Physicochemical Evaluation of Micellar Solution and Lyotropic Phases Formed by Self-Assembled Aggregates of Morpholinium Geminis

Avinash Bhadani,* Ananda Kafle,† Setsuko Koura,‡ Kenichi Sakai,‡ Hideki Sakai,† and Masahiko Abe*†

†Research Institute for Science and Technology and Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
‡Department of Applied Chemistry, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-8588, Japan

Supporting Information

ABSTRACT: The micellar solution and the lyotropic liquid crystalline phases formed by gemini surfactants containing morpholinium headgroups are investigated for their self-aggregation and physicochemical properties in water. These gemini surfactants demonstrated good surface activity because they are able to undergo micellization at lower concentration and form nanosized micellar aggregates in dilute aqueous solution. The binary mixture of the morpholinium gemini surfactant—water system is investigated over a wide range of concentrations. The micellar solution of the morpholinium gemini surfactants demonstrated Newtonian fluidlike behavior between 10 and 50 wt % as the observed viscosities were independent of the applied shear rate. At higher concentration, morpholinium geminis formed self-assembled lyotropic phases in water. These liquid crystalline phases were characterized by small-angle X-ray scattering and polarized optical microscopy techniques.

1. INTRODUCTION

Gemini surfactants are being increasingly investigated for various applications ranging from materials science to biomedical sciences.¹ These surfactants demonstrate superior physicochemical properties compared to monomeric surfactants and are able to self-aggregate into micelles at relatively lower concentration compared to their monomeric analogues.¹ Cationic geminis are an important category of surfactants containing two positively charged headgroups and two hydrophobic tails often connected by a spacer.² These surfactants are able to interact with a wide variety of molecules and materials in nature and possess unique characteristics.³ They are able to interact with a wide range of biomolecules/bioactive molecules such as peptides,⁴ proteins,⁵,⁶ drugs,⁷ and nucleic acids⁸ and often find applications as a drug delivery agent, nonviral gene delivery vectors, and an antifungal and antimicrobial agent.⁹,¹⁰ Because of their ability to self-aggregate in water, they are used as a soft template for the synthesis of hollow inorganic materials¹¹ and for the stabilization of microemulsions.¹² In recent years, several functionalized derivatives of these cationic gemini surfactants have been developed, containing different types of cationic headgroups. Among the various structural derivatives of these gemini surfactants, the conventional bisquaternary ammonium² is widely investigated along with the heterocyclic headgroup containing gemini cationic surfactants, that is, pyridinium,¹³⁻¹⁶ imidazolium¹⁷⁻¹⁹ pyrrolidinium²⁰⁻²¹ and piperidinium.²⁶,²⁷ Morpholinium gemini surfactant is another important category of heterocyclic cationic gemini surfactants.²⁸,²⁹ Recent reports have established their effectiveness as a corrosion inhibitor³⁰ and a drug-solubilizing agent.³¹ These surfactants are unique compared to other categories of cationic gemini surfactants. In our previous studies, while investigating gemini surfactants with different headgroups, we found that the gemini surfactant with the morpholinium headgroup possesses unique physicochemical characteristics combined with the exceptional water solubility at low temperature and high surfactant concentration.³² Unlike other conventional gemini surfactants, these morpholinium geminis are capable of forming hydrogen bonding with water because of the presence of pairs of nonbonding electrons on the O atom present in morpholinium headgroups. Thus, the polar morpholinium headgroups capable
of forming hydrogen bonds with water are able to get solubilized at relatively lower temperature in water. Further, self-aggregation and micellization properties of only limited structural varieties of morpholinium geminis are reported in the literature, and there is limited information about their phase and rheological behaviors. This prompted us to further investigate new structural derivatives of morpholinium gemini surfactants in detail. In the present paper, we have synthesized new ester-functionalized morpholinium gemini surfactants via a two-step synthetic process and characterized these new gemini surfactants by spectroscopic techniques. These gemini surfactants were investigated for their self-aggregation properties by surface tension, conductivity method, and dynamic light scattering (DLS) method. Further, the concentration-dependent viscosity behavior of these surfactants was investigated in aqueous solution. These surfactants were able to form lyotropic liquid crystalline phases at higher concentration, which was investigated by small-angle X-ray scattering (SAXS) and polarized optical microscopy (POM) techniques.

