

Solution Properties of Gemini Surfactant of Decanediyl-1-10-bis (dimethyltetradecylammonium bromide) in Aqueous Medium

Hiomichi Nakahara, Atsuko Hasegawa, Seina Uehara, Hideo Akisada and Osamu Shibata*

Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7 Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan

Abstract: The solution properties of a typical gemini surfactant of decanediyl-1-10-bis (dimethyltetradecylammonium bromide) (abbrev. 14-10-14,2Br⁻) were examined in an aqueous medium at temperatures of 288.2, 298.2, and 308.2 K. The characterization was performed by employing surface tension measurements, electrical conductivity measurements, steady-state fluorescence quenching (SSFQ), and dynamic light scattering (DLS). The surface tension was measured with the drop volume method, in which an improved tensiometer was used and the experimental operation was modified. The resultant data were well reproducible and the equilibrium adsorption time after producing the droplet onto the tip of the capillary was on the order of minutes. In addition, the critical micelle concentration obtained from the surface tension data is in good agreement with that obtained from the conductivity data. Using the conductivity variation as a function of surfactant concentration, the thermodynamic parameters of micellization were calculated. Furthermore, the SSFQ method suggests a small and constant aggregation number, irrespective of temperature. The formation of small-size micelles was also confirmed by DLS measurements.

Key words: gemini surfactant, 14-10-14,2Br⁻, surface tension, conductivity, steady-state fluorescence quenching, dynamic light scattering

1 INTRODUCTION

Gemini or dimeric surfactants consist of two hydrophobic chains and two hydrophilic headgroups in a molecule. The hydrophobic chains are covalently connected at the level of or in close vicinity to the headgroups by a spacer^{1,2)}. Gemini surfactants have gained much interest over the past few decades because of their much lower critical micelle concentration (cmc), which is 1–2 orders of magnitude lower than that of conventional monomeric surfactants. Gemini surfactants also exhibit superior surface activity, better lime-soap dispersing, more useful viscoelastic properties, and better wetting properties than conventional monomeric surfactants^{3–6)}. The most studied gemini surfactant with regard to biological activities and physicochemical properties is the cationic type m - s - m ,2Br⁻, which has two quaternary ammonium species [C_mH_{2m+1}N⁺(CH₃)₂] linked by a hydrocarbon spacer (–C_sH_{2s}–). The impact of hydrophobic chain length and structure of the spacer on the adsorption and aggregation behavior of gemini surfac-

tants has been studied in detail^{3–5)}. Generally, in an aqueous medium, the combination of m and s produces unique or unusual aggregation morphologies such as spherical and elongated micelles^{7–9)}. The m - s - m ,2Br⁻ cationic surfactants show a stronger biological activity than the corresponding monomers and are consequently more active on both a molar and a weight scale in terms of germicidal activity¹⁰⁾. In addition, the gemini surfactants have potential as DNA transfection and drug delivery agents^{11–15)}. To our knowledge, however, there is no report on the solution properties of 14- s -14,2Br⁻, although homologous surfactants of m - s - m ,2Br⁻ with $m = 12$ and 16 have been investigated, as mentioned above.

The aqueous solution behavior of gemini surfactants has been investigated employing a variety of methods such as tensiometry^{1, 4, 10)}, conductivity^{10, 16)}, spectroscopy^{17, 18)}, neutron scattering^{19, 20)}, and electron microscopy^{8, 21)}, similar to the methods used to investigate typical monomeric surfactants. One of the most fundamental and con-

*Correspondence to: Osamu Shibata, Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7 Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan

