Influence of Nanoparticle Addition on the Properties of Wormlike Micellar Solutions

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The addition of positively charged, 30 nm diameter silica nanoparticles to cationic wormlike micellar solutions of cetyltrimethylammonium bromide and sodium nitrate is studied using a combination of rheology, small angle neutron scattering, dynamic light scattering, and cryo-transmission electron microscopy. The mixtures are single phase up to particle volume fractions of 1%. The addition of like-charged particles significantly increases the wormlike micelle (WLM) solution’s zero shear rate viscosity, longest relaxation time, and storage modulus. The changes are hypothesized to originate from a close association of the particles with the micellar mesh. Small angle neutron scattering measurements with contrast matching demonstrate associations between particles mitigated by the WLMs. The effective interparticle interactions measured by SANS can explain the observed phase behavior. Dynamic light scattering measurements confirm the dynamic coupling of the particles to the micellar mesh.

Introduction

Surfactant molecules self-assemble in solution above the critical micelle concentration (cmc) into micelles. In many cases, these micelles grow into long, semiflexible chains often called wormlike micelles (WLMs).1–5 The growth of these WLMs depends on surfactant geometry,6,7 which in the case of ionic surfactants depends on the effective headgroup charge and is, therefore, a function of salt concentration. So-called hydrotropic salts, that act as salts with a hydrophobic moiety, prove very effective to induce rapid micellar growth due to their strong binding to the micelles and therefore the effective screening of the headgroup charge.4,6

Beyond the overlap concentration, an entangled WLM network is formed and such solutions exhibit viscoelastic properties. Upon the increasing surfactant or salt concentration even further, the entangled network transitions to a branched network and eventually reaches a saturation point leading to phase separation.4,6–8,14

The viscoelasticity of these WLM networks at low to intermediate frequencies can often be described by a simple Maxwell model, wherein the stress relaxation is exponential with a single relaxation time \( \lambda_r \). This response is a direct result of the equilibrium nature of wormlike micelles2,4,15 which undergo dynamic breakage and recombination on a time scale that is often much faster than the characteristic time of stress relaxation (in the case of polymers, the reptation time). Rheology measurements can therefore be used to study the length and time scales in WLM networks.16

Adding nanoparticles or colloids to surfactant solutions, such as lamellar phases,17–21 can lead to significant changes in macroscopic properties and phase behavior. Colloidal as well as non-Brownian particles are added to WLM solutions at very low concentrations to probe the local structure and viscoelasticity of the network22–25 in a technique called microrheology.26,27 In

References

these examples, the particles are typically larger than the characteristic length scale of the micelle or micellar network (such as the mesh size) and are used at volume fractions low enough so as not to influence the rheological properties of the micellar network. In one particular study, changes in macroscopic behavior were observed when adding polystyrene particles (particle volume fractions of \( \sim 1\% \)) to a like-charged anionic surfactant wormlike micellar system.\(^{29}\) The authors specifically studied the phase behavior and gel collapse kinetics of the particle micellar mixtures and observed interesting correlations between micellar length and sample stability, leading to the conclusion that the phase behavior of these mixtures is governed by a depletion interaction. In contrast to the study presented here, the polystyrene particles were substantially larger than the mesh size in WLM solutions. Besides being of significant fundamental interest, this question is relevant to applications in personal care and cosmetic products. A stable, single phase regime is identified, and the shear rheological properties, which are both sensitive probes of microstructural changes as well as of practical relevance, are studied as a function of particle volume fraction and network density of the micellar solution. Contrast matching small angle neutron scattering (SANS) experiments are performed to directly identify these microstructural modifications due to the nanoparticle addition as well as to probe the potential of mean force acting between the nanoparticles via the application of liquid state theories. The diffusion of the nanoparticles in the WLM network is studied by dynamic light scattering. Based on these measurements, a hypothesis for nanoparticle addition to the WLM network is proposed. Cryo-transmission electron microscopy provides corroborative evidence for this structuring. A short overview of the most pertinent theoretical results and experimental procedures used is provided prior to presenting and discussing the results.

