Fluorescence Probe Studies of Gelatin–Sodium Dodecyl Sulfate Interactions

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The characteristics of sodium dodecyl sulfate (SDS) micelles bound to gelatin have been studied by fluorescence using 8-anilino-1-naphthalene sulfonic acid (ANS) as probe. Like gelatin, ANS binds in the region of the micelle occupied by the hydrated headgroups, the palisade layer. The gelatin used in this study can bind an average of up to three SDS micelles. The fluorescence characteristics of ANS solubilized in the first micelle to bind to gelatin are very different from those exhibited in the second and third micelles to bind to the gelatin. This distinction arises because the first micelle to bind does so predominantly through an electrostatic interaction between the anionic surfactant and cationic residues, leading to a highly hydrophobic environment. Subsequent micelles bind through a combination of both electrostatic and hydrophobic interactions. We show that the bulk properties (principally viscosity) of the solution are intimately related to the (microscopic) structure of the palisade layer.

Introduction

The interaction between gelatin and surfactants is being studied intensively in this laboratory.1-3 Gelatin is a proteinaceous material, soluble in water with a range of both hydrophobic and hydrophilic sidechains, and behaves as a polyampholyte over a wide range of pH. The properties of gelatin depend on its source and the manufacturing process. The bovine osslein gelatin used here is extracted as a polyampholyte over a wide range of pH. The properties of gelatin used in this study can bind an average of up to three SDS micelles. The fluorescence characteristics of ANS solubilized in the first micelle to bind to gelatin are very different from those exhibited in the second and third micelles to bind to the gelatin. This distinction arises because the first micelle to bind does so predominantly through an electrostatic interaction between the anionic surfactant and cationic residues, leading to a highly hydrophobic environment. Subsequent micelles bind through a combination of both electrostatic and hydrophobic interactions. We show that the bulk properties (principally viscosity) of the solution are intimately related to the (microscopic) structure of the palisade layer.

9 Griffiths, P. C., unpublished results.
solution under the same prevailing conditions of ionic strength and pH.1

Many of these features are similar to those observed for other commonly studied polymer- and surfactant-containing solutions, for example, poly(ethylene oxide) PEO/SDS.10 One significant difference is how the onset of micellization responds to added electrolyte. For simple anionic surfactants, an increase in ionic strength substantially reduces the CMC. The scaling behavior of CMC versus ionic strength in the absence of PEO is very similar to that of CMC(1) in the presence of PEO, that is, their log-log plots are parallel.11 In other words, both the CMC of SDS and CMC(1) of PEO-SDS decrease equivalently because of the shielding of the surfactant headgroup repulsion. In contrast, in the gelatin–SDS case, comparable increases in bulk ionic strength have little or no effect on CMC(1), except at very low gelatin concentrations. It appears that gelatin therefore shields the bound micelle from the effects of the added salt. This “shielding” must occur within the palisade region.

Fluorescence probes can be used to study the microenvironment of the probe and, by inference, the structure of the polymer–surfactant complex. For instance, the fluorescence behavior of 8-anilino-1-naphthalene sulfonic acid (ANS) and related dyes is a qualitative indication of the polarity of the probe environment.12 This feature enables their use in the determination of CMC or CMC(1) through changes in polarity. Estimates of the CMC of SDS measured by ANS fluorescence compare favorably with those determined by other techniques, and therefore the probe does not perturb the structure of the micelle significantly.

