General rules for the scaling behavior of linear wormlike micelles formed in catanionic surfactant systems

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A B S T R A C T

We report in this work on the scaling behavior of wormlike micelles formed in a series of mixed systems of oppositely charged surfactants, including sodium decanote (SD)/hexadecyltrimethylammonium bromide (CTAB), sodium laurate (SL)/hexadecyltrimethylammonium bromide, sodium didecaminocystine (SDDC)/hexadecyltrimethylammonium bromide, and sodium dilauraminocystine (SDL)/hexadecyltrimethylammonium bromide. Steady and dynamic rheological measurements were performed to characterize these wormlike micelles. The scaling behavior for these systems at various mixing ratios was systematically investigated and was compared with that given by the Cates model. It was found that the Cates law can be applied in these systems simply by manipulating the mixing ratio or the surfactant structure. Energetic analysis demonstrates that the scaling behavior of wormlike micelles in nonequimolar mixed cationic and anionic surfactant systems can be close to that predicted by the Cates model, if the electrostatic contribution is below a threshold value.

1. Introduction

Wormlike micelles have attracted considerable attention in both fundamental and applied science due to their special rheological properties [1–10]. These types of micelles, with contour lengths ranging from several nanometers up to several micrometers, are usually self-assembled from aqueous surfactant solutions. They may overlap and entangle to form three-dimensional network structures, which exhibit viscoelastic properties. In this sense, wormlike micelles are similar to polymer chains [2]. However, unlike polymer chains, which formed out of covalent bonds, wormlike micelles are assemblies of small amphiphiles held together by weak noncovalent hydrophobic interactions. The micelles are in thermal equilibrium with surfactant monomers in the bulk and can break and recombine spontaneously in a characteristic time scale.

In the past two decades, the rheological behavior of wormlike micelles has been quantitatively described by measuring the linear mechanical response of these solutions [11–16]. An attractive result is that the viscoelasticity of wormlike micelles can be characterized by a single relaxation time, which is rather unusual for complex fluids [17]. On the basis of the reptation model of polymer dynamics while taking into account the effect of reversible scission kinetics, Cates and co-workers developed a model to understand this unique rheological behavior [18–21]. According to Cates et al., the rheological behaviors of wormlike micelles can be predicted by using the scaling laws

\[ \eta_0 \propto \phi^{3.5}; \quad G_0 \propto \phi^{2.25}, \]

where \( \eta_0 \) is the zero-shear viscosity, \( G_0 \) plateau modulus, and \( \phi \) the concentration of the surfactants. However, experimental results prove that the Cates model is applicable only to wormlike micelles formed by nonionic surfactants. The scaling exponents of wormlike micelles formed by ionic surfactants were found to deviate significantly from that predicted by the model [22,23]. This is considered to be due to the presence of strong electrostatic interactions in the ionic surfactant systems. On addition of inorganic salts to shield the charges, these electrostatic interactions can be effectively overcome.

So far studies on the scaling behavior for charged wormlike micelles are rather sparse, and many important problems have not been tackled, such as the effect of surfactant structure, and the role of the hydrophobic interaction on the rheological behaviors. This is in contradiction to the increasing development of charged wormlike micelles both in fundamental and in practical aspects. Therefore, we focus our attention in this work on the systematic study of factors that affect the scaling behavior of the ionic wormlike micelles.

The wormlike micelles in this study are formed in mixed systems of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) with different anionic surfactants, including the conventional surfactants sodium decanote (SD) and sodium laurate.
3. Results and discussion

3.1. Rheological behaviors of the wormlike micelles

As well-known in the literature, wormlike micellar systems are usually transparent and viscoelastic. So, mixed systems of CTAB and anionic surfactants possessing such features were chosen for study in this work.

