Micellar structure of an oligopeptide surfactant “trimeric \(N\)-dodecanoyl-l-proline potassium salt” in aqueous solution – small-angle neutron scattering study

Abstract Structures of the micelles which are formed by the chiral oligopeptide surfactant \(N\)-dodecanoyl-l-proline tripeptide anions have been examined using small-angle neutron scattering spectral analysis. Results show that the chiral \(N\)-dodecanoyl-l-proline trimeric anions may form a spherical micelle with an aggregation number of 36 and that the oligopeptide portions with a poly-l-proline I-type helical structure are saturated with water.

Key words Micelles · Chiral oligopeptide surfactant · SANS

Introduction

In previous work [1], the small-angle neutron scattering (SANS) spectra for micellar solutions of \(N\)-decanoylglycine and \(N\)-decanoyl-l-alanine oligomeric K-salts were measured and analyzed in order to elucidate the correlation between the secondary structure of the oligomeric portion and the observed SANS spectra. For micelles formed by the trimeric salts, a helical structural model provided the best fit to the observed SANS intensity, while for micelles of the monomeric and dimeric salts, a \(\beta\)-sheet model provided the best fit to the observed data. In particular, it was emphasized that for the trimeric micelles, the aggregation number depends upon the species of amino acid residue.

In this present study, for an aqueous micellar solution of an oligopeptide surfactant, \(N\)-dodecanoyl-l-proline trimeric anions with a helical structure, the structure of the micelles, obtained using SANS spectral analysis, is discussed.

Experimental

Materials

Chiral \(N\)-dodecanoyl-l-prolyl-l-prolyl-l-proline was synthesized by the stepwise procedure previously described [2]. The acid-type oligomer was identified by \(^1\)H NMR. The chiral oligomeric acid-type was then dissolved in methanol–water and the pH of the solution was adjusted to 7.0 by slow addition of dilute KOH–H\(_2\)O at 273 K. The potassium salt of this chiral trimer (DoP3K) was collected by lyophilization and dried under high vacuum at room temperature over P\(_2\)O\(_5\).
Critical micelle concentration measurements

The critical micelle concentration (cmc) of DoP3K was determined by the refractive index method using an Abbé refractometer (Atago Optical Works) at room temperature (around 298 K). The cmc of DoP3K thus obtained is 3.8 × 10⁻² mol/L.

Neutron scattering measurements

SANS measurements were carried out using the SANS-U installed at the JRR-3M reactor at the neutron scattering laboratory in the Institute for Solid State Physics of the University of Tokyo, Tokyo, Japan. The sample solutions were placed in a quartz cell of 4-mm path length at 298 K. The scattering length density (ρ) of each component was calculated using the following equation,

\[ ρ = \sum b_i/V \, , \tag{1} \]

where \( b_i \) is the scattering length of atom \( i \) and \( V \) is the molecular volume. The \( Σb_i \) values quoted from Ref. [3] and the \( V \) values calculated from the partial molar volume data [4-6] are listed in Table 1. The magnitude of the momentum transfer \( Q \) is given by Eq. (2),

\[ Q = \frac{4πr}{\lambda} \sin \left( \frac{θ}{2} \right) \, , \tag{2} \]

where \( λ \) is the incident wavelength (5 Å for SANS-U). The intensity of the scattered neutrons was recorded on a position-sensitive 2D detector. Normalization of the data to an absolute intensity scale was made by using the transmission of a 1-mm water sample. Corrections for the attenuation were also made.

Results and discussion

The dependence of the neutron scattering intensity on the magnitude of the scattering factor, \( Q \), depends upon both the particle structure factor, \( P(Q) \), and the interparticle structure factor, \( S'(Q) \). \( S'(Q) \) is a function of the diameter, \( δ \), the charge, \( Z \), and the number density of a particle and of the dielectric constant of the solvent.

For a monodispersed system of charged hard particles, the scattering intensity can be expressed as the product of \( S'(Q) \) and \( P(Q) \) in the following form,

\[ \frac{dΣ(Q)}{dΩ} = n_p 10^{-16} \left( \left( ρ_p - ρ_c \right) V_c + \left( ρ_s - ρ_p \right) V_m \right) \, S'(Q) \, , \tag{3} \]

\[ n_p = \frac{(c - \text{cmc})N_A}{1000n} \left( \text{cm}^{-1} \right) \, , \tag{4} \]

where \( n_p \) denotes the number density of the particles and \( n \) the average aggregation number of a micelle, and

\[ P(Q) = \int_0^1 \left| F(Q, μ) \right|^2 dμ \, , \tag{5} \]

\[ F(Q, μ) = x \frac{3\left[ \sin(QR_1) - QR_1 \cos(QR_1) \right]}{(QR_1)^3} + (1 - x) \frac{3\left[ \sin(QR_2) - QR_2 \cos(QR_2) \right]}{(QR_2)^3} \, , \tag{6} \]

\[ x = \frac{\left( ρ_p - ρ_c \right)V_c}{\left( ρ_p - ρ_s \right)V_c + \left( ρ_s - ρ_p \right)V_m} \, , \tag{7} \]

where \( V_c(\text{Å}³) \) and \( V_m(\text{Å}³) \) are the volumes of the micellar core and the overall micelle, respectively. \( ρ_p(\text{Å}⁻²), ρ_c(\text{Å}⁻²) \) and \( ρ_s(\text{Å}⁻²) \) are the average neutron scattering length densities of the polar shell, the hydrophobic core and the solvent, respectively.

When the micellar shape is spherical, \( R_1 \) and \( R_2 \) are given by

\[ R_1 = b \, , \tag{8} \]

\[ R_2 = b + t \, , \tag{9} \]

where \( b \) is the diameter of the micellar axes and \( t \) the diameter of the polar group.

\( S'(Q) \) can be calculated approximately by use of the following equation

\[ S'(Q) = 1 + β(Q, μ)[S(Q) - 1] \, , \tag{10} \]

where

\[ β(Q, μ) = \frac{\left| F(Q, μ) \right|^2}{\left\langle F(Q, μ)^2 \right\rangle} \, , \tag{11} \]

and

\[ S(Q) = \frac{1}{1 - 24μa(Q)} \, , \tag{12} \]

Table 1 Partial molar volumes \((V)\) and scattering length \((Σb_{coh})\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(V) (Å³)</th>
<th>(Σb_{coh}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>42.6⁴</td>
<td>-4.57 × 10⁻⁵</td>
</tr>
<tr>
<td>CH₂</td>
<td>28.2⁵</td>
<td>-8.32 × 10⁻⁶</td>
</tr>
<tr>
<td>-N(CH₂CH₂CH₂)CH-CO-</td>
<td>112.3⁶</td>
<td>2.23 × 10⁻⁴</td>
</tr>
<tr>
<td>COO⁻</td>
<td>25.7⁶</td>
<td>1.83 × 10⁻⁴</td>
</tr>
<tr>
<td>K⁺</td>
<td>9.85⁶</td>
<td>3.71 × 10⁻⁵</td>
</tr>
</tbody>
</table>

⁴ Ref. [4]  
⁵ Ref. [5]  
⁶ Ref. [6]