

Structure of Dilute Micellar Water Solutions of Nonionic Dimeric Surfactant Study by Small Angle Neutron Scattering Method

A. RAJEWSKA^{a,b,*} AND K.A. WILK^c

^aNational Centre for Nuclear Research, A. Sołtana 7, 05-400 Otwock-Świerk, Poland

^bJoint Institute for Nuclear Research, LNP, 141980 Dubna, Russia

^cDepartment of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

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The new sugar gemini nonionic surfactant — bis(C12LA) [(C₅₆H₁₁₀N₄O₂₂)] was investigated by small angle neutron scattering method for six dilute solutions with concentrations: 20 CMC, 50 CMC, 75 CMC, 100 CMC, 125 CMC and 150 CMC (CMC = 7.3 × 10⁻⁶ mol/dm³, CMC = critical micellar concentration) and three temperatures (20 °C, 40 °C and 60 °C) for the q range 0.003–0.4 Å⁻¹. The aim of experiment was to determine the size and shape of micelles as a function of concentration and temperature in heavy water micellar solutions of nonionic dimeric surfactant bis(C12LA).

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1. Introduction

The dimeric or gemini surfactants are composed of two conventional surfactants joined by a spacer (group which can be hydrophobic or hydrophilic, flexible or rigid) at or near the head group as they exhibit much lower critical micelle concentrations (CMC's) that can be achieved by conventional surfactants with the same hydrophilic and hydrophobic groups. They reveal very special physical properties: they are about three orders of magnitude more efficient at adsorbing at the surface (and consequently reducing the surface tension) and somewhat more than two orders of magnitude more efficient at forming micelles, because of an outstanding low CMC [1–6].

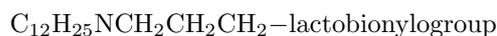
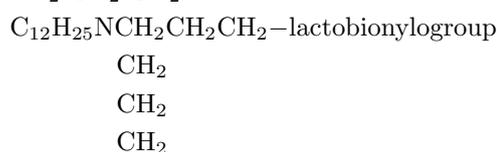
At concentrations above the CMC surfactants tend to self-associate in water to form micelles. The micelles are generally spherical or spheroidal at concentrations slightly above the CMC. For most surfactants micelles tend to grow and in this process change shape when the appropriate parameter is modified. Thus an increase in concentration and temperature bring about micellar growth.

This paper deals with the small angle scattering study of the micellization of nonionic gemini surfactant bis(C12LA) [7, 8]. We have studied the effect of concentration and temperature on the structure of isotropic solution as well as the micelle shape and size in wide range of dimeric surfactant low concentrations (no salts added) of heavy water solutions and for temperatures between 20 °C and 60 °C.

2. Experimental

2.1. Materials

Surfactant bis(C₁₂LA), i.e. *N,N'*-bis(dodecyl)-*N,N'*-bis(3lactobionamido) propyloethylenodamine (C₅₆H₁₁₀N₄O₂₂), $M = 1191.52$ g/mol, $\rho = 1.10$ g/cm³, CMC = 7.3 × 10⁻⁶ mol/dm³, $V \approx 3176$ Å³ was synthesized by a group of chemists from Wrocław University of Technology (Chemical Department) according to synthetic methodologies described in [9–11]. The material has an unusual structure for a nonionic surfactant with two identical lactobionyl hydrophilic heads and two *n*-dodecyl tails for bis(C₁₂LA) with the spacer -N-CH₂-CH₂-CH₂-N-:



All the surfactant solutions were made using D₂O as a solvent (99.9% deuterated). D₂O instead of H₂O was used (99%, from Sigma-Aldrich) to the better contrast of the surfactant from the solvent.

2.2. Small angle neutron scattering (SANS) technique

The new gemini nonionic surfactant — bis(C12LA) [(C₅₆H₁₁₀N₄O₂₂)] was investigated at the Intense Pulsed Neutron Source at Argonne National Laboratory, Argonne, IL (USA) using the small-angle diffractometer SAND for the scattering vector q range 0.003–0.4 Å⁻¹. For SANS experiment [12] the sample solutions were held in standard quartz cells with the path length of 0.2 cm. Neutrons were produced in pulses by spallation from 450 MeV protons followed

*corresponding author; e-mail: zaldona24@hotmail.com

by moderation by solid methane (18 K) to produce wavelengths of 0.5 to 14 Å. The 64×64 array position sensitive multidetector was used to detect neutrons scattered by the sample while the wavelength of the neutrons (λ) was determined by time-of-flight.