3.1.1. Steady-state rheological results

Fig. 1a and b shows the representative steady shear viscosities for the conventional surfactant mixed system of SD/CTAB and the gemini-containing surfactant mixed system of SDDC/CTAB at various mixing ratios. In both systems, a Newtonian plateau at low shear rates followed by shear thinning at higher shear rates occurs (Fig. 1a and b), characterizing the formation of wormlike micelles [1,2]. In addition, the zero-shear viscosities (plateau viscosities) against mixing ratios exhibit a peak for both systems (Fig. 1c), suggesting that the wormlike micelles have a maximum contour length at a threshold mixing ratio. It is well-known that the micelles grow while staying linear up to the maximum, whereas beyond the maximum, branching [25–27] or shrinking [28] of the wormlike micelles occurs. In the branched wormlike micelles, the intermicellar junctions that can slide along the cylindrical body serve as stress-release points, so that the viscosity is reduced. Theoretical studies have predicted that branching of worms should lower the viscosity, and so there is a foundation for this hypothesis. Recently, Croce et al. [29] indeed observed the branching of wormlike micelles using cryo-TEM at the surfactant composition beyond the peak. However, Ziserman et al. [30] found that branching already occurs at the peak composition. Nevertheless, most cryo-TEM results in literature confirm that linear wormlike micelles are indeed formed prior to the peak. Therefore, to avoid running into the disputation of the structures beyond the peak, we focus our discussion at mixing ratios below 0.35 for the SDDC/CTAB and 0.40 the SD/CTAB mixed system, respectively, where both systems are unquestionable in the linear wormlike micellar region. The smaller mixing ratio at which the viscosity maximum occurs in the SDDC/CTAB system is the first sign that the structure of the surfactant affects the rheological property of wormlike micelles. We will discuss it in further details in Section 2.

3.1.2. Dynamic rheological behavior

Fig. 2a–d demonstrates typical oscillatory-shear measurements for the two wormlike micellar systems. Clearly, the storage moduli ($G'$) and the loss modulus ($G''$) have one crossover in both systems. At frequencies below the crossover $G'$ and $G''$ increase with $\omega^2$ and $\omega$, respectively, whereas the complex viscosity $|\eta| = \eta'$ is constant. In this region, the data points of $G'$, $G''$, and $|\eta|$ were well fitted to the Maxwell model given by the equations [29]

\[
G'(\omega) = \frac{G_0(\omega \tau_R)^2}{1 + (\omega \tau_R)^2},
\]

\[
G''(\omega) = \frac{G_0 \omega \tau_R}{1 + (\omega \tau_R)^2},
\]

\[
|\eta'| = \frac{G_0 \tau_R}{\sqrt{1 + (\omega \tau_R)^2}},
\]

where $G_0$ is the plateau modulus and $\tau_R$ the relaxation time which is determined from the interval of the frequency at the crossover of $G'$ and $G''$ [30]. The zero-shear viscosity $\eta_0$ correlates well with the product of $G_0$ and $\tau_R$, as expected for a Maxwell fluid [31]. It is shown in Fig. 2e that the relaxation times also exhibit maxima in both the SDDC/CTAB and the SD/CTAB mixed systems. The positions
of the two maxima in Fig. 2e agree very well with those in Fig. 1c, demonstrating that the longest wormlike micelles are formed at critical mixing ratios in each system. It is noteworthy that the experimental data (symbols) for G and G' deviate from the Maxwell model at high frequencies, which is generally considered to be caused by Rouse-like behavior of the entanglement points [32]. Since we are only interested in the linear wormlike micelles, in the following we focus our discussion on the scaling behavior of the wormlike micelles before the peak occurs, i.e., systems with mixing ratios below the maximum.

3.2. Scaling behavior of the linear wormlike micelles

First, the power law dependence of the zero-shear viscosity (\( \eta_0 \)) and the plateau moduli (\( G_0 \)) on the overall surfactant concentration (wt.% \( \phi \)) for the SD/CTAB and SDDC/CTAB systems was analyzed. As stated above, this investigation was focused only on the linear wormlike micelles. Therefore, the power laws for the mixed systems within a mixing ratio range of 0.25–0.35 for SDDC/CTAB and 0.25–0.40 for SD/CTAB were studied.

