Chapter 5

Solubilization of Gelatin by Water-AOT-Isooctane Reverse Micelles Studied by Dynamic Laser Light Scattering

5.1. Abstract

The water cores of reverse micelles of water-AOT-isooctane were characterized through dynamic laser light scattering and viscometry measurements performed at room temperature $T = 25 \, ^\circ C$. The water to isooctane ratio, $W_0$, was chosen between 30 and 50, and AOT concentration was varied from 100 mM to 500 mM. Gelatin molecules of hydrodynamic radius, $R_h = 14.5$ nm (for a 0.5% (w/v) solution) were hosted inside these water cores. Three regimes were explored, water core radius, $R_w$ less than $R_h$, equal to $R_h$ and greater than $R_h$. Measurements revealed that when $R_w \leq R_h$, there was substantial rearrangement of the AOT molecules enabling volume expansion of the water core to accommodate the guest gelatin molecules. Viscometry studies showed nonspheroideal conformations for these micelles. Results have been discussed in the light of short-range and perturbation type of intermicellar potentials.

5.2. Introduction

Reverse micelles are formed when amphiphilic molecules are dissolved in a mixed solvent of polar and nonpolar constituents. An extensive overview of these surfactants can be found in the book of Fendler [1], and also in many excellent reviews [2-10]. The
The most studied amphiphilic molecule is AOT, sodium bis (2-ethylhexyl) sulfosuccinate and the popular nonpolar solvents normally chosen are n-octane, isoctane, heptane, cyclohexane, benzene, halogenated benzene and halogenated alkanes such as chloroform, and of course water is the chosen polar solvent in most of these studies. The AOT molecules lock themselves at the interface between these two non-mixing solvents providing stability to the solution [11,12]. When the water to AOT ratio is changed, one observes a dispersion of nano-sized reverse micelles in the bulk oil medium. Since, it is a free energy driven process, the sizes of these reverse micelles are uniform with a narrow particle size distribution dependent only on \([\text{H}_2\text{O}]/[\text{AOT}] = W_0\) ratio and temperature of the solution. The choice of AOT facilitates the formation of reverse micelles in the absence of a co-surfactant and secondly, the water pool inside the core of the reverse micelles is normally large. These have been characterized extensively in the past [13-16].

The water core of these structures can be used as micro-reactors for carrying out wet chemical reactions and, also for dissolving water-soluble proteins, enzymes etc. [17-20]. Luisi et al. [21] have given a review of these possibilities. Some basic questions were raised by these authors which, remain either partly or fully unanswered till date. These are (i) what are the driving forces responsible for such solubilizations (ii) what are the kinetic steps involved (iii) does the reverse micelles undergo conformational changes to host these polymeric guest molecules (iv) does the relative size of the host compared to that of the polymer (guest) play any role in the solubilization process. And, finally if any universal generalization is possible. Another associated problem is the localization of the guest molecules inside the water core. One of the simplest ways to determine this is to monitor the water core radius from the ratio of total water pool volume to the total interfacial area (assuming all surfactant molecules to be bound). Experimental evidence exists for solubilization of 3,4-dinitrophenol [22], p-nitrophenol [23], chlorophyll [19], DMS (dimethylsulfoxide) [17] etc. in reverse micellar cores. Solubilization of biopolymers offers an additional challenge because of their large sizes and associated preferential conformations in aqueous phase. Biopolymers like lysozyme, Ribonuclease A, Cytochrome C, \(\alpha\)-chymotrypsin, trypsin, pepsin etc. [24-
26] could be hosted inside these reverse micelles successfully. And various experimental techniques like ultracentrifugation, NMR, fluorescence, small angle neutron scattering (SANS) etc. have been adopted to quantify these processes [27-29].