3. Theory

3.1. The IFT method for determination of PDDF function

The intensity of scattered radiation as a function of the magnitude of the scattering vector q is represented for monodisperse particles by [13]:

$$I(Q) = nP(Q)S(Q),$$

where n is the number density of particles, $P(Q)$ is the particle form factor and contains the effect of particle size, shape and scattering power on scattered intensity, $S(Q)$ is the structure factor and accounts for interparticle interactions, $S(Q) \rightarrow 1$ for no interacting particles or in the limit of a very dilute solution. The micelle shape was determined with the generalized indirect Fourier transformation (GIFT) method [14]. The conventional Fourier transformation of $I(Q)$ involves the integral

$$p(r) = \frac{1}{2\pi^2} \int I(q)qr \sin(qr) dq,$$

which yields the pair distance distribution function $p(r)$, where r is the distance in real space. The point, at which the $p(r)$ falls to zero, represents the particle maximum dimension. The functional form of $I(Q)$ or $p(r)$ can be used to determine the shape and the internal structure of the scattering object. The $p(r)$ was evaluated from the measured $I(q)$ using the indirect Fourier transformation method (program IFT) [15, 16] and its extension named generalized indirect Fourier transformation method (GIFT) [17–20] (for semidilute systems). IFT is a completely model-free method which can only be applied for the “dilute” systems where interparticle interactions can be neglected. At higher concentrations of scattering particles interparticle correlations strongly affect the scattering intensity $I(q)$ and must be taken into account during the evaluation procedure using recently developed GIFT technique.

4. Results and discussion

The sugar gemini nonionic surfactant – bis(C12LA) [(C₅₆H₁₁₀N₄O₂₂)] was investigated on SAND diffractometer in Argonne National Laboratory (USA) for six low concentrations: 20 CMC, 50 CMC, 75 CMC, 100 CMC, 125 CMC and 150 CMC in heavy water solutions and three temperatures 20°C, 40°C and 60°C within the q range 0.005–0.4 Å⁻¹. Figure 1 shows the typical SANS data for all the D₂O solutions. According to our results we observed that the SANS pattern of the surfactant is dependent on the concentration of surfactant but independent of temperature.

In the investigated low concentrations the micellization process of bis(C12LA) takes place and molecules of the surfactant self-assemble in the spherical micelles. According to Tanford [21] equation the maximum length (nm) of a fully extended hydrocarbon chain of surfactant is $l = 015 + 0127 n_c$ (where n_c is number of carbon atoms) in our case it gave $l = R = 35.1$ Å. Table shows that the change of radius of micelles with increase of surfactant concentration in heavy water solutions is very small and micelles have the uniform structure.

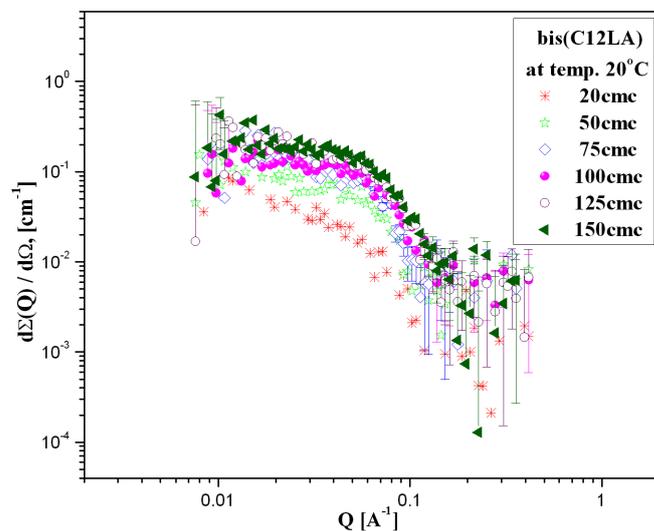


Fig. 1. Intensity of neutron scattering vs. scattering vector for nonionic sugar gemini surfactant bis(C₁₂LA) in heavy water only for concentrations: 20 CMC, water only for concentrations: 20 CMC, 50 CMC, 75 CMC, 100 CMC, 125 CMC, 150 CMC at temperature 20 °C.

TABLE

The radius of micelles for the six concentrations of the bis(C12LA) surfactant (CMC = 7.3×10^{-6} mol/dm³).

C [× CMC]	20	50	75	100	125	150
R [Å]	15.7±1.4	16.8±1.6	16.5±1.3	17.1±1.7	17.0±1.2	18.3±1.8

5. Conclusions

This paper reports measurements of neutron cross-sections of the micellar solutions of bis(C12LA) in D₂O over the wide range of dilute surfactant concentrations and temperatures in the single phase region. Measurements have covered the q range from 0.003 to 0.4 Å⁻¹. It was assumed from our analysis that bis(C12LA) micelles are spherical and have the uniform structure. The change of radius with increase of concentration is very small. The radius of micelles in investigated solutions was shorter than the length of full extended tail of surfactant molecules equal to $l = R = 35.1$ Å

is the confirmation of the spherical aggregates. The temperature has no influence on the change of structure of all micellar solutions. The small micelles are spherical and can grow up to maximum radius of fully extended molecule tail. Nevertheless, their growth can be accompanied with a shape deformation (to prolate ellipsoid and then cylinder or to oblate ellipsoid turning into disc).

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