Figs. 3 and 4 demonstrate the power law of \( \eta_0 \) and \( G_0 \), respectively. It is very clear that the scaling exponents for the SD/CTAB systems are highly mixing ratio dependent. As the mixing ratio increases, i.e., moves toward charge neutral, both the exponents for \( \eta_0 \) and \( G_0 \) decrease and shift toward the values predicted by the Cates model, namely, 3.5 for \( \eta_0 \) and 2.25 for \( G_0 \), respectively, as illustrated with dotted lines in Figs. 3 and 4, respectively. At a mixing ratio of 0.35, the scaling exponents for \( \eta_0 \) (3.6) and \( G_0 \) (3.0) can be regarded as in reasonable agreement with those obtained by the Cates model. This means that at small mixing ratios, where the wormlike micelles are considerably charged, the rheological behavior deviates significantly from that of nonionic surfactants due to the presence of electrostatic forces. With increasing mixing ratio, the net charges on the surface of the wormlike micelles are effectively decreased which allows the system to take the features of nonionic wormlike micelles.

However, the scaling exponents for the SDDC/CTAB systems change only slightly as the mixing ratio increases from \( X = 0.25 \) to 0.30. It is revealed in Fig. 4 that at \( X = 0.25 \), the exponents for \( \eta_0 \) (4.08) and \( G_0 \) (2.85) are very close to the model values (3.5 for \( \eta_0 \) and 2.25 for \( G_0 \), dotted line in Figs. 3a and b, respectively). This result suggests that in the gemini surfactant-containing system, the surface charge density is much lower than that in the conventional surfactant system at given charge ratios. Even at a bulk mixing ratio far away from equimolar mixing, the ratio of the negative to positive charges in the wormlike micelles containing gemini surfactant is close to 1. This means that the structure of the surfactant has significant influence on the rheological behavior of the wormlike micelles.

The reason for this effect can be probably ascribed to the different CMCs of the two types of surfactants. The CMCs of gemini surfactants are usually two orders of magnitude smaller than those of the conventional unimers. In the present study, the CMCs of SDDC and SD are 0.750 and 74.5 mM [24], respectively. According to regular solution theory, the components with lower CMC will be enriched in the micelles in a mixed surfactant system [33]. Therefore, the relative content of SDDC is more than that of SD in the corresponding wormlike micelles. As a result, the charge density for wormlike micelles containing SDDC is close to electroneutral than that for the micelles containing SD. One should note that such CMC effect should be negligible given that the CMCs of the two components are very close to each other, or the bulk concentration is much higher than the CMCs. However, in the present study, the CMC of SD is 74.5 mM, which corresponds to a log \( \phi \) about −1.84. This concentration is of the same magnitude as that of the bulk concentration in this study. Therefore, the effect of CMC on the micellar composition indeed plays an important role.

Since variation of the chain length of surfactants can also affect their CMC, we carried out similar experiments for the mixed systems.
of CTAB with SL and SDLC, respectively. With increasing the chain length, the CMCs of SL (9.55 mM [24]) and SDLC (0.022 mM [24]) are lower than those of SD and SDDC, respectively. Indeed, we found lower exponents in both systems when compared with the SD and SDDC systems, as illustrated with arrows in Fig. 5. It can be found in Fig. 5 that the scaling exponents in both the conventional and the gemini-containing catanionic surfactant mixed systems can be tuned close to those from the Cates model by either changing the mixing ratio or modifying the structure of the surfactant. This is a common rule in catanionic surfactant wormlike micellar systems which is in contrast with the previous reports that only some sparse examples can be described by the Cates model, e.g., ionic surfactant systems at high salt concentrations [1,34], lecithin reverse micelles [35,36], metallic salts in organic solvents [37], and supramolecular polymers [38]. In these systems, the scaling exponents are in a range of 3.20–3.84 for the zero-shear viscosity ($\eta_0$) and in a range of 1.8–2.91 for the plateau modulus ($G_0$). In the present study, the two exponents can be down to 3.72 and 2.85 in the SDDC/CTAB system at mixing ratios of 0.3, and 3.60 and 3.01 in the SD/CTAB system at a ratio of 0.35, respectively. Obviously, by adjusting the initial molar ratio ($X$) and the structure of the surfactants, the scaling behavior in catanionic surfactant systems without shielding of the excess charge can also be in good agreement with the Cates model. It should be pointed out that in gemini-containing catanionic surfactant systems, variations of the mixing ratio and chain length have less effect on the rheological behaviors of wormlike micelles. This is because the very low CMC of the gemini surfactants makes them enriched in the micelles, which leads to very low charge density for the micelles. As a result, further decrease of the charge density becomes difficult, and the electrostatic interaction is hardly changed on these variations.