**Theory**

Rheology and SANS measurements are combined with models for semiflexible, living polymers to determine the length and time scales of the WLM solutions, as is summarized elsewhere.\(^{16}\) Only the final relations are presented here: The Cates model\(^{4,15,29}\) for the dynamics of WLMs considers two primary relaxation times associated with the reptation of a micelle, \( \lambda_{\text{rep}} \), and micellar breakage, \( \lambda_{\text{br}} \). In the limit of fast breakage (\( \lambda_{\text{br}} \ll \lambda_{\text{rep}} \)), this leads to Maxwellian linear viscoelastic rheology with a single relaxation time as the geometric mean of \( \lambda_{\text{rep}} \) and \( \lambda_{\text{br}} \):

\[
\lambda_t = \sqrt{\lambda_{\text{rep}} \lambda_{\text{br}}} \tag{1}
\]

This mean relaxation time is identified with the crossover in the viscoelastic spectra. The frequency where \( \omega = \lambda_{\text{br}}^{-1} \) corresponds to a local minimum in \( G'' \), which also defines the plateau modulus \( G'_p \). Rubber elasticity relates the mesh size \( \xi_M \) directly to the plateau modulus and the network density \( \nu \) as:

\[
G'_p = \nu k_B T \frac{\lambda_p T}{\xi_M} \frac{\nu}{3} \tag{2}
\]

The loss modulus at the minimum is related to the contour length \( \bar{L} \) and entanglement length \( l_c \) as:

\[
\frac{G'_p}{G_{\min}} = \frac{\bar{L}}{l_c} \tag{3}
\]

The entanglement length is related to the mesh size and persistence length by:

\[
l_c = \frac{\xi_M^{5/3}}{l_p^{2/3}} \tag{4}
\]

The persistence length \( l_p \) can be measured by using, for example, flow birefringence,\(^{30}\) static and dynamic light scattering,\(^{31–33}\) high frequency rheology,\(^{34,35}\) or neutron spin echo measurements.\(^{36}\)

The scattering of WLMs can be described by the form factor of a semiflexible chain (SFC) taking excluded volume effects into account.\(^{37,38}\) At high scattering vectors, \( q \), the spectra exhibit oscillations resulting from the cross-sectional dimension of the WLM. At intermediate \( q \), the intensity decreases as \( q^{-2} \), which is a signature of linearly extended rigid objects such as wormlike micelles. At lower \( q \), there is a transition to a regime where the intensity changes as \( q^{-1.2} \) to \( q^{-2} \). The scattering vector at which this transition occurs is approximately the inverse of the persistence length \( l_p \). Network density fluctuations and inter-particle correlations often lead to strong deviations from simple SFC scattering at lower scattering vectors in the form of correlation peaks.

For mixed systems of wormlike micelles and particles, the scattering is a convolution of scattering from both components in terms of partial structure factors.\(^{39,40}\) With contrast matching by selective deuteration, these partial structure factors are determined.\(^{41}\) Here, we consider two limits achieved by varying the H\(_2\)O/D\(_2\)O ratio in the suspending medium, namely particle matching such that only the WLMs are evident and WLM matching such that the spatial arrangement of the particles is probed.

A model for the interparticle interactions employed herein is the idealized square well potential (SQW), for which phase diagrams are readily available.\(^{42–44}\) For a SQW fluid of particles with a hard sphere radius of \( R_{hs} \), the potential is defined as:

\[
V(r) = \begin{cases} 
0, & r > R_{hs} \\
\infty, & r \leq R_{hs} 
\end{cases}
\]

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\]
were vortex mixed and left to equilibrate overnight. All experiments to the presence of the particles and are not a result of added electrolyte. Changes in properties of the WLM mixtures with particles are due
mixtures were prepared without the silica phase to examine the
approach can be used to probe the local effective viscosity of
both components scatter light, two modes are observed in the
diffusive motion of the nanoparticles in the WLM solutions. As
g
m(2), 331–346.

The resulting structure factor was derived by Sharma and

ε
2

h

r

s

A

τ

exp(−Dq2τ).