Whitesides and Miller4 have studied the interaction between gelatin and SDS at low polymer concentrations (<0.5 wt %) in some detail, using fluorescence probe studies with ANS in combination with other techniques. They invoked a model proposing that micelle formation occurs in multiple stages to account for their observed fluorescence data. At low surfactant concentrations, C < CMC(1), the intensity of the ANS fluorescence remained constant. At C = CMC(1), a sharp increase in fluorescence was observed because of the presence of hydrophobic domains, which increases the quantum yield. This increase reached a plateau at a SDS concentration that was dependent on the gelatin concentration and pH. The intensity at this plateau also increased with both ANS and gelatin concentration. At C = CMC(2), the intensity increased more sharply. Within their multiple-stage binding model, Whitesides and Miller theorized that the partitioning of the negatively charged ANS into gelatin-bound micelles is affected by the charge associated with the (negatively charged) bound micelle–gelatin complex and by the number of micelles bound to a (single) gelatin strand. From this, they concluded that the binding of ANS per micelle decreases as the number of micelles per strand increases. Accordingly, their model predicted a maximum in the ANS intensity, yet none was observed in their study. In this paper, we extend their analysis, and do observe the predicted maximum.

**Materials, Samples Preparation and Equipment**

The gelatin, denoted as “standard gelatin”, is an alkali-processed pollysperse bone gelatin (Kodak European R&D) that has been deionized and had its pH raised from the isoelectric point of pH = 4.9 to pH = 5.8 with NaOH.

SDS (98% purity from Aldrich Chemical Co.) was purified before use by several recrystallizations from ethanol. PEO (Mw = 100000 kDa) sodium tetradecylsulphate (STS), sodium hexadecylsulphate (SHS), and ANS were all obtained from Aldrich and used without further purification.

A stock gelatin solution was prepared by warming to 45 °C the required amount of gelatin and distilled water containing 2 × 10−5 M ANS and, unless specified otherwise, a phosphate buffer (pH = 6.6, 34 mM ionic strength). The solution was maintained at that temperature for 30 min with occasional stirring.

The fluorescence measurements were carried out using a Perkin-Elmer LB 50 luminescence spectrophotometer. ANS emission spectra were obtained on samples at 45 °C (±1 °C). Excitation was at 320 nm and the emission integrated over the range 490 to 520 nm.

**Results**

**Simple Surfactant Solutions.** The emission intensity of ANS dissolved in micellar solutions of the sodium alkyl sulfates increases dramatically at a well-defined surfactant concentration. For the dodecyl (SDS), tetradecyl (STS), and hexadecyl surfactants (SHS), this increase in intensity occurs at the cmc (Figure 1). Analogous behavior for the octyl surfactant is observed, but in this case, the increase in intensity does not occur around the CMC. We conclude therefore that ANS perturbs the micellization process for the octyl surfactant, and we cannot use this approach to study the micelle formed.

For alkyl chain lengths greater than octyl and at concentrations greater than the CMC, ANS associates predominantly with the micelle, executing rapid motion between the polar shell and the surrounding aqueous pseudophase. Because the fluorescence intensity of ANS increases with increasing hydrophobicity, the observed fluorescence is an average of the intensity within the polar shell and in the aqueous pseudophase, each weighted by the probability of finding the probe in the respective regions. Assuming that this probability is proportional to the polar shell volume, the increase in the observed fluorescence intensity (Iobs) ought to be proportional to...
the total volume of polar shell available, viz:

\[ V_p = \frac{4\pi}{3} R_c^3 \]

\[ N_A V_{tail} = \frac{4\pi}{3} R_c^3 \]

\[ V_p = \frac{4\pi}{3N_A} (R_{m}^3 - R_c^3) \]

Table 1. Parameters for Calculation of \( V_p \) for SNS

<table>
<thead>
<tr>
<th>( N = N_c )</th>
<th>cmc, mM</th>
<th>( N_A )</th>
<th>( V_{tail}, \text{Å}^3 )</th>
<th>( V_p, \text{Å}^3 )</th>
<th>( N_A^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>8.0</td>
<td>57</td>
<td>350.2</td>
<td>414</td>
<td>62</td>
</tr>
<tr>
<td>14</td>
<td>2.5</td>
<td>80</td>
<td>404.0</td>
<td>391</td>
<td>75</td>
</tr>
<tr>
<td>16</td>
<td>0.58</td>
<td>98</td>
<td>457.8</td>
<td>388</td>
<td>91</td>
</tr>
</tbody>
</table>

\( ^a \) Assumption of constant area per headgroup.