Here, we discuss the solubilization of a polypeptide (gelatin) in the water core of water-AOT-isooctane reverse micelles. The W₀ values were carefully chosen so that the water core size ranged from larger than the hydrodynamic radius of gelatin to smaller than the same. The micellar sizes were measured through dynamic light scattering (DLS) and viscometry. Prior to this, a systematic characterization of the reverse micelles was performed. The major problem encountered in these type of studies is that the filled micelles often alter the radii of the reverse micelles by a very small amount. This demands higher sensitivity on the experimental technique used. Here dynamic light scattering has an edge over other conventional techniques [30,31].

5.3. Results and Discussion

The sample preparation and the method of analyzing the date for dynamic light scattering are fully described in Chapters 2 and 3. The measured hydrodynamic radii values of the reverse micelles at 25 °C at different W₀ are listed in Table 5.1. In Tables 5.2, 5.3 and 5.4, the same for gelatin filled reverse micelles are given.

Table 5.1. Sizes of Water-AOT-isooctane reverse micelles (Rₘ) in nm, measured at various water to AOT concentration ratio (W₀) with the AOT concentration specified as above at (25 ± 1)°C.

<table>
<thead>
<tr>
<th>W₀</th>
<th>[AOT] (mM)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>4000</td>
</tr>
<tr>
<td>30</td>
<td>6.5±0.2ᵇ</td>
<td>6.5±0.2ᵇ</td>
<td>10±0.6ᵇ</td>
<td>18±1ᶜ</td>
</tr>
<tr>
<td>40</td>
<td>10±0.7ᵇ</td>
<td>12±1ᵇ</td>
<td>17±1ᶜ</td>
<td>21±1ᶜ</td>
</tr>
<tr>
<td>50</td>
<td>13±1ᵈ</td>
<td>15±1ᵈ</td>
<td>19±1ᶜ</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ The length of the aliphatic tail of AOT molecule is ~ 1.0 nm, which was the typical experimental error in the estimations of Rₘ values for data points in footnotes ᶜ and ᵈ. Hence,
R_m can be approximated to be the radius of the water core for qualitative discussions. \( b \) correspond to \( R_m < R_h \), the hydrodynamic radius of gelatin at 0.5\%(w/v); \( c \) correspond to \( R_m > R_h \) and \( d \) correspond to \( R_m \sim R_h \). See text for details.

Table 5.2. Sizes of Water-AOT-isooctane reverse micelles (\( R_m' \)) in nm, with gelatin chain trapped inside the water core. Gelatin concentration chosen was 0.5\% (w/v)\( a \).

<table>
<thead>
<tr>
<th>( W_0 )</th>
<th>[AOT] (mM)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>12±1( b )</td>
<td>20±1( b )</td>
<td>16±1( b )</td>
<td>19±1( c )</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>14±1( b )</td>
<td>20±1( b )</td>
<td>22±1( c )</td>
<td>21±1( c )</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>16±1( d )</td>
<td>21±1( d )</td>
<td>24±1( c )</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) The length of the aliphatic tail of AOT molecule is \( \sim 1.0 \) nm, which was the typical experimental error in the estimations of \( R_m \) values for data points in footnotes \( c \) and \( d \). Hence, \( R_m \) can be approximated to be the radius of the water core for qualitative discussions. \( b \) correspond to \( R_m < R_h \), the hydrodynamic radius of gelatin at 0.5\%(w/v); \( c \) correspond to \( R_m > R_h \) and \( d \) correspond to \( R_m \sim R_h \). See text for details.

Table 5.3. Sizes of Water-AOT-isooctane reverse micelles (\( R_m' \)) with gelatin chain trapped inside the water core. Gelatin concentration chosen was 1\% (w/v)\( a \).