2. RESULTS AND DISCUSSION

2.1. Characterization of Morpholinium Gemini Surfactants. Two different types of morpholinium gemini surfactants containing 12-hydrocarbon tails—4,4′-(hexane-1,6-diylbis(oxy))bis(2-octadecylmorpholin-4-ium) dibromide ([C12MOR(6)C12MOR]2Br) and 14-hydrocarbon tail—4,4′-(hexane-1,6-diylbis(oxy))bis(2-octadecylmorpholin-4-ium) dibromide ([C14MOR(6)C14MOR]2Br) (Figure 1) were synthesized.

![Molecular structure of morpholinium gemini surfactants](image)

Figure 1. Molecular structure of morpholinium gemini surfactants synthesized and investigated.

The molecular structure of the morpholinium gemini surfactants was confirmed by 1H and 13C NMR spectroscopy and high-resolution mass spectroscopy (HRMS). The 1H NMR spectra for the surfactants confirmed total 82 protons for [C12MOR(6)C12MOR]2Br and 90 protons for [C14MOR(6)C14MOR]2Br. Each individual proton signal was assigned based on confirmation by 2D heteronuclear chemical shift correlation and 2D correlation spectroscopy experiments. The signal for methylene protons present between ester functionality and positively charged nitrogen of the morpholinium headgroup (−COOCH₂N⁺) was observed as a singlet between δ 5.33 and 5.38 ppm for the morpholinium gemini surfactants. The protons adjacent to the positively charged nitrogen which are part of the heterocyclic ring are diastereotopic in nature and were observed as two independent signals at δ 4.47–4.53 ppm for −CH₂H₂N⁺CH₂H₂− and at δ 3.80–3.84 ppm for −CH₂H₂N⁺CH₂H₂−. The latter signals were observed along with the protons directly attached to the quaternary nitrogen, which are part of the hydrophobic alkyl chain length (−CH₂CH₂N⁺). The methylene protons of the heterocyclic headgroup adjacent to the oxygen atom are also diastereotopic in nature and were observed as two independent signals at δ 4.34–4.36 ppm for −CH₂H₂OCH₂H₂− and at δ 3.97–4.02 ppm for −CH₂H₂OCH₂H₂−. The signals for the methylene protons adjacent to ester functionality which are part of spacer units were observed as triplet at δ 4.26 ppm, whereas the signals for the other methylene protons of spacer units were observed between δ 1.52 and 1.72 ppm. In 13C NMR spectra, the characteristic signals for the carbonyl carbon of the ester group were observed at δ 164.38 ppm for [C12MOR(6)C12MOR]2Br and at 164.31 ppm for [C14MOR(6)C14MOR]2Br. The molecular structure of the morpholinium gemini surfactants was further confirmed by the HRMS. The observed values for the parent ion peak for both surfactant molecules closely matched with the calculated values. The purity of both the new surfactants was confirmed by the elemental analysis.

2.2. Surface Tension Measurements. The surfactant properties of the morpholinium gemini surfactants were determined by surface tension measurements. The length of the hydrophobic tail influences the surface properties of these surfactants. The critical micelle concentration (cmc) values of these surfactants decrease with increase in hydrophobic alkyl chain length (Table 1). Figure 2 shows the surface tension versus log of concentration plot of [C12MOR(6)C12MOR]2Br and [C14MOR(6)C14MOR]2Br at 25 °C.