E-mail: wosamu@niu.ac.jp

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venient methods is tensiometry, which allows us to determine the cmc, the surface excess concentration, and the occupied area per molecule. The change in surface tension as a function of surfactant concentration is usually measured with the Wilhelmy plate method, the Du Nöuy ring method, or the drop volume method. With regard to the measurements for gemini surfactant solutions, the drop volume method has been employed to a lesser extent. It is well known that with the drop volume method, it is not easy to measure the surface tension of gemini surfactant solutions at concentrations below the cmc. At these concentrations, the value of the surface tension obtained is significantly smaller than the correct value, and the subsequent droplets measured do not provide reproducible data. This is considered to be caused by the capillary tip being coated with a slight amount of the gemini surfactant during or after measurement of the first drop. For this reason, many researchers in surface and colloid sciences have utilized the Wilhelmy plate method^{22–25)} and the Du Nöuy ring method^{26–29)} rather than the drop volume method to measure the surface tension of gemini surfactant solutions³⁰⁾. However, it often takes a few hours to obtain the equilibrium surface tension of gemini surfactant solutions below the cmc with the Wilhelmy method. Considering the fact that gemini surfactants are also ionic surfactants, the lengthy adsorption time is problematic.

We report the solution behavior of a gemini surfactant of the bis-quaternary dimeric surfactant (14-10-14,2Br[−]) in an aqueous medium at 288.2, 298.2, and 308.2 K. The surface tension measurement was carried out employing the drop volume method with a modified apparatus (see Experimental section) for a wide range of surfactant concentrations, including quite low concentrations, where the surface tension is almost the same as that of pure water. In addition, the electrical conductivity of the solutions was measured in order to check the cmc value obtained from the drop volume method (DVM). As further characterization of the 14-10-14,2Br[−] micelles, the mean aggregation number and hydrodynamic diameter were determined with steady-state fluorescence quenching (SSFQ) and dynamic light scattering (DLS), respectively.

2 EXPERIMENTAL

2.1 Materials

Decanediyl-1-10-bis(dimethyltetradecylammonium bromide) [$C_{14}H_{29}(CH_3)_2N(CH_2)_{10}N(CH_3)_2C_{14}H_{29}$]Br₂ (abbr. 14-10-14,2Br[−]) was synthesized via a procedure reported previously³⁾. The obtained crude crystal of 14-10-14,2Br[−] was purified by thrice recrystallization from an acetone/ethanol mixed solvent (99/1, v/v). The identification was checked by ¹H NMR, ¹³C NMR (JNM-AL400, Jeol, Tokyo, Japan), and elemental analysis: C, 63.89(64.43); H, 11.59

(11.59); N, 3.51(3.58), where the values in parentheses are the calculated ones. Pyrene (98%), used as a fluorescent probe, and 1-hexadecylpyridinium chloride (cetylpyridinium chloride, abbr. CPC), used as a quencher, were purchased from nacalai tesque (Kyoto, Japan) and Aldrich (St. Louis, MO), respectively. Pyrene and CPC were purified by thrice recrystallization from benzene and an acetone/ethanol mixed solvent (8/1, v/v), respectively. The water used throughout the syntheses and measurements was thrice-distilled water (surface tension of 71.99 mN m^{−1} at 298.2 K and electrical resistivity of 18 MΩcm).

2.2 Methods

2.2.1 Surface tension (DVM)

The surface tension (γ) of the surfactant solutions was determined at 288.2, 298.2, and 308.2 ± 0.01 K by using a drop volume tensiometer (YHC-2010, YTS, Tokushima, Japan). This tensiometer measures the volume of a drop detaching from a glass capillary of known diameter (~2.0 mm). The head of the capillary was siliconized with dimethylpolysiloxane (Siliconize L-25, Fuji Systems Corp., Tokyo) and then the capillary tip was ground with sandpaper to remove the adhesive materials. The surfactant solutions were put into the capillary with a Hamilton syringe (1.0 mL) under computer control. After equilibration of the apparatus with a thermostat, the following procedures were done as a first run to measure the surface tension. First, the first and the second droplets were successively dropped at high speed to remove a coated film of the surfactant in the tip of the capillary. Then, the third droplet was used for the surface tension measurement. With regard to the measurement, 60–90% of the total drop volume was produced depending on surfactant concentration. After formation of the droplet, the droplet was allowed 1–3 min to attain further adsorption equilibrium, and then the total volume was determined by continuing to slowly push the droplet out. This procedure was repeated at least five times per loading of surfactant solutions into the syringe (one cycle). In this study, each γ value of surfactant solutions is expressed as the mean of three cycles. The temperature was kept constant within ± 0.01 K by means of a thermostat chamber. The experimental error for the surface tension was ± 0.05 mN m^{−1}.