H2O was replaced by D2O at the National Institute for Standards and Technology (NIST).

Instrument equipped with a goniometer allowing angle dependent measurements at a wavelength of 488 nm.

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as previously mentioned, this process was on the order of several months.

Sample Stability. Samples were prepared over a range of surfactant and salt concentrations, and various amounts of particles were included. The phase diagrams were determined by visual inspection in water baths at T = 25 ± 1 °C. Figure 1 presents the results at three ratios of salt to surfactant concentrations (c/s/cd) where the nanoparticle volume fraction and salt concentrations are varied. Increasing particle volume fraction (Φp) or surfactant concentrations (cd) leads to phase separation into an opaque soft sediment and a low viscosity supernatant. As the ratio of salt to surfactant increases, the unstable region expands. The samples separate into a particle rich sediment and particle free supernatant. This transition is thermally reversible. This was tested for a solution of 40 mM CTAB and 140 mM NaNO3, and the transition temperature was found to be about 40 °C. Structural and rheological measurements were only made on samples that did not phase separate during the time of experimentation, that is, on time scales of several days. Note that the sample at 1 vol % particles eventually phase separated, but this process was on the order of several months.

Rheology. The influence of nanoparticle addition on the rheological properties of wormlike micellar solutions was studied using a 100 mM CTAB/200 mM NaNO3 sample containing 0.1, 0.5, and 1 vol % silica particles (Figures 2 and 3). The neat WLM solution (no silica particles) exhibits a plateau at low shear rates.

Dynamic light scattering (DLS) was performed on a Brookhaven instrument equipped with a goniometer allowing angle dependent measurements at a wavelength of 488 nm.

Neutron scattering experiments were performed at the NG-3 and NG-7 beamlines at the NIST Center for Neutron Research (NCNR) at the National Institute for Standards and Technology (NIST). To obtain sufficient scattering contrast, H2O was replaced by D2O (Cambridge Isotopes). For the contrast variation measurements, two different H2O/D2O mixtures were prepared as suspending media. A 35:65 (w/w) H2O/D2O mixture was used to match the scattering of the silica spheres, and a 95.5 (w/w) H2O/D2O mixture was used to match the scattering of the micelles. In the case of matching the silica spheres, the suspending medium composition was calculated from the density of silica (2.2 g/cm3) and the scattering length densities of the components at a wavelength of 6 Å. In the case of matching the surfactant I(0), was measured for a series of WLM solutions in suspending mediums with 70–100 wt % H2O to determine the match point. Data were corrected for background scattering, normalized using standard procedures, and averaged using software provided by NIST.46,48,49

Samples for cryo transmission electron microscopy (cryo-TEM) were examined using a Techni 12 transmission electron microscope at an acceleration voltage of 120 keV. Specimens were prepared using a Vitrobot Mark II instrument. Quantifoil grids were submerged in the liquid sample, blotted to produce a thin liquid film, and allowed adequate relaxation time before vitrification in liquid ethane held at its freezing temperature. Grids were held below −170 °C during investigation in the transmission electron microscope, and images were recorded using a Gatan multispec charge-coupled device (CCD) camera and processed with Digital Micrograph software.

Experimental Section

Samples were prepared from cetyltrimethylammonium bromide (CTAB) sodium nitrate (NaNO3) in distilled, deionized water to which the silica particles were added in the form of the supplied stock solution. Surfactant and salt were purchased from Aldrich and used as received. NaNO3 is not a hydrotrope, so its addition to the suspending medium around the particle.

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The stability of the particle dispersions was observed by visually inspecting sealed, quiescent samples over several months. All samples of particle volume fractions up to 1% were stable over the period of inspection. Particle volume fractions above 1% were observed to develop an opaque sediment and a clear, low viscosity supernatant, indicating a loss of stability on the time scale of days.

Rheological data were collected using a stress-controlled AR-G2 rheometer (TA instruments) in cone-and-plate geometry (4°, 40 mm). Dynamic light scattering (DLS) was performed on a Brookhaven instrument equipped with a goniometer allowing angle dependent measurements at a wavelength of 488 nm.