<table>
<thead>
<tr>
<th>( W_0 )</th>
<th>[AOT]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mM</td>
<td>200 mM</td>
</tr>
<tr>
<td>30</td>
<td>10±1( b )</td>
</tr>
<tr>
<td>40</td>
<td>15±1( b )</td>
</tr>
<tr>
<td>50</td>
<td>17±1( d )</td>
</tr>
</tbody>
</table>

\( a \) The length of the aliphatic tail of AOT molecule is \( \sim 1.0 \) nm, which was the typical experimental error in the estimations of \( R_m \) values for data points in footnotes \( c \) and \( d \). Hence, \( R_m \) can be approximated to be the radius of the water core for qualitative discussions. \( b \) correspond to \( R_m < R_h \), the hydrodynamic radius of gelatin at 0.5\%(w/v); \( c \) correspond to \( R_m > R_h \) and \( d \) correspond to \( R_m \sim R_h \). See text for details.
Table 5.4. Sizes of Water-AOT-isooctane reverse micelles \( (R_m) \) with gelatin chain trapped inside the water core. Gelatin concentration chosen was 1.5% (w/v)\(^a\).

<table>
<thead>
<tr>
<th>( W_0 )</th>
<th>[AOT]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 mM</td>
</tr>
<tr>
<td>30</td>
<td>11±1(^b)</td>
</tr>
<tr>
<td>40</td>
<td>14±1(^b)</td>
</tr>
<tr>
<td>50</td>
<td>16±1(^d)</td>
</tr>
</tbody>
</table>

\(^a\) The length of the aliphatic tail of AOT molecule is \(~1.0\) nm, which was the typical experimental error in the estimations of \( R_m \) values for data points in footnotes \(^c\) and \(^d\). Hence, \( R_m \) can be approximated to be the radius of the water core for qualitative discussions. \(^b\) correspond to \( R_m < R_h \), the hydrodynamic radius of gelatin at 0.5% (w/v); \(^c\) correspond to \( R_m > R_h \) and \(^d\) correspond to \( R_m \sim R_h \). See text for details.

The variation of translational diffusion coefficient \( (D) \) with the volume fraction of the dispersed phase \( \phi \) is shown in Fig. 5.1 for a fixed \( W_0 \) value and different gelatin concentrations. Fig. 5.2 depicts the same for a fixed gelatin concentration and different \( W_0 \) values. Fig. 5.3 shows a master plot of the reduced viscosity \( \eta_r \) versus \( \phi \) for 0.5% (w/v) gelatin sample.

![Graph of translational diffusion coefficient vs volume fraction for different gelatin concentrations](image)

Fig. 5.1. Variation of translational diffusion coefficient, \( D \), with the volume fraction of the dispersed phase \( \phi \) for \( W_0=50 \) and 0.5%, 1% and 1.5% (w/v) gelatin concentrations measured at \( T = 25 \pm 1 \) °C. Solid lines are guides to the eye.
Fig. 5.2. Variation of translational diffusion coefficient, $D$, as a function of the volume fraction of dispersed phase $\phi$ for 1.5% (w/v) gelatin concentration and different $W_0$ values measured at $T = 25 \pm 1 \, ^\circ C$. Solid lines are guides to the eye.

Fig. 5.3. Variation of reduced viscosity $\eta_r$ as a function of volume fraction of dispersed phase $\phi$, for 0.5% (w/v) gelatin concentration and different $W_0$ values measured at $T = 25 \pm 1 \, ^\circ C$. The solid line is a fit to Eq. (5.4) and the fitting parameters are discussed in the text.
Table 5.1 characterizes the radii ($R_m$) of reverse micelles at $W_0 =$ 30, 40 and 50 and for AOT concentrations 100 mM, 200 mM, 300 mM and 400 mM. The apparent hydrodynamic radius of gelatin was measured to be $R_h = (14.5 \pm 0.5)$ nm. The actual hydrodynamic radius (in the infinite dilution limit) was measured to be $\approx 26$ nm [30]. However, for the present studies, it suffices to use 14.5 nm as the representative size of gelatin in a 0.5% (w/v) aqueous solution. The errors in the estimations of $R_m$ values in most of these measurements were typically ±1 nm, which is approximately same as the length of the hydrophobic tail of AOT molecules. Hence, in these studies, we made no distinction between the water core radius $R_w$ and micellar radius $R_m$. Thus there were three distinct situations as described below.