2.2.2 Electrical conductivity

The specific conductivity (κ) of the surfactant solution was measured as a function of the concentration using a conductivity meter (CM-30R, DKK-TOA Corp., Tokyo, Japan). The surfactant concentration was successively increased by a stepwise addition of 1 mL of the concentrated 14-10-14,2Br[−] solution into 30–50 g of pure water that had been placed in a glass cell which is immersed in a thermostat bath. The temperature was kept constant to within ± 0.01 K using a modified thermostat system (YHC-2000, YTS). After the respective injections, the solution was

stirred to ensure homogeneous mixing and then subjected to the conductivity measurement. The cell constant was 104.4 m⁻¹. The conductivity measurements were carried out at temperatures of 288.2, 298.2, and 308.2 K. Measurements of a minimum of eight runs were made at each temperature. The data analysis was carried out with the software KaleidaGraph ver. 4.1 (Synergy Software, PA, USA).

2.2.3 Steady-state fluorescence quenching (SSFQ)

Fluorescence quenching of pyrene by CPC was monitored in a spectrofluorometer (Model FP-6200, Jasco, Tokyo, Japan). The pyrene concentration was low enough (1.0×10^{-6} M) to avoid excimer formation and the CPC concentration was varied from 1.0×10^{-5} to 1.5×10^{-4} M. The [probe]/[micelles] and [quencher]/[micelles] values were low enough to ensure Poisson distributions^{31–33}. The fluorescence spectra were measured at 288.2, 298.2, and 308.2 ± 0.1 K by a water-flow thermostat connected to the cell compartment. A fluorescence excitation wavelength of 335 nm was used. The emission spectra wavelength ranged from 350 to 500 nm and slit widths for both emission and excitation were fixed at 5 nm. The value of the fluorescence intensity of pyrene was chosen at a wavelength of 395 nm.

2.2.4 Dynamic light scattering (DLS)

DLS measurements were performed with a Zetaser Nano-S (Malvern Instrument Ltd., Worcestershire, UK) using a 5 mW He–Ne laser ($\lambda = 633$ nm). Prior to the measurement, all surfactant solutions were filtered through a 0.1 μ m pore-size membrane filter. The measurements were carried out at temperatures of 288.2, 298.2, and 308.2 ± 0.1 K. The measurements were repeated at least five times at each temperature. The apparent hydrodynamic diameter (d_H) of the surfactant micelles was calculated according to the Einstein–Stokes relation:

$$d_H = \frac{k_B T}{3\pi\eta D_0} \quad (1)$$

where D_0 is the diffusion coefficient extrapolated to zero concentration, k_B is the Boltzmann constant, T is the Kelvin temperature, and η is the viscosity of the medium.

3 RESULTS AND DISCUSSION

3.1 Surface tension

Plots of the surface tension (γ) versus the logarithm of the 14-10-14,2Br⁻ concentration (c in mM) at 288.2, 298.2, and 308.2 K are shown in Fig. 1. The γ values decreased slowly with increasing concentration up to ~0.01 mM and then decreased steeply as the concentration increased to the critical micelle concentration (cmc). Above the cmc, the values were relatively constant. The adsorption equilibrium time after producing a droplet on the capillary tip was less than 3 min for all concentrations. It is worthwhile to mention that the γ values can be accurately measured at