Figure 2. Aggregation numbers of sodium alkyl sulfates (\( \bigcirc \)) and sodium alkyl sulfonates (\( \bigotimes \)) vs alkyl chain length taken from the literature. The lines are least-squares fits as follows: \( N_A = -49 + 9.0 \ N_c \) (sulfonates) and \( N_A = -44 + 8.4 \ N_c \) (sulfates), showing that in both cases the aggregation number increases by about 8—9 molecules per additional methylene group. Values of \( N_A \) vs \( N_c \) for the sulfates corresponding to an assumption of constant surface area per headgroup (final column of Table 1).

temperature, the surfactant, and electrolyte concentrations and the measurement technique. Unfortunately, there are no reliable relative values for sodium alkyl sulfates in the range \( N = 8, 12, 14, \) and 16 at 45 °C, as these have not been measured by the same technique in the same laboratory. Fortunately, we shall see that the absolute values of \( N_A \) are relatively unimportant for our purposes here. Figure 2 shows aggregation numbers for a series of sodium alkyl sulfates and sulfonates versus the chain length. The straight lines are linear least-squares fits with slopes of about 8 (sulfates) and 9 (sulfonates) molecules per additional methylene group. We adopt light-scattering data for \( N_A \) for \( N = 8 \) and 12, use the value \( N_A = 80 \) by interpolation for \( N = 16 \), and tentatively extrapolate to estimate \( N_A = 98 \) for \( N = 16 \). Aggregation numbers increase with increasing micelle concentration and decrease with increasing temperature. To first order, we ignore these factors because they affect each of the surfactants similarly.

Figure 3 shows the results of calculations of \( V_p \). For each surfactant, the symbol shows the result for the value of \( N_A \) given in the second column of Table 1 and the solid lines are computed extending from \( N_A \pm 10\% \). It is clear for \( N = 12, 14, \) and 16 that the values of \( V_p \) are rather insensitive to the values of \( N_A \) from the upper extreme

References


for $N$ to the lower for $N$, $V_p$ varies by only $(12\%$ from the average of the two extremes.

Figure 4 shows a plot of $I_{obs}$ versus $V_p([SNS]_{total} - [SNS]_{free})$, which, according to eq 1, ought to be a universal, straight line for the three surfactants. Given the approximate nature of the model, the results are more than satisfactory. However, if we further assume that $V_p$ is the same ($= 400 \text{ Å}^3$) for the SNS studied here, $8 \leq N \leq 16$, that is, a constant surface area per headgroup, reasonable values for $N_A$ are obtained in all cases. We conclude therefore that ANS is an effective probe of the micelle surface, provided the micelle is significantly larger than the probe molecule, and adopt this approach for studying polymer–SDS complexes.

**Gelatin–SDS Solutions.** There are substantial changes in the ANS fluorescence intensity dependent on

the surfactant and gelatin concentrations, as shown in Figure 5. In the absence of SDS, the intensity is independent of the presence of gelatin and we can conclude that there is no association of ANS with gelatin. Similarly, the intensity is unaffected by unimeric SDS (i.e., for $[SDS] < \text{CMC}(1)$ and $[SDS] < \text{CMC}$); hence we also conclude that there is no association between ANS and unimeric SDS. However, the intensity does increase significantly in the presence of SDS micelles for both the gelatin-free and gelatin-containing solutions as ANS partitions into a more hydrophobic environment.

In the presence of micelles ($[SDS] > \text{CMC}(1)$), the fluorescence intensity depends on the concentration of gelatin. For dilute gelatin solutions (0.5 and 0.75 wt %), the intensity increases to a plateau at $7-10 \text{ mM SDS}$. After this plateau, the intensity starts to rise once more. The concentration at which the second increase in intensity occurs corresponds to $\text{CMC}(2)$. The probe intensity is different in free and bound micelles because the free micelles have no gelatin groups in the micelle palisade layer and are larger than bound micelles. These are the same conclusions drawn by Whitesides and Miller.4