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Results

Sample Stability. Samples were prepared over a range of surfactant and salt concentrations, and various amounts of particles were included. The phase diagrams were determined by visual inspection in water baths at T = 25 ± 1 °C. Figure 1 presents the results at three ratios of salt to surfactant concentrations (c/s/cd) where the nanoparticle volume fraction and salt concentrations are varied. Increasing particle volume fraction (Φp) or surfactant concentrations (cd) leads to phase separation into an opaque soft sediment and a low viscosity supernatant. As the ratio of salt to surfactant increases, the unstable region expands. The samples separate into a particle rich sediment and particle free supernatant. This transition is thermally reversible. This was tested for a solution of 40 mM CTAB and 140 mM NaNO3, and the transition temperature was found to be about 40 °C. Structural and rheological measurements were only made on samples that did not phase separate during the time of experimentation, that is, on time scales of several days. Note that the sample at 1 vol % particles eventually phase separated, but this process was on the order of several months.

Rheology. The influence of nanoparticle addition on the rheological properties of wormlike micellar solutions was studied using a 100 mM CTAB/200 mM NaNO3 sample containing 0.1, 0.5, and 1 vol % silica particles (Figures 2 and 3). The neat WLM solution (no silica particles) exhibits a plateau at low shear rates.
and significant shear thinning at shear rates above 5 s\(^{-1}\). The onset of shear thinning at a shear rate \(\gamma^*\) identifies the relaxation time \(\lambda_r (\gamma^*)\). The relaxation times and zero shear viscosities were obtained by fitting a Carreau model\(^{50}\) to the shear viscosity.

The surfactant solution exhibits moderate viscoelasticity, as seen in Figure 3. The lines represent fits to a Maxwell fluid model with an additional term to account for the high frequency deviations from the simple form of the Maxwell model. Such deviations at frequencies above the crossover frequency indicate that the semiflexible surfactant micelles are relatively short. Thus, the longest bending modes of the micelles are significant at frequencies just above the longest relaxation time. The Cole–Cole plot (Figure 3) demonstrates the expected deviations from Maxwellian behavior at higher frequencies and identifies the breakage time as the local minimum in \(G''\). Table 1 summarizes the length and time scales extracted from these data, where the persistence length is taken to be 24 nm.\(^{30,51}\)

Adding just \(\Phi_p = 0.001\) of nanoparticles does not substantially change the shear viscosity or plateau modulus, and only a slight shift of the crossover frequency to a lower value is observed. The measurement of \(\lambda_{br}\) from the minimum in \(G''\) is difficult, especially for the pure WLM sample. However, no significant change in the position of the minimum is observed upon further particle addition, and it is therefore assumed to remain largely unchanged. Thus, the observed increase in \(\lambda_r\) upon nanoparticle addition is primarily due to an increase in \(\lambda_{rep}\).

Significant changes occur upon adding \(\Phi_p = 0.01\) of nanoparticles. The zero shear rate viscosity increases by a factor of nearly 2, and the onset of shear thinning shifts to lower shear rates. The dynamic measurements show an increase in both plateau modulus and reptation time. However, the breakage times do not change, within measurement accuracy, with nanoparticle addition. A comparative summary of all the length and time scales is given in Table 1.