The cmc values of these ester-functionalized morpholinium geminis are lower compared to their structural analogue with a...
The affinity to reduce surface tension at cmc ($\gamma_{\text{cmc}}$) by this group of surfactants significantly varies with increase in hydrophobic alkyl chain length. The $\gamma_{\text{cmc}}$ values of the new gemini morpholinium surfactants [C12MOR(6)C12MOR]2Br and [C14MOR(6)C14MOR]2Br are comparatively lower compared to those of previously reported gemini morpholinium surfactants. Generally, the $\gamma_{\text{cmc}}$ values decrease with increase in hydrophobic alkyl chain length for the conventional surfactants. However, the $\gamma_{\text{cmc}}$ values observed for the ester-functionalized gemini morpholinium surfactants increase with increase in hydrophobic alkyl chain length, and consequently, the gemini surfactant with longer hydrophobic tail (14 carbon) demonstrates less efficiency in reducing the surface tension of water compared to its analogue with smaller hydrocarbon tail (12 carbon). Recent report suggests that the unconventional diversely functionalized gemini surfactants containing polar ester, amide, and hydroxyl groups behave differently, and the affinity to reduce surface tension generally decreases with increase in hydrophobic alkyl chain length for these groups of gemini surfactants. Similar trend has been reported for the amide-functionalized cationic surfactants constituting morpholinium headgroups as the affinity to reduce surface tension drastically decreases with increase in hydrophobic alkyl chain length. Li et al. have recently investigated and explained the observed trend of increasing $\gamma_{\text{cmc}}$ and $A_{\text{min}}$ values with increasing hydrophobic alkyl chain length for gemini surfactants based on the detailed analysis by neutron reflectometry. The investigation suggests that the anomalous behavior for the observed surface tension trend for gemini surfactants is probably due to poor packing of the gemini side chains between adjacent molecules. The longer the side chain, the more they interfere with each other and thus are less effective in reducing the surface tension at the air–water interface. Recent report on quaternary ammonium gemini surfactants containing multiple polar functional groups has also confirmed the affinity of these surfactants to form hydrogen bonding in aqueous solution. The observed $\gamma_{\text{cmc}}$ trend for the new ester-functionalized gemini morpholinium surfactants is in accordance with the trend observed for the functionalized gemini surfactants containing polar functional groups and may also be attributed to the affinity of these types of gemini surfactants to form a hydrogen-bonding network in water. Such types of interactions combined with poor packing of gemini side chains may significantly influence the overall dynamics of the system, thereby affecting the self-aggregation and physicochemical properties.

The maximum surface excess concentration at the air–water interface, $\Gamma_{\text{max}}$ is calculated by applying the Gibbs adsorption isotherm equation

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left( \frac{d\gamma}{d \log C} \right)_T$$  \hspace{1cm} (1)

where $\gamma$ denotes the surface tension, $R$ is the gas constant, $T$ is the absolute temperature, and $C$ is the surfactant concentration. $n$ is a constant which depends on the number of species constituting the surfactant which are adsorbed at the air–water interface. The value of $n$ for gemini surfactants is generally considered to be 3. However, recent investigation has shown that the use of $n = 3$ in eq 1 can lead to area per molecule that is unrealistically large relative to the molecular size and high surface activity of the geminis. Neutron reflectometry studies and surface potential have shown that $n$ is a variable depending upon the hydrophobic alkyl chain length. We in the current studies have calculated the values of $\Gamma_{\text{max}}$ and $A_{\text{min}}$, considering $n$ to be 2 and 3. The area occupied per surfactant molecule ($A_{\text{min}}$) at the air–water interface is obtained by using the following equation

$$A_{\text{min}} = 1/N \Gamma_{\text{max}}$$  \hspace{1cm} (2)