The fluorescence intensity of ANS in the more concentrated gelatin solutions (2.5 and 5 wt %) shows a pronounced maximum before decreasing sharply on increasing SDS concentration. The SDS concentration at the maximum increases approximately linearly with gelatin concentration: for example, from 20 to 40 mM SDS corresponding to 2.5 and 5 wt % gelatin, respectively. It is interesting that the maximum in fluorescence intensity occurs at approximately the same SDS concentration as the maximum in the solution viscosity, a stoichiometry corresponding to 1 SDS micelle per gelatin molecule. The concentrated gelatin solutions show no second increase in intensity even though the SDS concentrations studied are well in excess of $\text{CMC}(2)$. 

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**Figure 3.** Volume per surfactant molecule in the polar shell vs the aggregation number for SNS micelles for $N = 12$ ($\square$), 14 ($\Delta$), and 16 ($\diamond$). The symbols correspond to the values of $N_A$ in Table 1 and the lines extend to $\pm 10\%$ of those values of $N_A$.

**Figure 4.** Fluorescence intensity vs total volume in the polar shell for SNS micelles for $N = 12$ ($\square$), 14 ($\Delta$), and 16 ($\diamond$). The horizontal error bars correspond to $\pm 10\%$ uncertainty in values of $N_A$, i.e., to the extremes of the solid lines in Figure 3.

For $N = 12$ the lower for $N = 16$, $V_p$ varies by only $\pm 12\%$ from the average of the two extremes.

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against the concentration of micellized surfactant, normalized by the micellar shell volume and are plotted PEO-SDS data for comparison. The intensities have been greater than 34 mM, adding appropriate SDS-only and PGSE-NMR, are always less than approximations, measured by a dodecyl sulfate ion-selective electrode. This approximation is entirely valid as the unimer concentration has been taken as equal to CMC(1) for ease. This number and the area per headgroup are constant, and thus errors in these values will not affect the conclusions of this study. The value of the free unimer concentration has been taken as equal to CMC(1) for CMC(1) for (a) 5 wt % standard gelatin in buffer (pH = 6.6, 34 mM ionic strength); (b) 2.5 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (c) 0.75 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (d) 0.5 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (e) 0.75 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (f) 0.5 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (g) 0.75 wt % standard gelatin in buffer (pH = 6.6, 34 mM); (h) 0.5 wt % standard gelatin in buffer (pH = 6.6, 34 mM). In the concentrated gelatin solutions, small increases are observed in the maximum fluorescence intensity when the ionic strength is increased. In the dilute gelatin cases, C_gelatin < 1 wt %, much larger increases are observed. As proposed by Whitesides and Miller, these effects arise because of the increasing ionic strength introducing an electrostatic screening between the negatively charged dye and the negative surfactant, resulting in an increase in binding.

To evaluate the nature of the interaction between SDS micelles and gelatin, we need to treat our results in terms of the composition of the micelle palisade layer according to the approach described above. For gelatin-containing solutions, values of N_A have been derived from fluorescence-quenching studies.1 The volume of the polar shell in the gelatin systems has been calculated using an average of the experimentally determined aggregation numbers, N_A = 50, adopting the figure of 400 Å^2 per headgroup from aqueous studies. Both the aggregation number and the area per headgroup are constant, and thus errors in these values will not affect the conclusions of this study. The value of the free unimer concentration has been taken as equal to CMC(1) for CMC(1) for the free micelle at an equivalent concentration, irrespective of the nature of any added polymer. The same conclusion was reached in our electron paramagnetic resonance (EPR) studies.2 At low SDS concentrations, the gelatin-SDS behavior is quite different from those of the SDS-only and PEO-SDS systems, which are mutually very similar. This implies that the first few micelles adsorbed onto the PEO molecules have a character comparable to nonadsorbed micelles. However, the first few micelles to bind to the gelatin molecules are much more hydrophobic, and the hydrophobicity increases with increasing gelatin concentration, albeit rather weakly. At higher SDS concentrations, the micellar environment is very similar for all systems, whether bound to PEO or gelatin or indeed, not adsorbed to either polymer.