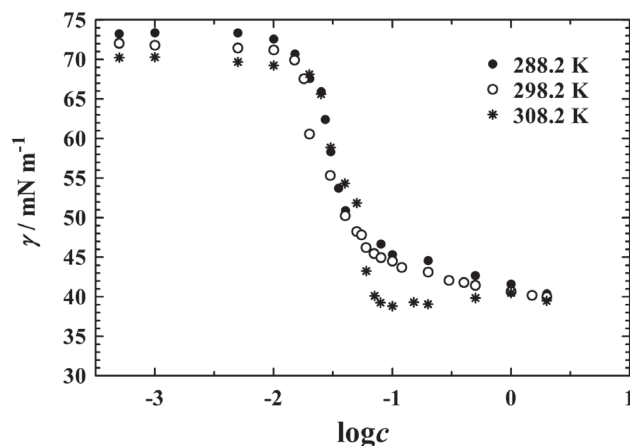


Fig. 1 Variation in surface tension with logarithm of surfactant concentration for 14-10-14,2Br⁻ at 288.2, 298.2, and 308.2 K.

lower concentrations near 0.01 mM. Generally, it is not easy to obtain such high γ values for gemini surfactant solutions using the Wilhelmy plate method^{34, 35}. By using the Gibbs adsorption equation (Eq. 2) and Eq. 3, several parameters were determined from the γ -log c plots for comparison to the parameters reported for *m-s-m*,2Br⁻: the cmc, the surface tension at the cmc (γ_{cmc}), the maximum surface excess concentration (Γ_{max}), and the minimum area per molecule (A_{min}) at the surface.

$$\Gamma_{max} = -\frac{1}{n \times 2.303RT} \left(\frac{\partial \gamma}{\partial \log c} \right)_T \quad (2)$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (3)$$

The value of n , the number of adsorption (ionic) species whose concentration at the interface changes with the surfactant concentration, is 2 or 3 for gemini surfactant solutions in the absence of an added electrolyte. In the present study, we calculated the value of Γ_{max} on the basis of $n = 3$, where complete dissociation of the surfactant and the two bromide counterions is assumed^{4, 25, 36, 37}. R is the gas constant and N_A is Avogadro's number. The resultant values of cmc, γ_{cmc} , Γ_{max} , and A_{min} are summarized in Table 1. The cmc value increased with increasing temperature due to the destruction of the water structure surrounding the alkyl chains, as well as to the improvement of the molecular motion of the surfactants. It has been reported that the

Table 1 Parameters Obtained from the Tensiometry (DVM).

T (K)	cmc (mM)	γ_{cmc} (mN m ⁻¹)	$10^6 \Gamma_{max}$ (mol m ⁻²)	A_{min} (nm ²)
288.2	0.0467	47.2	3.67	0.453
298.2	0.0555	44.9	2.46	0.674
308.2	0.0761	38.9	3.05	0.545

cmc values of homologous gemini surfactant solutions of 12-10-12,2Br⁻ and 16-10-16,2Br⁻ are 0.32–0.63 mM (at 298.2 K)^{3, 4, 29} and 0.027 mM (at 303.2 K)¹⁹, respectively. The cmc values here are included in the values between 12-10-12,2Br⁻ and 16-10-16,2Br⁻, which substantiates the reasonableness of the cmc values attained for the 14-10-14,2Br⁻ solutions. The γ_{cmc} value of 14-10-14,2Br⁻ is almost the same as that of 12-10-12,2Br⁻⁴). Interestingly, there is a significant difference in A_{min} between 14-10-14,2Br⁻ and 12-10-12,2Br⁻. This implies that the resultant values from the current study are more accurate than those reported previously. In this study, with the improved drop volume method, two droplets were successively dropped at high speed prior to the γ measurement so that the coated film on the capillary tip was removed. In a previous study, we reported the validity of the method using a typical anionic surfactant, sodium dodecyl sulfate (SDS), where one droplet was dropped before measurement³⁸). That is, use of the DVM here enabled us to easily measure the surface tension of gemini surfactant solutions similar to monomeric surfactant solutions.