5.4. Analysis of Gelatin Entrapments

5.4.1. Water core size less than gelatin size ($R_w < R_h$)

This situation corresponded to samples with $W_0 =$ 30 and 40, and [AOT] = 100 mM, 200 mM and 300 mM respectively. Here $R_m$ varied from 6 nm to 12 nm which was much smaller than $R_h = 14.5$ nm. The filled micelles were observed to have radii ($R'_m$) values typically increased by 50% of their unfilled values. Yet, the hydrodynamic radii values of these micelles did not reach the gelatin radius value of $R_h = 14.5$ nm. It can be argued that the size 14.5 nm includes the thickness of hydration layer surrounding the gelatin chain. Since, in our experiments, gelatin solutions rather than gelatin powder was added to the solutions of AOT-isooctane; these polymer molecules entered the dispersion phase with their own hydration layer. Since, the micellar core could not accommodate such large hydrated particles, a re-organization of water and AOT surfactants among the existing reverse micelles was the only possibility. In this process, some hydration water from gelatin molecules could have been released, thus reducing its size to a value acceptable to the re-organized micelles. Since, this was a purely free energy driven process the equilibrium radii that emerged (of the filled micelles) was a compromise between $R_h = 14.5$ nm and corresponding $R_w$. Thus we observed that the
filled micelles had radii values (Tables 5.2, 5.3 and 5.4) 50% larger than before (Table 5.1). Here, a tightly fitted gelatin molecule inside the water core is visualized see Fig. 5.4. This trend remained more or less same for all gelatin concentrations undertaken in these studies. Here it is worthwhile to discuss the corresponding changes in the number density of AOT surfactants when the swelling of the micelles takes place because of the gelatin in take of water cores.

![Diagram of reverse micelle, gelatin with hydration water, and gelatin tightly packed inside the water core.](image)

Fig. 5.4. The physical situation, where the hydrodynamic radius of reverse micelles, $R_m$, are smaller than that of gelatin ($R_h$). Some hydration water from gelatin molecules could have been released thus reducing their size to a value acceptable to the reorganized micelles, having radius $R'_m$. Here, gelatin molecule is tightly packed inside the water core. The water core undergoes significant expansion here.

As the size of the filled reverse micelles $R'_m$ are known it is possible to estimate the number of AOT molecules attached to every reverse micelle for a given $W_0$ and AOT concentration. The number of reverse micelles formed is $N$,

$$N = \frac{nV_m + V_w + V_g}{\left(\frac{4\pi}{3}\right)R_m^3}$$  \hspace{1cm} (5.1)

where $n$ is the number of AOT molecules present in the solution, $V_m$ is the volume of each AOT monomer, $V_w$ is the total added water volume, and $V_g$ is the total volume of added gelatin. Assuming a conical structure for the AOT molecule, and the fact that its head group area is 0.55 (nm)$^2$ and each molecule has a length of 1.2 nm one can assign
a volume = 0.22 (nm)³ to each of these molecules [16], [31]. The number density of AOT molecules \( \sigma \) will be

\[
\sigma = \frac{n}{N}
\]

(5.2)

Our estimation gives, \( \sigma = 29 \times 10^3 \) for \( W_0 = 30 \), \([\text{AOT}] = 100 \text{ mM} \) and gelatin concentration = 0.5% (w/v). The \( \sigma \) value increases to \( = 130 \times 10^3 \) for \( W_0 = 40 \), \([\text{AOT}] = 200 \text{ mM} \) and 0.5% (w/v) gelatin concentration. This trend was observed to repeat in the entire domain where \( R_w < R_h \). It is possible to estimate the head group area \((f)\) actually in contact with the water core of the reverse micelles. This is defined as

\[
\frac{\text{Total surface area of water core}}{\text{Total surface area covered by AOT molecules}} = f
\]

(5.3)