**Discussion**

The fluorescence data exhibit many distinct features, several of which appear in the viscosity behavior; this is illustrated in Figure 7 for 2.5 wt % gelatin solutions as a function of SDS concentration. Particularly obvious are the coincidence of the onset of the increase in fluorescence intensity and the onset of the viscosification, and broad maxima in both the viscosity and fluorescence intensity around 20–30 mM SDS. This similarity suggests that the bulk behavior has a microscopic basis. In this section we attempt to show the link.

The first micelle to bind to gelatin does so predominantly through the 50 or so cationic residues on the gelatin. The
gelatin adopts a localized conformation similar to that of the micelle. For the same [gelatin]/[SDS] concentration ratio, this may be achieved by the gelatin collapsing onto the micelle surface (dilute gelatin solutions) or bridging between adjacent micelles (concentrated gelatin solutions) to induce the same degree of electrostatic and hydrophobic interaction.

Binding of the gelatin necessarily displaces some water from the palisade layer. Charge neutralization between the anionic headgroups and the cationic residues also occurs. Both of these factors contribute to the explanation of the rather “dry”, rigid”, and hydrophobic headgroup environment as perceived by an EPR spin-probe and the fluorescent probe discussed here. We tacitly assume that any change in entropy due to the release (or otherwise) of bound counterions is much smaller than the entropy change associated with breaking any water structure around both the gelatin and micelle surface.

The number of cationic groups on the gelatin available to the second or third micelle is significantly reduced. The pH and therefore negative charge on the gelatin has increased. The gelatin rearranges its conformation to maximize the hydrophobic interaction yet minimize the electrostatic interaction with the negatively charged micelle. The surfaces of the second and third micelles that bind to gelatin are more hydrated and “fluid”. The fluorescence intensity from an ANS molecule located in the second or third micelle is therefore less, and thus the average or overall intensity detected decreases.

The CMC(1) and CMC(2) values for SDS in the presence of gelatin are given in Table 2 for several ionic strengths. For the most dilute gelatin solutions, there is a slight decrease in CMC(1) on increasing ionic strength from no added salt to 34 mM. No further change is detectable on increasing the ionic strength to 100 mM. At high gelatin concentrations (2.5 and 5 wt %), no change in CMC(1) is observed at all as the inherent ionic strength of gelatin swamps the effect. There are two competing factors affecting the electrostatic interactions in the dilute gelatin solutions. Here, the solution pH ranges between 5.5 and 6.5, just above the isoelectric point of gelatin (pH = 4.9), and therefore gelatin is negatively charged. However, for low gelatin concentrations, certainly for SDS concentrations around CMC(1), the pH drops when the ionic strength is increased, as fewer protons condense onto the weak acid carboxylate groups. The pH drop renders the gelatin less negatively charged and CMC(1) would be expected to decrease. These factors effectively cancel each other, except at very low gelatin concentrations.

Notwithstanding the above, both CMC(1) and CMC(2) are largely unaffected by the presence of any added electrolyte, but the amount of surfactant bound to the gelatin increases significantly with increasing ionic strength. At CMC(2), the unimer concentration equals the CMC under the prevailing (solution) conditions of pH and ionic strength. The free CMC falls with increasing ionic strength and thus the amount bound, that is, CMC(2) - CMC(1), increases. The scaling behaviors of CMC(2) versus ionic strength for gelatin-SDS is similar to that of CMC versus ionic strength for simple SDS, highlighting the electrostatic component to the process that determines saturation.

### Conclusions

This study confirms that ANS is a suitable molecular probe for investigating the characteristics of both free micelles and polymer-bound micelles (gelatin-PEO) of sodium alkyl sulfates. This is facilitated by the observation that the fluorescence intensity is unaffected by unimer either in the absence or presence of polymer.

In the absence of polymer, the observed fluorescence intensity is proportional to the total volume of the micellar polar shell available (within experimental error), provided the length of the alkyl chain of the alkyl sulfate, N, is greater than 8. This finding is consistent with a constant surface area per headgroup in the palisade layer of the micelle.