**Table 1. Rheological Parameters of 100 mM CTAB and 200 mM NaNO\(_3\) in H\(_2\)O**

<table>
<thead>
<tr>
<th>100 mM CTAB/ 200 mM NaNO(_3)</th>
<th>no particles</th>
<th>(\Phi_p = 0.001)</th>
<th>(\Phi_p = 0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta_0/Pa\cdot s)</td>
<td>2.1</td>
<td>2.3</td>
<td>4.5</td>
</tr>
<tr>
<td>((G_0)/Pa\cdot s)</td>
<td>(2)</td>
<td>(2.3)</td>
<td>(5.1)</td>
</tr>
<tr>
<td>(\lambda_r/s)</td>
<td>0.19</td>
<td>0.17</td>
<td>1.05</td>
</tr>
<tr>
<td>(G_0/Pa)</td>
<td>17</td>
<td>17.4</td>
<td>23.2</td>
</tr>
<tr>
<td>(G_{max}/Pa)</td>
<td>6.6</td>
<td>7</td>
<td>6.5</td>
</tr>
<tr>
<td>(l_p/nm)</td>
<td>24</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>(\xi_{air}/nm)</td>
<td>62</td>
<td>62</td>
<td>56</td>
</tr>
<tr>
<td>(l_c)</td>
<td>120</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>(L_c)</td>
<td>310</td>
<td>310</td>
<td>350</td>
</tr>
<tr>
<td>(\lambda_r/s) (dyn. exp.)</td>
<td>0.12</td>
<td>0.13</td>
<td>0.22</td>
</tr>
<tr>
<td>(\lambda_{br}/s) (dyn. exp.)</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>(\lambda_{rep}/s) (dyn. exp.)</td>
<td>0.9</td>
<td>1.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

---


adding display weak shear thinning (see Figures 4 and 5). Here, even viscosity is only about 30 times that of water. The sample does WLM solution does not exhibit any viscoelasticity and its similarly examined (Table 2). At this low surfactant concentration, viscoelastic properties, a more dilute WLM solution, 50 mM CTAB and 150 mM NaNO3 as a function of silica volume fraction.

As only 1 vol % particle addition greatly increases the solution’s viscoelastic properties, a more dilute WLM solution, 50 mM CTAB/150 mM NaNO3, with a lower network density was examined (Table 2). At this low surfactant concentration, the WLM solution does not exhibit any viscoelasticity and its viscosity is only about 30 times that of water. The sample does display weak shear thinning (see Figures 4 and 5). Here, even adding \( \Phi_p = 0.001 \) has a noticeable effect on the shear viscosity, and with the addition of \( \Phi_p = 0.01 \) the sample is noticeably viscoelastic. Note that, with only 1 vol % nanoparticles added, the zero shear rate viscosity increases by a factor of 25.

**Small Angle Neutron Scattering.** SANS measurements were performed on the 100 mM CTAB/200 mM NaNO3 sample with and without nanoparticles under three contrast conditions, namely full (pure D2O), micelle and nanoparticle contrast as defined above.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>50 mM CTAB/150 mM NaNO3 no particles</th>
<th>50 mM CTAB/150 mM NaNO3 1 vol % silica particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{pA} )</td>
<td>0.03</td>
<td>0.625</td>
</tr>
<tr>
<td>( \eta_{pS} )</td>
<td>0.01</td>
<td>0.37</td>
</tr>
<tr>
<td>( G_\eta/\eta_{0} )</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>( l_\eta/\eta_{0} )</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>( \xi_{w}/l_\eta )</td>
<td>120</td>
<td>340</td>
</tr>
<tr>
<td>( L_\eta/l_\eta )</td>
<td>610</td>
<td>610</td>
</tr>
<tr>
<td>( \lambda_\eta/l_\eta ) (dyn. exp.)</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>( \lambda_{p}/l_\eta ) (dyn. exp.)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>( \lambda_{p}/l_\eta ) (dyn. exp.)</td>
<td>1.25</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.** Steady state viscosity of a wormlike micellar solution of 50 mM CTAB and 150 mM NaNO3 as a function of silica volume fraction.

**Figure 5.** Linear viscoelastic spectrum of 50 mM CTAB and 150 mM NaNO3 as a function of silica volume fraction and Cole–Cole representations of the same data. Lines represent fits to the Maxwell model.

The pure WLM sample in full contrast displays the typical features of a semiflexible chain (Figure 6). The scattering at high \( q \) can be fit by a cylindrical form factor yielding the cross-sectional radius \( r_{cs} \) of 2.5 nm. In agreement with the cylindrical symmetry of the WLM, the slope in the intermediate \( q \)-range is close to \(-1\). This region is, however, not very pronounced, which could be the result of network correlations that lead to a decrease in intensity at lower \( q \) as well as the relatively short contour length. The correlation length of the 100 mM CTAB/200 mM NaNO3 sample is known from the plateau modulus from dynamic rheology to be on the order of 60 nm. Thus, correlations at \( q > 2\pi/\xi_{w} = 0.01 \AA^{-1} \) are expected to lead to a reduction in scattering intensity.