3.2 Conductivity

The electrical conductivity (κ) for the 14-10-14,2Br⁻ solutions was measured to ensure the validity of the cmc value obtained from the DVM. The κ - c plots for the solutions in the temperature range from 288.2 to 308.2 K are shown in Fig. 2. The κ value shows a gradual increase with increasing temperatures. This is attributed to an incremental increase in the thermal energy of the molecule itself. It is well known that a break in the plot reflects the onset of micelle formation. Therefore, it is possible to estimate the cmc value of the surfactant from the intersection of two linear intercepts below and above the break. However, in this study, the break was somewhat unclear for the cmc determination, which implies either the formation of quite small micelles or the polydispersity of micelles. As a result, the former is the present case (see the latter section). The cmc is also defined as the surfactant concentration corresponding to the maximum variation in κ - c curves³⁹).

$$\left(\frac{d^3\kappa}{dc^3}\right)_{c=\text{cmc}} = 0 \quad (4)$$

The cmc values were determined at each temperature with Eq. 4 and the results are listed in Table 2. The cmc values

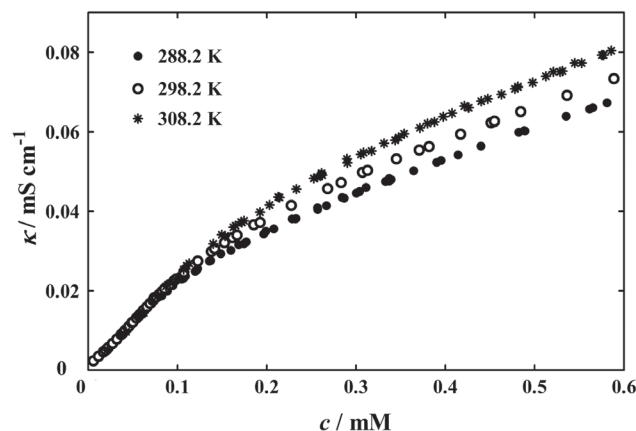


Fig. 2 Variation in electrical conductivity with surfactant concentration for 14-10-14,2Br⁻ at 288.2, 298.2, and 308.2 K.

obtained from the conductivity measurements are in good agreement with those obtained from the DVM (Table 1). This supports the accuracy of the γ measurement here. In addition, the degree of ionization of the 14-10-14,2Br⁻ micelles (α) was estimated from the ratio of slopes of the two intersecting lines below and above the cmc. The α values increased slightly with an increase in temperature. The values of 14-10-14,2Br⁻ correspond to those of 12-6-12,2Br⁻ ($\alpha = 0.33$ at 298.2 K) and 16-3-16,2Br⁻ ($\alpha = 0.32$ – 0.39 at 298.2 K)³). Furthermore, the standard Gibbs free energy of micellization (ΔG_m^0) for gemini surfactants with monovalent counterions is related to the cmc and α according to the following equation⁴⁰:

$$\Delta G_m^0 = RT \left(\frac{3}{2} - \alpha \right) \ln X_{\text{cmc}} \quad (5)$$

where X_{cmc} is the cmc value expressed in mole fraction. The standard enthalpy of micellization (ΔH_m^0) can be derived from the ΔG_m^0 values as a function of temperature by applying the Gibbs–Helmholtz equation (Eq. 6).

$$\Delta H_m^0 = \left[\frac{\partial(\Delta G_m^0/T)}{\partial(1/T)} \right]_P \quad (6)$$

In this study, the variation of $\Delta G_m^0/T$ against $1/T$ was fitted with a first-order approximation and the ΔH_m^0 value was subsequently estimated from the slope. Then, the standard entropy of micellization (ΔS_m^0) was calculated from the following relation (Eq. 7):

Table 2 Parameters Obtained from the Conductivity Measurements.