In this study the relative hydrophobicity of the palisade layer has been defined in terms of the relative fluorescence intensity per unit volume of the micellar polar shell; the higher the value the greater the hydrophobicity. This enables comparisons of hydrophobicity to be made between different polymer-surfactant systems at varying concentrations.

For the gelatin-SDS system, the hydrophobicity is very sensitive to the amount of micellized surfactant. Clearly the main case of interest is comparing low and high concentrations of micellized surfactant to contrast the structure of the first and last micelle to bind to the same gelatin molecule. The first micelle to bind to gelatin appears to be much more hydrophobic than a nonadsorbed micelle. At higher surfactant concentrations, this difference decreases such that at C_{SDS} = CMC(2), the bound micelles are indistinguishable from nonadsorbed micelle, or indeed SDS micelles bound to PEO. Taking into account previous studies, these observations have been rationalized in terms of the relative electrostatic and hydrophobic interactions between gelatin strands and micelles. In contrast, the PEO-SDS systems, which possess no equivalent electrostatic interactions, merely show the same singular decrease in hydrophobicity with increasing

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### Table 2. CMC(1) and CMC(2) Values for Gelatin-SDS Solutions at 45 °C

<table>
<thead>
<tr>
<th>C_{gelatin} (wt %)</th>
<th>Ionic strength/mM</th>
<th>pH</th>
<th>CMC(1)/mM</th>
<th>CMC(2)/mM</th>
<th>bound surfactant (mM)</th>
<th>[CMC(2) - CMC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0</td>
<td>5.8–6.2</td>
<td>0.7 ± 0.1</td>
<td>N/a</td>
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<tr>
<td>0.25</td>
<td>34</td>
<td>6.6</td>
<td>0.4 ± 0.1</td>
<td>N/a</td>
<td>14 ± 2.5</td>
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<tr>
<td>0.5</td>
<td>0</td>
<td>5.8–6.5</td>
<td>0.7 ± 0.1</td>
<td>22 ± 3</td>
<td>16.3 ± 2.5</td>
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<td>0.4 ± 0.1</td>
<td>42 ± 5</td>
<td>39.9 ± 5</td>
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<tr>
<td>2.5</td>
<td>34</td>
<td>6.6</td>
<td>0.4 ± 0.1</td>
<td>N/a</td>
<td>150 ± 20</td>
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<tr>
<td>5</td>
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<td>5.8–6.5</td>
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<td>N/a</td>
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</tr>
<tr>
<td>5</td>
<td>34</td>
<td>6.6</td>
<td>0.5 ± 0.1</td>
<td>150 ± 20</td>
<td>148.5 ± 20</td>
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<tr>
<td>5</td>
<td>100</td>
<td>6.6</td>
<td>0.5 ± 0.1</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>

a By pyrene fluorescence. b By ANS fluorescence. c By PGSE-NMR. This technique is sensitive to the onset of micellization only in dilute polymer solutions. CMC values of SDS at ambient and 34 and 100 mM ionic strength were measured by surface tension and fluorescence (pyrene or ANS). The CMC at 8 mM ionic strength was taken from literature values.
concentration over all concentrations, as exhibited by simple SDS solutions.

In general, the ANS results show clearly that the localized structure of the gelatin–SDS complex depends on the relative gelatin and SDS concentrations (a conclusion also drawn from our previous studies with an EPR spin probe). For instance, for the same [gelatin]/[SDS] ratio below CMC(2), the gelatin can either collapse onto the micelle surface or bridge between adjacent micelles depending on the gelatin concentration. The bridging mechanism is believed to be responsible for the pronounced maximum in fluorescence intensity with SDS concentration, found in this study with the more concentrated gelatin solutions. This fluorescence maximum is shown to coincide approximately with the same maximum found in the solution viscosity, which is thought to be due to a maximum in efficiency of bridging between gelatin molecules by micelles with micellar concentration.

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