At high scattering vectors (\( q \geq 3 \times 10^{-2} \AA^{-1} \)), the addition of nanoparticles does not affect the scattered intensity, and thus, the micellar structure on length scales of \( r_{cs} \) up to \(~20 \text{ nm} \) remains unperturbed. At lower scattering vectors, an increase in scattered intensity with nanoparticle addition is observed, as expected. The form factor for a sphere of 15 nm mean radius with a Schulz size distribution with a standard deviation of 10% is also shown for reference in Figure 6. Clearly, the increase in scattering intensity for the mixture at lower scattering vectors is consistent with the presence of dispersed nanoparticles contributing to the overall scattering intensity.

To determine whether the presence of particles has any influence on the micelle network structure, contrast matching of the nanoparticles was performed using a 39 wt % mixture of H2O in D2O with 1 vol % silica particles. Under these conditions, only the micelles in the mixture scatter. Figure 7 compares this measurement to that from the pure wormlike micelles in D2O. The preservation of local structure is confirmed at high \( q \) (\( q \geq 6 \times 10^{-2} \AA^{-1} \)). The only effect of the nanoparticles on the micelle structure apparent in the SANS measurements is a weak suppression in the low \( q \) scattering intensity.

Contrast matching the micelles using 95 wt % H2O in D2O as the suspending medium probes the spatial arrangement of the nanoparticles in the WLM solution. Figure 8 compares the scattering of 0.1 and 1 vol % silica particles in 100 mM CTAB/200 mM NaNO3 using 95 wt % H2O in D2O as the suspending medium along with the scattering of the silica particles at 1 vol % in D2O. In the presence of the WLMs, the nanoparticle scattering shows evidence of an upturn at low scattering vectors indicative of weak attractive interactions.

The intensity was fit to a polydisperse but homogeneous sphere model using a form factor comprising a Schultz size
distribution with a standard deviation in size of 10%. The incoherent background was included as a floating parameter. The structure factor calculated from liquid state theory using a square well potential was used to describe particle–particle interactions.45 The fits are shown in Figure 8, and the parameters are listed in Table 3. Note that the particle radius \( r \) determined from the fit increases by 0.5 nm in the presence of surfactant, presumably due to surfactant adsorption. Interestingly, a weak square well attraction was required to accurately describe the nanoparticle scattering in \( \text{D}_2\text{O} \), suggesting some weak attractions are evident due to ubiquitous London–van der Waals interactions. To simplify the fitting and enable comparison between the data sets, a square well width of \(\lambda = 1.375\) was found to best describe particle–particle interactions.\(^4\) The fits are shown in Figure 8, and the parameters are listed in Table 3. The scattering length density of the particles was calculated using the measured density of 2.2 g/cm\(^3\) for silica, and the suspending medium’s length density of the particles was calculated using the measured density of 2.2 g/cm\(^3\) for silica, and the suspending medium’s

**Discussion**

Nanoparticle addition to wormlike micellar solutions, where the particles are of the same charge as the surfactant, leads to stable solutions at low particle concentrations. At high particle volume fractions, reversible phase separation is observed with the formation of a dense, soft solid precipitate. In the stable, one phase regime, nanoparticle addition increases both the zero shear rate viscosity and the storage modulus. Indeed, we have demonstrated that nanoparticle addition can even create viscoelasticity in dilute, entangled WLM solutions. For viscoelastic WLM solutions, particle addition moves the crossover frequency to lower frequencies, but the position of the minimum in \(G''\) remains roughly constant. Particle contrast matching SANS measurements show that adding nanoparticles slightly decreases the forward scattering from the micelles whereas the structure of the micellar solutions on the length scale of the worm cross section remains unchanged. Surfactant contrast matching SANS measurements indicate that the particles are dispersed but have an apparent attractive particle–particle interaction mediated by the WLMs. The diffusion of the particles in the mesh as measured by DLS (see the Supporting Information) is significantly hindered as compared to that expected from a medium with the zero shear rate viscosity of the bulk WLM solution.