T (K)	cmc (mM)	α	ΔG_m^0 (kJ mol ⁻¹)	ΔH_m^0 (kJ mol ⁻¹)	$-T\Delta S_m^0$ (kJ mol ⁻¹)
288.2	0.0586	0.33	-38.7	-29.7	-8.97
298.2	0.0600	0.33	-39.9	-29.7	-10.1
308.2	0.104	0.34	-39.3	-29.7	-9.58

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (7)$$

These thermodynamic parameters for 14-10-14,2Br⁻ are presented in Table 2. The ΔH_m^0 value indicates that the micellization process is exothermic. The value is also larger in magnitude than an entropy term ($-T\Delta S_m^0$), which means that the contribution of ΔH_m^0 to ΔG_m^0 is dominant for the micellization as compared to ΔS_m^0 . Thus, it is suggested that the micelle formation process for 14-10-14,2Br⁻ is enthalpy-driven in the temperature region treated here.

3.3 Aggregation number of micelles

The mean aggregation number (N_{agg}) of 14-10-14,2Br⁻ micelles in the aqueous solution was determined by the fluorescence quenching method using pyrene as a fluorescent probe and CPC as a quencher. Shown in Fig. 3 are the fluorescence spectra of pyrene in the 14-10-14,2Br⁻ solution (2.0 mM) with and without different amounts of CPC. The spectrum intensity decreased with increasing CPC concentrations. Herein, the value of the fluorescence intensity of pyrene was chosen at a wavelength of 395 nm. The peak shift was not caused by the CPC addition. The N_{agg} value can be calculated from the slope of the plot of $\ln(I_0/I)$ versus CPC concentration [CPC] in the 14-10-14,2Br⁻ solution according to the following equation^{31-33,41}:

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{agg}[CPC]}{c - cmc} \quad (8)$$

where I_0 and I are the fluorescence intensities in the absence and presence of a quencher, respectively. The main assumptions of this method are as follows. First, the quencher and probe are completely solubilized in the micelle phase. Second, the random distribution of the probe and quencher in the micelles obeys a Poisson distribution. The addition of CPC gradually decreased the fluorescence intensity of pyrene (Fig. 3). Figure 4 shows the plots of the logarithm of the pyrene intensity ratio (I_0/I) versus the CPC concentration at 288.2, 298.2, and 308.2 K for the 14-10-14,2Br⁻ solution. The $\ln(I_0/I)$ value indicates a good linear relationship with the CPC concentration. Thus, according to Eq. 8, N_{agg} was calculated to be 11 ± 1 for all temperatures, where the cmc values obtained from both the DVM and conductivity are utilized (Tables 1 and 2). The value of N_{agg} is not temperature-dependent, which is similar to the case for 12-8-12,2Br⁻ micelles⁸). The N_{agg} values of 14-10-14,2Br⁻ micelles are smaller than those of 12-7-12,2Br⁻, 12-9-12,2Br⁻, and 12-11-12,2Br⁻ micelles ($N_{agg} = 21, 18, \text{ and } 18$, respectively)⁴²), which suggests the formation of smaller micelles for 14-10-14,2Br⁻. It has been pointed out that the steady-state fluorescence quenching (SSFQ) method generates smaller values of N_{agg} due to the microviscosity of the aggregates as compared to the time-resolved fluorescence quenching (TRFQ) method⁴³). In addition, it is widely accepted that an increase in gemini surfactant concentration causes incremental increases in the