where $N$ is Avogadro’s number and $A_{\text{min}}$ is in square nanometer. The values of $\Gamma_{\text{max}}$ and $A_{\text{min}}$ are shown in Table 1. The $A_{\text{min}}$ values of the morpholinium gemini surfactant increase with the increase in hydrophobic alkyl tail length. Generally, the $A_{\text{min}}$ value decreases with increase in hydrophobic alkyl chain length for conventional monomeric quaternary ammonium surfactants. However, anomalous behavior is evident for gemini surfactants as they demonstrate the ability to form premicellar aggregates. As the electrical conductance varies with increasing surfactant concentration, the molar conductivity when plotted against $\sqrt{C}$ gives significant information about the presence of the existence of premicellar aggregates in the surfactant solution. Such plot shows a small upward curvature or a maximum if the premicellar aggregates are formed in solution because the equivalent conductivity of small aggregates is larger than the sum of the equivalent conductivities of the ions constituting it. The plot of molar conductivity versus $\sqrt{C}$ for the gemini morpholinium surfactants having a similar hydrophobic tail and spacer units and conventional quaternary ammonium gemini surfactants containing multiple polar functional groups has also confirmed the above observation.

**Figure 2.** Surface tension vs log C plot for the morpholinium gemini surfactants.
surfactant indicates the absence of premicellar aggregates for [C12MOR(6)C12MOR]2Br containing 12-carbon hydrophobic tail, as the maximum is absent in this case (see Figure S5, Supporting Information). However, the gemini morpholinium surfactant [C14MOR(6)C14MOR]2Br containing 14-carbon tail demonstrated some peculiarities at lower concentration, and maximum is observed confirming the existence of premicellar aggregates in the surfactant solution (see Figure S6, Supporting Information). Hence, [C14MOR(6)C14MOR]-2Br has lower A_{min} value compared to [C12MOR(6)-C12MOR]2Br. The observed trend for A_{min} values is also supported by the fact that the gemini surfactants containing longer hydrophobic alky alkanoyl chain demonstrate poor packing at the air–water interface.41 The in-depth analysis of gemini surfactants by neutron reflectometry studies has recently established that the gemini surfactants containing longer hydrocarbon tail demonstrate poor packing of the gemini side chains between adjacent molecules.41

2.3. Conductivity Measurements. The micellar solution of morpholinium gemini surfactants was further evaluated by conductivity measurements. The classical method adopted to determine the cmc values from conductivity data involves intersecting the lines fitted in the diluted and concentrated regions before and after the cmc. This method gives independence in selection of the point denoting cmc value, and hence, notable errors can occur in determining the cmc values. To overcome this limitation, we adopted a mathematical procedure proposed by Carpena et al. to determine the cmc values of the morpholinium gemini surfactants.45,46 This procedure is based on the assumption that the first derivative of specific conductivity versus concentration is a Boltzmann-type sigmoidal function

$$f(x) = \frac{A_1 - A_2}{1 + e^{-x/\Delta x}} + A_2$$  \hspace{1cm} (3)

where $A_1$ ($A_2$) is the asymptotic value for small (large) values of the surfactant concentration, $x_0$ is the center of the sigmoidal curve (central point of the transition), and $\Delta x$ is the width of the transition. The integration of eq 3 gives the following equation

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln \left( \frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right)$$  \hspace{1cm} (4)

where $F(0)$ is the value of specific conductivity when $x$ is 0 and $A_1$ and $A_2$ are the slopes obtained in the premicellar and postmicellar segments, respectively. Equation 4 is obtained by performing the integration of a Boltzmann-type sigmoidal function shown in eq 3. Figure 3 shows standard specific conductivity versus concentration plot and the plot derived using the mathematical procedure proposed by Carpena et al. Similarly, the above-mentioned method is used for deriving the cmc values for [C14MOR(6)C14MOR]2Br; however, the complexities arising due to the formation of premicellar aggregates result in uneven sigmoid plot as the equivalent conductivity of small premicellar aggregates formed below cmc value is always larger than the sum of the equivalent conductivities of the ions constituting it (see Figure S7, Supporting Information).