Our calculation consistently showed that \( f \) was close to 1/10 implying that only 10% of the head group surface of AOT molecules were in actual contact with the water core. If the head group area is taken as 0.55 (nm)² only 0.055 (nm)² is in contact with the water core. This remained valid almost in the entire \( W_0 = 30 \) and 40 and, \([\text{AOT}] = 100 \text{ mM} \). These arguments further implied that since more AOT molecules populated the gelatin hosted reverse micellar surfaces at higher AOT concentrations, the micellar surface layer formed with 1.5% (w/v) gelatin concentrations had rigid surface as compared to the fragile surfaces observed for 0.5% (w/v) gelatin solutions. This was true for \([\text{AOT}] \geq 300 \text{ mM} \). Such fragile surfaces are more susceptible to deformation. However for \([\text{AOT}] < 300 \text{ mM} \), the \( \sigma \) - values were almost same for 0.5 % and 1.5% gelatin solutions.

5.4.2. Water core size comparable to gelatin \((R_w \approx R_h)\)

The second scenario involved a situation where the water core had the required space to accommodate a \( R_h = 14.5 \text{ nm} \) gelatin molecule. There was only one value of \( W_0 = 50 \)
([AOT] = 100 mM and 200 mM) where we measured $R_w$ values close to $R_h$. Here, we envisaged a one-to-one matching between the sizes and, hence the gelatin molecules could be hosted inside the water cores without losing their hydration water (Fig. 5.5). The filled micelles were observed to have sizes ($R'_m$) that were \( \sim 20\% \) larger than their initial values. The filled reverse micellar sizes did not show any dependence on the gelatin concentration. As has already been discussed, the incoming gelatin molecules with their hydration water came to thermodynamic equilibrium with the available AOT molecules in a way that enhanced $R'_m$ by $\sim 20\%$.

The number density of AOT molecules ($\sigma$) was estimated as $\sim 80 \times 10^3$, $85 \times 10^3$, and $80 \times 10^3$ for $W_0 = 50$ and [AOT] = 100 mM at gelatin concentration of 0.5%, 1% and 1.5% (w/v). These changed to $\sim 175 \times 10^3$, $120 \times 10^3$ and $150 \times 10^3$ for [AOT] = 200 mM at the same $W_0$ value, and the corresponding gelatin concentration. Thus, the number density of AOT molecules increased almost by a factor of 2. Correspondingly, the fraction of head group area of AOT molecules in contact with the surface of the water core, $f$ (Eq. 5.3) was estimated as $f = 1/15$. In the previous case where $R_w < R_h$, $f$
was 1/10. Here it has reduced further. Hence, the typical area of AOT head group in contact with the water core surface \( \equiv 0.04 \text{ (nm)}^2 \).

### 5.4.3. Water-core size larger than gelatin \((R_w > R_h)\)

As has been shown in Table 5.1 for \( W_0 = 30, 40 \) and 50 and for AOT concentrations of 400 mM, 300 mM, and 300 mM respectively, sizes of reverse micelles \( R_w > R_h \) were observed. The measured \( R_w \) values varied from 17 nm to 21 nm and these were bigger than \( R_h = 14.5 \text{ nm} \). Hence, the entrapment was trivial. The gelatin molecules could reside inside the water cores of these large micelles without causing further swelling to their cores, as were the cases earlier. Here, the filled micelles had sizes, \( R'_m \) and these were comparable to their initial values \( (R_m) \) within the accuracy of experimental error. The trapped gelatin molecules did not have to shed a portion of their hydration water alike in previous cases, see Fig. 5.6.

![Diagram](image)

Fig. 5.6. Here the hydrodynamic radius of reverse micelles are larger than gelatin hydrodynamic radius \((R_h)\). The gelatin molecules could reside inside the water cores of these large micelles without causing further swelling to their cores. Thus, gelatin can be hosted inside the water core comfortably. See text for details.
The gelatin samples used were polydisperse, and hence it is possible that more than one molecule could have got occluded inside some of the cores. However, we rule out this happening on a large scale because in such a scenario, the droplet size would be very large. This was not revealed in any of our measurements.