To explain these observations, we hypothesize that the nanoparticles physically participate in the WLM network as shown in Figure 9. Despite being like-charged as the surfactant, hydrophobic interactions between the cationic surfactant and the net positively charged nanoparticle can drive adsorption. In particular, WLMs grow linearly with the addition of surfactant because of the unfavorable energy of formation of endcaps relative to cylinders. Consequently, it is plausible that the nanoparticles would first associate with the energetically unfavorable endcaps, and therefore, it is plausible that the nanoparticles become “junctions” between WLMs.

This simple physical picture of nanoparticle–micelle association is consistent with the static and dynamic data presented herein and the cryo-TEM micrographs in the Supporting Information. Reversible phase separation at higher nanoparticle concentrations can be simply a consequence of the particle–particle attractions mediated by the WLMs. These attractions are envisioned to be similar to those observed in polymer bridging.\(^5\) Indeed, phase separation is promoted by the addition of salt, which leads to micellar growth and hence stronger bridging attractions (note that the nanoparticles are stable at these salt concentrations in the absence of surfactant). Three additional physical observations were made that are relevant to this discussion. First, anionic silica particles of similar composition were inherently unstable in the cationic WLM solutions, as expected. Second, larger silica nanoparticles with a diameter of 50 nm and similar surface potential were also not stable in the cationic WLMs. Third, the addition of hydrotropic salts, which generate longer worms by increasing the energy difference for endcap formation relative to the formation of cylinders, also resulted in phase separation over the range of particle, surfactant, and salt concentrations examined here. Thus, these observations of phase separation are suggestive of effective attractions between the particles introduced by the presence of the micelles.

Depletion interactions arising from the WLMs could potentially be a source of attractive interactions leading to possible phase separation without surfactant adsorption onto the nanoparticles.\(^2\) However, depletion interactions at the low particle loadings are too weak in comparison to the viscoelasticity of the WLM solution.

Figures 7 and 8. Scattering cross sections of 100 mM CTAB/200 mM NaNO\(_3\) with 1 vol % silica particles in 39 wt % \(\text{H}_2\text{O}/\text{D}_2\text{O}\).
The lines for bare silica particles in D2O (shown for reference. The results of a square well fit to the data of bare particles that freely diffuse through the network. The Einstein relation predicts that addition of 1 vol % of a colloid would increase the viscosity by 2.5% instead of the 300% increase observed. The enhancement of the plateau storage modulus upon nanoparticle addition can be interpreted as an increase in network density, that is, by assuming that the silica nanoparticles act as new network junctions. A simple estimate illustrates that the observed increase is in semiquantitative agreement with this physical picture. From eq 2, the network density \( \nu \) of the pure 100 mM CTAB/200 mM NaNO3 micellar system is \( 4 \times 10^{21} \) m\(^{-3} \). A nanoparticle volume fraction of \( \Phi_p = 0.01 \) corresponds to a number density of \( 0.7 \times 10^{21} \) m\(^{-3} \). Thus, if each particle served as a new network junction, this would account for a 20% increase in \( G' \), which compares well with the observed 30% increase (Table 1). Alternatively, one can estimate the mesh volume from rheology, and the change in the plateau modulus should then correspond to a change in particles per mesh volume. This number turns out to be 0.1 for this sample, indicating that only a fraction of junctions is established by the particles.

Considering the more dilute WLM system of 50 mM CTAB that is below the entanglement conditions in the absence of nanoparticles, the strong viscoelasticity arising upon addition of only 1% nanoparticles is consistent with the nanoparticles bridging WLMs and participating in the WLM network. Here again, the measured plateau modulus of the order of 2 Pa is quantitatively consistent with the number of nanoparticles present. Assuming that each particle forms a network junction, one would expect \( G_p = 3 \) Pa. Since the pure WLM solution does not exhibit any elasticity, hence one should expect the particle per mesh volume to be very close to unity. However, the value is 1.4, indicating that some particles do not contribute to network formation. On the other hand, it is not possible to explain these strong increases in viscoelasticity by considering only stress contributions from dispersed nanoparticles at these concentrations (the viscosity of 1% particle dispersion has a viscosity of 1.14 mPa·s, very close to the Einstein prediction); that is, by assuming that the silica nanoparticles act as new network junctions, one would expect a 20% increase in \( G_p \). This number turns out to be 0.1 for this sample, indicating that only a fraction of junctions is established by the particles.