The cmc values of the morpholinium gemini surfactants determined by the conductivity methods slightly differ from those determined by the surface tension experiments (Table 1). Depending on the nature of the surfactant under investigation, the determined cmc values may differ when evaluated by two different techniques.47,48 Such behavior has been often observed for different types of cationic gemini surfactants and has been previously reported by several research groups.36,43,49,50 Differences in the observed cmc values when evaluated by different techniques have been attributed to the affinity to form premicellar aggregates by the surfactants in aqueous solution.48,49 We in our current studies have found that [C14MOR(6)C14MOR]2Br containing 14-carbon tail is able to form premicellar aggregates. However, unlike [C14MOR(6)C14MOR]2Br, [C12MOR(6)C12MOR]2Br containing 12-carbon tail is not able to form a premicellar aggregate, but yet irregularity is observed in the determined cmc values by two different techniques. However, the difference in cmc calculated by surface tension and conductivity can be explained on the basis of affinity of [C14MOR(6)C14MOR]-2Br to form premicellar aggregates at lower surfactant concentration in water. The provided explanation cannot justify the observed results for [C12MOR(6)C12MOR]2Br as this surfactant does not form premicellar aggregates. The traces of surface-active impurities if present in the surfactant sample may also significantly influence the observed cmc values by two different techniques. Although such impurities may be present in traces that cannot be detected in proton NMR, they can have marked influence on the observed cmc values observed by the surface tension technique. Often if traces of impurities are present in a surfactant sample, a minimum (dip) is observed in the surface tension versus surfactant concentration plots.51 However, we in our current studies are not able to observe a minimum for morpholinium gemini surfactants. Most recently, Thomas et al. summarized the limitations of surface tension experiments for evaluating cationic surfactants.50 It has been established that the observed surfactant properties may vary depending upon the method used for evaluating cationic surfactants. The positively charged cationic surfactants when evaluated by the Wilhelmy plate method generally demonstrate some peculiarities in calculated surface properties, and the observed results considerably differ when compared with the results evident from other techniques.52 The negative charge on the material (Pt–Ir or Pt) utilized for designing the Wilhelmy plate has significant influence on the observed results, especially when oppositely charged surfactants are evaluated using such materials. On the basis of the anomalous behavior of cationic surfactants when evaluated by this method, Thomas et al. concluded that the wetting may be
both incomplete and significantly vary with the concentration of a positively charged cationic surfactant essentially because of the adsorption of cationic surfactants on negatively charged solid surfaces. In such cases, the self-aggregation is generally lower than the cmc as the interaction of a surfactant with the surface is favorable. Thus, the observed difference in the determined cmc values by two different techniques may be explained on the basis of affinity of the morpholinium gemini surfactants to form an adsorbed layer on the oppositely charged Wilhelmy plate. The error in estimating the surfactant properties including cmc values becomes even more complicated if the surfactants demonstrate the ability to form premicellar aggregates. Given the widespread use of the Wilhelmy plate method for investigating the surfactant properties and the practical limitation of using this method for investigating cationic surfactants, it is more desirable to determine the cmc values of the cationic gemini surfactant under investigation by another technique (as calculated by the conductivity method in current studies).

The degree of counterion binding (β) which represents the bromide counterions associated with the micelles in aqueous solution is calculated from the slope values of the region before and after the cmc values, observed in the conductivity plot. The β values of gemini surfactants indicate the amount of counterions present in the Stern layer of micelles to counterbalance the electrostatic force that oppose micelle formation. The β values of the morpholinium gemini surfactant under investigation decrease with increase in hydrophobic tail length. Similar trend had been previously reported for the polar group containing thioether-functionalized gemini pyridinium surfactants, hydroxyl-functionalized gemini pyridinium surfactants, ether-functionalized gemini pyridinium surfactants, amide-functionalized quaternary ammonium gemini surfactants, and ester-functionalized gemini piperidinium surfactants, while no specific trend was observed for gemini imidazolium surfactants. The observed trend of decrease in β values with increasing hydrophobic alkyl tail length for gemini imidazolium surfactants can be explained on the basis of balance between the electrostatic interactions between the headgroups and the hydrophobic effect. However, most of the functionalized gemini surfactants containing a polar functional group may also interact with water molecules via hydrogen bonding, and the new dynamics resulting from the combination of electrostatic interactions and hydrogen bond formation in the presence of negatively charged counterions may influence the observed β values. For the ester-based morpholinium gemini surfactant [C12MOR(6)C12MOR]-2Br containing 12-carbon hydrophobic tail, more counterions are required to reduce the effective nuclear charge between the headgroups which eventually decreases the repulsion between the headgroups. With increasing tail length, the hydrophobic effect becomes a prominent factor and a lesser number of counterions are required to reduce the effective nuclear charge between the headgroups. Hence, [C14MOR(6)C14MOR]-2Br containing 14-carbon tail has lower β values compared to its analogue containing 12-carbon hydrophobic tail.