For the situation $R_w > R_h$, $\sigma$ values were estimated as $\sigma \equiv 200 \times 10^3$ for $W_0 = 40$ and $[\text{AOT}] = 300$ mM for 0.5% and 1% (w/v) gelatin concentrations that increased to $\sim 230 \times 10^3$ for 1.5% (w/v) gelatin solution at the same $W_0$ value. For $W_0 = 40$ and $[\text{AOT}] = 400$ mM, we estimated it increasing from $180 \times 10^3$ (0.5%) to $373 \times 10^3$ for (1%) and (1.5%) gelatin solutions. From these numbers, we could estimate the fraction of the surface area of AOT head group in direct contact with water core surface and we got $f \equiv 1/20$. Hence, an effective area of $\sim 0.03$ (nm)$^2$ was in actual contact with the core water. We construe this as an artifact of the presence of gelatin inside the reverse micellar core.

5.5. Viscosity Studies

The relative viscosity $\eta_r$ values are plotted as function of volume fraction of the dispersed phase $\phi$ for 0.5% (w/v) gelatin in Fig. 5.3. For a nearly spherical particle, $\eta_r(\phi)$ can be expressed as \cite{34,35}

$$\eta_r(\phi) = (1 - \phi - \lambda \phi^2)^{-\delta}$$

(5.4)

where $\delta$ is a shape dependent parameter with a value 2.5 for spheres. For a given gelatin concentration all the $\eta_r(\phi)$ values corresponding to different $W_0$ could be plotted as a master curve as shown in Fig. 5.3. A least-squares fitting to Eq. (5.4) yielded $\lambda = 1.26, 1.28$ and 1.31; and $\delta = 1.60, 1.70$ and 1.80 for gelatin concentration 0.5%, 1% and 1.5% (w/v) respectively. Hence, the quadratic coefficient of $\phi$, $\lambda$ remained constant with a mean value $\lambda = (1.28 \pm 0.03)$ independent of gelatin concentration. The shape
parameter $\delta$ increased from 1.60 at 0.5% gelatin concentration to 1.70 at 1% and 1.80 at 1.5% (w/v) gelatin concentration. It appeared that at higher gelatin concentration, the dispersed micelles (filled) had shapes close to spheroids where as at lower gelatin concentrations these could be deformed spheroids. Our earlier discussions implied that at lower gelatin concentrations, there were fewer AOT molecules per reverse micelle. Hence, more of the surface was exposed to the oil phase. This could result in distorting the surface of these reverse micelles. The $\delta$ parameters showed that $\delta = 1.80$ for 1.5% (w/v) gelatin solutions which is much closer to the spheroid value of 2.5. On the contrary at lower gelatin concentrations (0.5% and 1% (w/v)), there were smaller number of AOT molecules on the surfaces of these gelatin hosted micelles. This reduced the rigidity of these surfaces and one would expect these micelles to have almost non-spherical shapes. This was observed in our viscosity experiments. Since, the capillary viscometry cannot resolve smaller viscosity changes the finer details of the 3-d structures of these polymer hosted micelles could not be explored further from these data set.

5.6. Intermicellar Interactions

The variations of translational diffusion coefficients $D$ with the volume fractions of the dispersed phase is shown in Figs. 5.1 and 5.2 for various gelatin concentrations and $W_0$, measured at room temperature, $T = 25 \degree C$. The concentration dependence of $D(\phi)$ could be expressed as

$$D(\phi) = D_0(1 + \alpha \phi)$$  \hspace{1cm} (5.5)

which is a linear approximation of the generalized expression [30,31]

$$D(\phi) = \frac{\phi}{(1 - \phi)} \frac{1}{f(\phi)} \left( \frac{\partial \mu}{\partial \phi} \right)_{p,T}$$  \hspace{1cm} (5.6)
where $\mu(\phi)$ is the chemical potential of the solution and $f(\phi)$ is the translational frictional coefficient of the dispersed particles. The intermicellar interactions are accounted for by the parameter $\alpha$ [36-38]. It contains contributions from osmotic virial part, Oseen tensor part, dipolar interactions part, short-range interactions part, perturbation contribution part etc. A detailed analysis relates $\alpha$ to the second virial coefficient ($A$) of $\mu(\phi)$ as

$$
\alpha = \begin{cases} 
1.56 + \frac{A}{2} + \frac{3A}{256} & \text{Short range perturbation potential} \\
1.56 + \frac{5A}{2} + \frac{93A}{7168} & \text{Perturbation potential } \sim r^{-6}
\end{cases}
$$