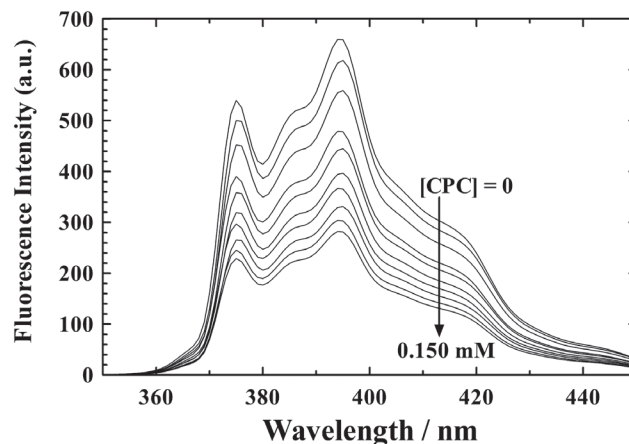


Fig. 3 Fluorescence spectra of pyrene (1.0×10^{-3} mM) at 298.2 K in 2.0 mM 14-10-14,2Br⁻ aqueous solutions in the presence of CPC; [CPC] = 0, 0.010, 0.030, 0.050, 0.065, 0.085, 0.100, 0.115, 0.135, and 0.150 mM.

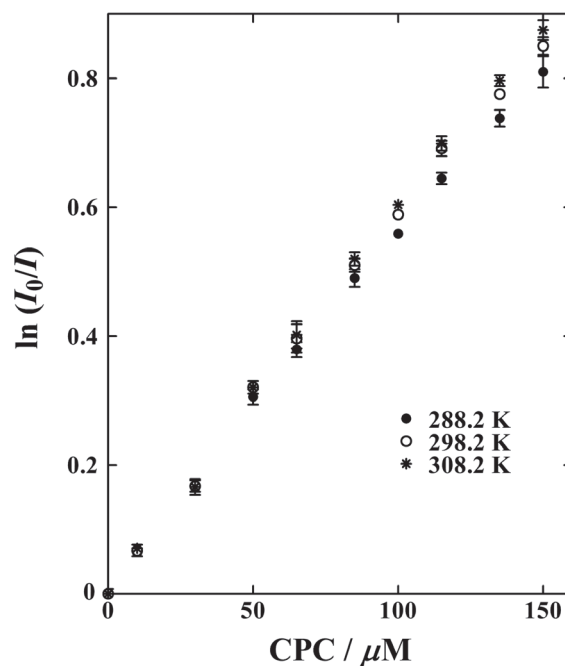


Fig. 4 Plots of $\ln(I_0/I)$ for pyrene (1.0×10^{-3} mM) against CPC concentration in 2.0 mM 14-10-14,2Br⁻ aqueous solutions at 288.2, 298.2, and 308.2 K.

N_{agg} value with regard to both methods, thus resulting in a transition of micellar shapes from spherical to elongated structures⁴²). It has also been determined from a transmission electron microscopy that the micellar shape depends strongly on the spacer length (s)⁸). In the present study, the N_{agg} value of 14-10-14,2Br⁻ micelles ($N_{agg} = \sim 11$) corresponds to 22 tetradecyl chains per micelle. Considering the

N_{agg} value of tetradecyltrimethylammonium bromide (TTAB) micelles in an aqueous medium ($N_{\text{agg}} = 58 - 60$ from SSFQ)^{43, 44}, the spacer moiety ($s = 10$) in 14-10-14,2Br⁻ was found to contribute strongly to the hydrophobic interaction for micelle formation. The N_{agg} value of 14-10-14,2Br⁻ micelles was also considerably smaller as compared to that calculated from Tanford's equation⁴⁵ for spherical micelles with a hydrophobic core radius equal to the length of a tetradecyl chain in the fully stretched conformation ($N_{\text{agg}} = 73$). Herein, the very low concentration of 2 mM was selected for the N_{agg} determination and consequently quite small N_{agg} values were obtained. These results suggest the micellar shape of 14-10-14,2Br⁻ to be spherical, which is discussed in a latter section.

