual data sets from figure 3b collapse onto a single master curve. The data points for lecithin/cyclohexane solutions are in quite good agreement with the curve $F_{h, \exp}(X)$ for synthetic polymers, although the polymer curve does not extended to low enough reduced concentrations to judge the behavior at low $X$. Figure 4b thus shows that we can not only quantitatively describe the static light scattering data using the application of polymer renormalization group theory, but that this approach also works for the dynamic light scattering data.

Conclusions.

We have presented a detailed analysis of the static and dynamic structure factor of polymer-like lecithin reverse micelles. Giant micellar aggregates exist in solutions with $w_0 \approx 10$ which results in a very large static correlation length $\xi_s$ at low concentrations $c \ll c^*$, and the intensity $I(Q)$ closely follows the theoretical prediction for the $Q$-dependence of polydisperse semiflexible chains with excluded volume interactions. This provides a firm basis for the application of a power law of the form $R_g \sim M^{0.588}$ to these systems. The dynamic structure factor exhibits both contributions from centre of mass diffusion and internal chain dynamics, which result in a $Q^3$-dependence of the initial decay $\langle F(Q) \rangle$ at $Q \cdot \xi_h \gg 1$. At $c \gg c^*$, the static and dynamic correlation lengths decrease with concentration as expected for semi-dilute polymer solutions, and due to the relatively limited $Q$-range of the light scattering experiments the $Q$-dependence of the intensity $I(Q)$ reduces to a simple Lorentzian scattering law, and $\langle F(Q) \rangle / Q^2$ is practically $Q$-independent.

We previously demonstrated that one can directly apply the results from conformation space renormalization group theory for semi-dilute 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 [1]. Based on the assumption of a power law of the form $M_w \sim c^a$ for the $c$-dependence of the micellar size, we were able to construct a universal curve $(M_w/RT) (\partial \Pi / \partial c)$ versus a reduced concentration $X \sim c/c^*$ from the experimentally determined values of the osmotic compressibility. We then concluded that one can thus obtain information from static light scattering experiments on the concentration dependence of both the micellar size distribution and the intermicellar interaction effects, i.e., on the weight average molecular weight $M_w(c)$ and the static structure factor $S(0, c)$.

The present study now provides an additional independent test and shows that this approach can be extended to the $Q$- and $c$-dependence of the static ($S(Q)$) and dynamic ($S(Q, t)$) structure factor. The concentration dependence of the initial $Q$-dependence of the intensity $I(Q)$, which can be described by a correlation length $\xi_s$, and of the initial $t$-dependence of the intensity autocorrelation function $g_2(t)$, which can be described by a correlation length $\xi_h$, are in quantitative agreement with the behavior found for synthetic polymers such as polystyrene over the entire range of concentrations studied. We can construct universal master curves for the dimensionless quantities $\xi / R_{\xi,o}$ and $\xi_h / R_{h,o}$ as a function of the reduced concentration $X$ only, which provides a further successful test of the previously obtained information on the concentration and composition dependence of the micellar size distribution.

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References

[20] In our discussion of the dynamic light scattering results we shall concentrate on the $Q$-dependence of the initial decay $\langle F(Q) \rangle$ of the intensity autocorrelation function as obtained for example using a second order cumulant analysis of the data. For this quantity, theoretical expressions have been derived for various concentration and solvent regimes [22].
[26] Cavaco C., Koper G. and Schurtenberger P., to be published.