(5.7)

Our values of infinite dilution diffusion coefficient $D_0$ and $\alpha$ are listed in Table 5.5 for various gelatin concentrations. The $\alpha$-values were negative in all these cases implying net attractive interactions between reverse micelles. The corresponding values of second virial coefficients ($A$) of the chemical potential $\mu(\phi)$ were deduced from Eq. (5.7) and these are listed in Table 5.5.

Table 5.5. Variation of infinite dilution diffusivity, $D_0$, interaction parameter $\alpha$, $A^{SR}$ and $A^{PR}$ with $W_0$ for various gelatin concentrations.

<table>
<thead>
<tr>
<th>$W_0$</th>
<th>$D_0 \times 10^7$ (cm$^2$/s)</th>
<th>$\alpha$</th>
<th>$A^{SR}$</th>
<th>$A^{PR}$</th>
<th>Gelatin Concentration (w/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.3±0.4</td>
<td>-2.72</td>
<td>-8.36</td>
<td>-1.703</td>
<td>0.5%</td>
</tr>
<tr>
<td>40</td>
<td>3.0±0.3</td>
<td>-2.57</td>
<td>-8.07</td>
<td>-1.64</td>
<td>1%</td>
</tr>
<tr>
<td>50</td>
<td>2.1±0.2</td>
<td>-2.32</td>
<td>-7.58</td>
<td>-1.54</td>
<td>1%</td>
</tr>
<tr>
<td>30</td>
<td>3.9±0.4</td>
<td>-2.93</td>
<td>-8.77</td>
<td>-1.78</td>
<td>1.5%</td>
</tr>
<tr>
<td>40</td>
<td>2.2±0.2</td>
<td>-2.64</td>
<td>-8.20</td>
<td>-1.58</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.1±0.2</td>
<td>-2.41</td>
<td>-7.75</td>
<td>-1.68</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.0±0.4</td>
<td>-2.51</td>
<td>-7.95</td>
<td>-1.62</td>
<td>1.5%</td>
</tr>
<tr>
<td>40</td>
<td>2.9±0.3</td>
<td>-2.52</td>
<td>-7.97</td>
<td>-1.62</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.4±0.2</td>
<td>-2.47</td>
<td>-7.87</td>
<td>-1.61</td>
<td></td>
</tr>
</tbody>
</table>
Both for 0.5% (w/v) and 1% (w/v) gelatin concentrations, $\alpha$ values increased by about 17% as $W_0$ increased from 30 to 50, whereas for 1.5% (w/v) gelatin samples these remained constant at $\alpha \approx -(2.5 \pm 0.02)$. Hence, the 1.5% (w/v) gelatin samples could be visualized as a relatively stable phase as compared to others. The $\alpha$ values are plotted as function of $W_0$ for various concentrations of gelatin in Fig. 5.7. Unfortunately our values could not be compared with any reported literature values because of paucity of similar data. Nonetheless, the $\alpha$ and $A$ values appeared to be reasonable when seen in the context of similar values reported for reverse micelles alone. The intermicellar interactions most probably depend on the population of AOT molecules on a reverse micellar surface. Though we have estimated these values ($\sigma$) from our measured reverse micellar sizes, yet it is not possible at this stage to correlate $\sigma$ with $\alpha$ though correlation seem plausible. Any theoretical model describing intermicellar interaction must have $\sigma$ as a tuning parameter among other things. Fig. 5.7 indicates abrupt change in plotted values close to $W_0 = 40$ which we could not explain at this stage.