3.4 Hydrodynamic diameter of micelles

The 14-10-14,2Br⁻ solution was characterized with dynamic light scattering (DLS) to elucidate the aggregation behavior. The hydrodynamic diameter (d_{H}) of 14-10-14,2Br⁻ micelles is plotted as a function of surfactant concentration and temperature in Fig. 5. All DLS results indicated a monodispersed size distribution with only one peak for all concentrations. The d_{H} values decreased with increasing surfactant concentrations. At 1.0 mM, the diameters and widths of the micelles were somewhat larger and broader than micelles at the other concentrations, respectively. This means that the micelles were unstable in terms of the kinetics of micelle formation due to the low micellar concentration. As the concentration increased further, the micellar size increased from 2 to 5 nm. In addition, the d_{H}

values increased with increasing temperature for all the concentrations. Considering the N_{agg} values given in the previous section, it is suggested that the hydration of 14-10-14,2Br⁻ micelles is accelerated by the increase in temperature. The size of the micelles at 2.0 mM was used to analyze the relation of d_{H} with N_{agg} . At 288.2 K, the micellar size can be estimated simply from the d_{H} value as $\sim 15 \text{ nm}^3/\text{micelle}$ under the assumption of spherical micelles. On the other hand, according to Tanford's equation⁴⁵, the volume occupied by one tetradecyl chain is $\sim 0.40 \text{ nm}^3$. Using the rough assumption of no spacer in 14-10-14,2Br⁻ and an N_{agg} value of 11, the micellar size was determined to be $\sim 8.9 \text{ nm}^3/\text{micelle}$. The difference in size between the two volumes is clearly attributed to the hydration of water molecules and the spacer conformation.

4 CONCLUSION

A typical gemini surfactant of 14-10-14,2Br⁻ was characterized in an aqueous medium at temperatures of 288.2, 298.2, and 308.2 K. The cmc values obtained from tensiometry with a modified apparatus employing the drop volume method (DVM) agree well with those from the conductivity. Thus, it is indicated that the drop volume method enables us to easily measure the surface tension of gemini surfactant solutions, similar to monomeric surfactant solutions. In addition, the N_{agg} value of the 14-10-14,2Br⁻ micelles was determined with the steady-state fluorescence quenching method to be ~ 11 , regardless of temperature. The DLS results also support the formation of micelles with a very small diameter above the cmc. These analyses suggest that the shape of the micelles is predominantly a sphere at low surfactant concentrations. The present results provide information on the design of gemini surfactants, including other types of surfactants with functionalized spacers.

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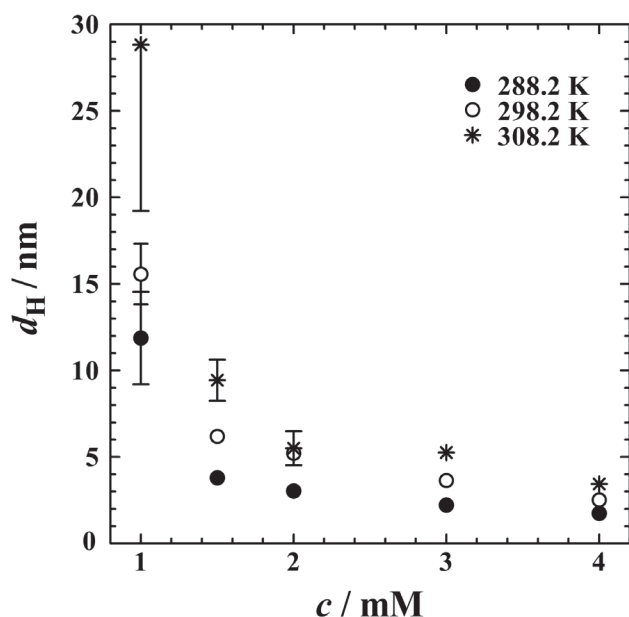


Fig. 5 Variation in hydrodynamic diameter (d_{H}) with surfactant concentration for 14-10-14,2Br⁻ at 288.2, 298.2, and 308.2 K.

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