The Gibbs free energy for micellization (ΔGmic°) denotes the work done to transfer the surfactant monomers from the air–water interface to the micellar phase and is calculated from the following equation

$$\Delta G_{mic}^o = RT(0.5 + \beta) \ln X_{cmc}$$ (5)

where R is the gas constant (8.314 J mol⁻¹ K⁻¹); T is the absolute temperature; and Xcmc is the cmc in molar fraction, Xcmc = cmc/55.4, where cmc is in mol/L and 55.4 comes from 1 L of water corresponding to 55.4 mol of water at 25 °C. β is the degree of counterion binding to micelles. The calculated values of ΔGmic° are negative, indicating that the micellization is an energetically favorable process for the morpholinium geminis.

2.4. DLS Measurements. The hydrodynamic radius of the micelles formed by morpholinium gemini surfactants, [C12MOR(6)C12MOR]-2Br and [C14MOR(6)C14MOR]-2Br, is determined by the DLS technique.

Figure 4 shows the size distribution of micelles formed by the gemini surfactants for different surfactant concentrations determined at 25 °C. The results indicate that the aggregates with different sizes and morphologies are formed depending on the length of a hydrophobic tail. A narrow single peak is observed for the micellar solution of [C12MOR(6)C12MOR]-2Br at different surfactant concentrations (i.e., 5, 10, and 20 mM). The determined micelle size represented by the hydrodynamic radius slightly varied from 1.55 to 1.60 nm depending on the surfactant concentration under investigation for [C12MOR(6)C12MOR]-2Br. Two different size distribution peaks were observed for [C14MOR(6)C14MOR]-2Br at 5 and 10 mM concentration, whereas single peak was observed for the same surfactant at 2.5 mM surfactant concentration. The size of the first peak indicating the hydrodynamic radius varied from 1.81 to 1.83 nm, whereas the size of the second peak varied from 61.8 to 69.9 nm. The observed results indicate that the surfactants with a longer hydrophobic tail are able to form different structural morphologies by varying the concentration.

The new morpholinium gemini surfactants are able to self-aggregate into relatively smaller nanosized micelles at low surfactant concentration above their respective cmc values. The hydrodynamic radii of the micelles formed by morpholinum
gemi surfactants in aqueous solution are smaller compared to that of the conventional quaternary ammonium gemini surfactants,¹ and different categories of heterocyclic cationic gemini surfactants are piperidinium gemini surfactants,² imidazolium gemini surfactants,³ pyrroldinium gemini surfactants,⁴ and pyridinium gemini surfactants.⁵ The ability of gemini morpholinium surfactants to form nanosized micellar aggregates in dilute aqueous solution can be explored for several emerging technical application areas.

2.5. Viscosity Measurements. The viscosities of the micellar solution of morpholinium gemini surfactants were investigated by a rheometer for different concentrations at 25 °C. The aqueous micellar solution of both [C12MOR(6)-C12MOR]2Br and [C14MOR(6)C14MOR]2Br demonstrated Newtonian fluid behavior between 10 and 50 wt % because the observed viscosities are independent of the applied shear rate. The viscosities of the aqueous micellar solution depend on the concentration of dissolved gemini surfactants and the length of the hydrophobic alkyl tail.