The terminal relaxation time determined from the crossover of \( G' \) and \( G'' \) increases with nanoparticle addition in accordance with the increase in zero shear rate viscosity and the plateau value of \( G' \). As the breakage time of the micelles does not change significantly, the increase in the terminal relaxation time is a consequence of an increase in reptation time. The reptation time strongly increases with the molecular weight of a wormlike micelle (of the order of \( L_c^3 \)), and so the creation of longer micelles through nanoparticle bridging of micellar endcaps will significantly increase the terminal relaxation time of the solution. The reptation time increasing by about a factor of 3 (Table 1) would require only a modest increase in the effective contour length \( L_c \) by nanoparticle bridging. It is plausible that nanoparticles bridging the wormlike micelles would not significantly influence the breakage time, because \( \lambda_{br} \approx L_c^{-1} \), which is a much weaker
Properties of Wormlike Micellar Solutions

Conclusions

The addition of nanoparticles of like charge to a cationic wormlike micellar solution leads to significant increases in viscosity and viscoelasticity and, at particle loadings of only a few percent, to thermodynamic phase separation. Indeed, nanoparticles can structure low viscosity, weakly entangled WLM solutions to become viscoelastic. The increases in viscoelasticity can be quantitatively accounted for by assuming that the nanoparticles incorporate into the WLM network and thereby increase both the reptation time of the micelles and the number of effective entanglements in the network. SANS measurements with contrast matching demonstrate that the nanoparticles do not disrupt the structure of the WLMs on length scales of the persistence length and less, which is also consistent with DLS measurements of the dynamics of the mixture. However, nanoparticle addition increases the osmotic compressibility of the WLM phase, which is consistent with the commensurate increase in mixture viscosity. DLS measurements also show that the nanoparticles diffuse through a medium with an effective viscosity greater than that of the mixture, which is again consistent with the nanoparticles being incorporated into the WLM network.

Focusing on the nanoparticle phase, the SANS measurements using surfactant contrast matching show the nanoparticles to be dispersed in the mixture and interacting with a potential of mean force that can be modeled by a square well potential. The strength of the interparticle attraction mediated by the WLMs is in semiquantitative agreement with the observed phase behavior and is consistent with the hypothesis of WLMs bridging nanoparticles. The dynamics and spatial arrangement of the nanoparticles in the WLM solutions are consistent with adsorption of the micelles onto the nanoparticles, which is likely to be due to hydrophobic interactions, as the surfactant and particles are of like charge.

A more quantitative agreement between the nanoparticle solution structure, dynamics, and phase behavior requires developing a more physical potential model for this unique system. The attractive potential of mean force acting between the nanoparticles that is thought to be mediated by bridging of wormlike micelles is novel and has not, to our knowledge, been solved theoretically. Consequently, we anticipate that our observations of the novel thermodynamics, rheology, and micromechanics of the nanoparticle surfactant mesophase will both provide a number of interesting observations for future investigations as well as motivate theoretical studies into the nature of WLM mediated interparticle interactions. Finally, we note that these results provide an initial road map for using nanoparticles as a means to control WLM solution rheology in industrial formulations.

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References

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**Supporting Information Available:** Autocorrelation functions of 100 mM CTAB/200 mM NaNO₃ in H₂O without and with 0.1 and 0.5 vol % silica particles and cryo-TEM micrographs of solutions containing 50 mM CTAB and 150 mM NaNO₃ and 50 mM CTAB, 150 mM NaNO₃, and 0.001 volume fraction silica particles. This material is available free of charge via the Internet at http://pubs.acs.org.