![Graph](image)

Fig. 5.7. Variation of $\alpha$ with $W_0$ for 0.5%, 1% and 1.5% (w/v) gelatin concentrations. Notice that there is an abrupt change in value of the interaction parameter $\alpha$ close to $W_0 = 40$. No physical explanation could be offered to this at this stage. Solid lines are guides to the eye.
5.7. Conclusions

Gelatin, which is denatured collagen, could be solubilized in the water core of reverse micelles of water-AOT-isooctane system. Three distinct domains have been identified, when the water core size was close to gelatin size, the biopolymer fitted tightly into the water core but forced an enhancement of water core radius by almost 50%. The AOT number density calculations showed that 1/10th of the surface area of AOT head group was actually in contact with the water surface. In the second domain the water cores size almost matched with gelatin size, hence the solubilization could be achieved with expansion of the host. Nonetheless, the water cores expanded by 20% in these cases. The AOT head group area in actual contact with the water surface was estimated to be 1/15 of the AOT head group area. When the micellar size was larger than the gelatin size, the solubilization was trivial and almost no size change of the host was noticed. Here, 1/20 of the AOT head group area was found to be in contact with the water core.

Viscosity measurements showed that the dispersed gelatin filled micelles were distorted spheroids with the degree of sphericity being higher for 1.5% (w/v) gelatin solution. For lower gelatin concentrations, the shapes were far from spherical conformations. The inter-particle interactions could be determined from the volume fraction dependence $\alpha$ of the translational diffusion coefficient data. This parameter $\alpha$ was related to the second virial coefficient $A$ of osmotic pressure both in the short range potential and perturbation potential models. Since, no comparison data was available in the literature for similar systems, these could not be compared. The stability of the gelatin hosted reverse micelles can be estimated from the free energy calculations. The free energy $G_1$ of the ensemble of $N$ droplets of radius $R$ in a liquid having surface tension $\gamma$ can be written as [35]

$$G_1 = M_0 g_0 + M_s g_s + M_w g_w + 4\pi N\gamma R^2 - \frac{4\pi NKR}{R_0} + 2\pi N K$$

(5.8)

where $M_0$, $M_s$ and $M_w$ are the mass of oil, surfactant and water present with their chemical potentials being $g_0$, $g_s$ and $g_w$. $K$ is a parameter that describes the rigidity of
the surface of the micelle having a curvature $1/R_0$. When gelatin-chain of mass $M_g$, (with end-to-end length $\bar{R}_e$) chemical potential $g_g$, gets hosted the above changes to $G_2$ written as

$$G_2 \equiv G_1 + M_g g_g + K_B T \left( \frac{3R_e^2}{2N_0 b^2} \right) + K_B T \frac{\nu N_0^2}{R_e^3}$$

(5.9)

Here, $K_B$ is the Boltzmann constant, $T$ is absolute temperature. The last term is the contribution of excluded volume $\nu$ to the free energy and the last but one term is the contribution arising from chain connectivity (entropic contribution)[37]. In principle the free energy term $G_2$ can be minimized for an equilibrium radius ($R_{eq}$) and $R_{eq}$ can be deduced exactly from

$$\frac{\partial G_2}{\partial R} = 0 \quad R = R_{eq}$$

(5.10)

yields

$$R_{eq}^5 \left( 108 \sqrt{6} K_B T R_0 + 48 \sqrt{6} \pi N_0 \nu \gamma b^2 R_0 \right) - (24 \sqrt{6} \pi NN_0 K_b^2) R_e^4 - 3K_B T \nu N_0^3 R_0 b^2 = 0$$

(5.11)

which can be evaluated. Yet, this would necessitate the knowledge of several other physical parameters of the dispersion medium and the dispersed phase (like, $\gamma$, $K$, $\nu$ etc.) that getting an exact estimate for $R_{eq}$ would not be trivial. Note that in the absence of excluded volume interactions ($\nu = 0$), Eq.(5.11) yields $R_{eq} = K_l/(2\gamma R_0)$, which was deduced by Robbin [36] while discussing hydrodynamic stability of reverse micelles and this has been discussed at length by de Gennes and Taupin [11].
References