It should be pointed out that in the above discussion we neglect the possible change of the chain packing in the wormlike micelles with increasing the fraction of the negatively charged surfactants.

**Fig. 2.** Small amplitude oscillatory rheology of SD/CTAB and SDDC/CTAB systems: (a) SD/CTAB, $X = 0.30$; (b) SD/CTAB, $X = 0.40$; (c) SDDC/CTAB, $X = 0.30$; (d) SDDC/CTAB, $X = 0.40$. The concentration of CTAB is 120 mM; (e) Variation of the relaxation time with mixing ratios in the two systems.
The packing mode of the mixed chains with increasing the fraction of the shorter anionic surfactants in the wormlike micelles should be inevitably changed, which normally favors the formation of smaller micelles according to the packing constrains [41]. However, this effect might be overcome by the decrease of the average head-group area, which favors the formation of larger micelles. The occurrence of peak viscosity and relaxation time in the investigated wormlike micellar systems indeed suggests that the wormlike micelles are growing with increasing the fraction of anionic surfactants in this work. This is also in line with literature results about wormlike micelles formed in catanionic surfactant systems [30].

Fig. 3. The zero-shear viscosity ($\eta_0$) (a) and plateau modulus ($G_0$) (b) as a function of total surfactant concentration (wt.%, $\phi$) in the SD/CTAB system at different molar ratios. (X): $X = 0.25$, square; $X = 0.30$, circles; $X = 0.35$, triangles. Straight lines are the best least-square fits to the experimental data. The dotted line in each figure demonstrates the slope predicted by the Cates model.

Fig. 4. The zero-shear viscosity ($\eta_0$) (a) and plateau modulus ($G_0$) (b) as a function of total surfactant concentration (wt.%, $\phi$) in SDDC/CTAB at the molar ratio $X = 0.25$ and 0.30. The solid symbols are the experimental data, and the straight lines the best least-square fits to the experiment data. The dotted line in each figure demonstrates the slope predicted by the Cates model.

Fig. 5. The scaling exponents of zero-shear viscosity ($\eta_0$) and plateau modulus ($G_0$) at different molar ratios ($X$) for SD/CTAB (open triangles), SL/CTAB (solid triangles), SDDC/CTAB (open squares), SDLC/CTAB (solid squares) systems.
3.3. Quantitative analysis of the role of electrostatic interaction on the scaling behavior of wormlike micelles

The above experimental results indicate that the essence for both the influence of the mixing ratio and the surfactant structure on wormlike micelles can be ascribed to electrostatic interactions. Variation of the mixing ratio changes the charge density of the micelles directly; whereas alteration of the surfactant structures changes their relative concentration in the micelles, which changes the net charge density of the micelles as well. Therefore, the electrostatic energy is the key factor that governs the rheological behavior of charged wormlike micelles. To understand the role of electrostatic energy on the wormlike micelles, we should consider the origin of micellar growth. For nonionic wormlike micelles, the scission energy ($E_{\text{scission}}$), which provides the driving force for the growth of wormlike micelles, is equal to the end-cap energy ($E_c$). However, the growth of charged wormlike micelles is more complicated than that for the neutral systems because the presence of electrostatic interaction introduces an additional electrostatic component ($E_e$) [39]. This leads to

$$E_{\text{scission}} = E_c(1 - E_e/E_c),$$

$$E_e = k_BTl/a\nu^2\phi^{-0.5},$$

where $l$ is the Bjerrum length, $a$ the radius of the micelles, and $\nu$ an effective charge number per unit length of the wormlike micelles. According to In et al. [40], the zero-shear viscosity of wormlike micelles can be related to $E_e$ and $E_c$:

$$\eta_0 \propto \phi \exp \left[ \frac{1}{2k_BT} \left( E_c - E_e \right) \right].$$

(6)

Eq. (7) is obtained on inserting Eq. (5) to Eq. (6):

$$\eta_0 \propto \phi \exp \left[ \frac{E_c}{2k_BT} \frac{la\nu^2}{2} \phi^{-0.5} \right].$$

(7)

Therefore, values for $E_c$ and $la\nu^2$ can be obtained from the fitting of the $\eta_0$ dependence on the total surfactant concentration $\phi^{-0.5}$. Fig. 6a shows the fitting plot for systems of SD/CTAB and SDDC/CTAB. If we assume that the micellar radius $a$ is equal to the average chain length of the surfactant that forms the wormlike micelles, by using the Bjerrum length $l = 0.7$ nm, the charge density per unit length for the wormlike micelles $\nu'$ is obtained. The fitting parameters for all the studied systems are listed in Table 1.

<table>
<thead>
<tr>
<th>Surfactant mixture</th>
<th>$E_c$ (kT)</th>
<th>$av^2$</th>
<th>$\nu'$ ($e$/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD/CTAB X = 0.25</td>
<td>35.8 ± 3.6</td>
<td>8.90 ± 0.84</td>
<td>0.22</td>
</tr>
<tr>
<td>SD/CTAB X = 0.30</td>
<td>25.6 ± 1.4</td>
<td>4.66 ± 0.31</td>
<td>0.16</td>
</tr>
<tr>
<td>SD/CTAB X = 0.35</td>
<td>23.0 ± 1.3</td>
<td>3.50 ± 0.30</td>
<td>0.14</td>
</tr>
<tr>
<td>SL/CTAB X = 0.25</td>
<td>30.4 ± 1.0</td>
<td>5.94 ± 0.23</td>
<td>0.18</td>
</tr>
<tr>
<td>SDDC/CTAB X = 0.25</td>
<td>21.7 ± 1.5</td>
<td>4.03 ± 0.34</td>
<td>0.15</td>
</tr>
<tr>
<td>SDDC/CTAB X = 0.30</td>
<td>21.3 ± 0.5</td>
<td>3.49 ± 0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>SDLC/CTAB X = 0.25</td>
<td>21.9 ± 0.5</td>
<td>3.41 ± 0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The parameters in Table 1 demonstrate that the deviation of the scaling exponents from the Cates model arose from electrostatic interaction is closely related to the values of $av^2$. Fig. 6b illustrates the variation of the scaling exponents for $\eta_0$ with the values of $av^2$ and $\nu'$ for all the mixed surfactant systems in this study. It can be seen that the scaling exponents become smaller with decreasing values of $av^2$ or $\nu'$ regardless of the structure of the surfactants. The effect of the radius of the wormlike micelles has no obvious effect on this tendency, which is reflected on the similar decay of the exponents with $av^2$ and that with $\nu'$ in Fig. 6b. Thus it is reasonable to neglect the radius of the micelles when considering the electrostatic forces between the wormlike micelles. This also explains why the effect of the mixed chain packing with increasing the fraction of the shorter chains has negligible effect on the scaling behavior. One may read from Fig. 6b that at $v^2$ values around 0.13, the scaling exponents are very close to those predicted by the Cates model.

4. Conclusion

In summary, we have described a common rule that is valid for the scaling behavior of wormlike micelles formed in catanionic surfactant mixed systems. Our results demonstrate that both the surfactant structure and the mixing ratio between the two oppositely charged component surfactants affect the scaling exponents of the rheological data. However, these two factors can be united in terms of electrostatic interactions. Variation in surfactant structures changes their CMCs. The one with a smaller CMC will be enriched in the wormlike micelles, which lowers the charge density of the wormlike micelles. Increasing the mixing ratio toward equimolar mixing lowers the charge density of the micelles as well.

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Fig. 6. (a) Linearization of Eq. (6) to obtain values for $E_c$ and $la\nu^2$ for the system SD/CTAB and SDDC/CTAB at $X = 0.30$. (b) Variation of the scaling exponents $\eta_0$ for all the mixed systems in Table 1 with $av^2$ and $\nu'$, respectively. The dashed line indicates the scaling exponent $\eta_0$ obtained from the Cates model.
Therefore, these effects, in essence, are control of electrostatic interactions between the wormlike micelles. By using the model of In et al., we found that the scaling exponents are mainly dependent on the charge density of the wormlike micelles regardless of the surfactant structure. It seems that once the charge density of wormlike micelles is low enough, the Cates model can be applied to describe the rheological behavior of these catanionic surfactant systems, regardless of the possible changes in the chain packing. We hope that this work may provide better understanding of the scaling behavior of wormlike micelles in catanionic surfactant systems and promote their practical applications.

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