The viscosities of the surfactant solution increase with increase in surfactant concentration as well as the increase in hydrophobic alkyl chain length. Figure 5 shows viscosity (η) versus shear rate (γ) plot for the aqueous micellar solution of the morpholinium gemini surfactants at 25 °C for various concentrations. There is a little difference in the observed viscosities for both the morpholinium gemini surfactants at lower surfactant concentration (10 wt %), and this difference becomes prominent at higher surfactant concentrations (i.e., 20–50 wt %). The micellar solution of the conventional quaternary ammonium gemini surfactant of \( m-s-m \) type generally demonstrates Newtonian fluid behavior at lower concentration (\( \leq 0.04 \text{ mol-L}^{-1} \) or \( \leq 2.46 \text{ wt} % \)) and is viscoelastic in nature at higher concentration.⁶ By contrast, the micellar solution of morpholinium gemini surfactants is Newtonian fluid up to surfactant concentration as high as 50 wt %. The Newtonian fluidlike behavior of the morpholinium gemini surfactant at high surfactant concentration can be attributed to the affinity of these surfactants to form hydrogen bonding with water. Recent reports suggest that the physicochemical and rheological properties of the micellar solution of cationic gemini surfactants containing polar functional groups may be influenced by the affinity of these molecules to form hydrogen bonding with water.⁷,⁸ Such surfactant solution may behave as Newtonian or non-Newtonian fluid depending upon the surfactant concentration and the temperature. Quaternary ammonium gemini surfactants behave as non-Newtonian fluid at higher surfactant concentration because these surfactants self-aggregate in aqueous solution above their cmc values into simple spherical micelles, which generally grow with increasing surfactant concentration and assume different forms such as rodlike micelles or flexible wormlike micelles and so forth.⁹ The formation of more complex entangled network structures changes the solution into a viscoelastic fluid; however, the concentrated aqueous solution of gemini morpholinium surfactants of surfactant concentration as high as 50 wt % does not demonstrate viscoelastic fluid nature. The observed nature of the morpholinium geminis can be explained on the basis of their ability to form nanosized micelles at dilute concentration which does not grow into wormlike micelles at higher concentration.

2.6. Phase Behavior of the Morpholinium Gemini Surfactant in Water. The phase behavior of the binary morpholinium gemini surfactant–water system was investigated at 25 °C. Figure 6 shows the phase diagram for the morpholinium gemini surfactant–H₂O system at 25 °C.

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**Figure 5.** Viscosity vs steady shear rate curves of (a) [C12MOR(6)C12MOR]2Br and (b) [C14MOR(6)C14MOR]2Br.

**Figure 6.** Phase diagram of (i) [C12MOR(6)C12MOR]2Br–H₂O system and (ii) [C14MOR(6)C14MOR]2Br–H₂O system at 25 °C. L₁ notifies micellar phase, H₁ notifies lyotropic hexagonal phase, and S notifies solid phase.
analyses. \([\text{C12MOR(6)C12MOR}]_2\text{Br}\) self-aggregates into \(\text{H}_1\) lyotropic phase between 68 and 96 wt %, whereas \([\text{C14MOR(6)C14MOR}]_2\text{Br}\) exists as \(\text{H}_1\) phase between 59 and 94 wt % in water. These \(\text{H}_1\) phases are observed as birefringent POM textures, which is characteristic for the lyotropic \(\text{H}_1\) phases (Figure 7).

The SAXS experiments further confirmed the existence of \(\text{H}_1\) phases for both the morpholinium gemini surfactants as the observed Bragg reflections correspond to hexagonal packing. The value of scattering vector \(q\) was found to be in the ratio \(q_1:/ q_2:/ q_3 = 1:\sqrt{3}:2\) for both the morpholinium gemini surfactants, confirming the existence of \(\text{H}_1\) phases. Figure 8a,b shows the SAXS patterns of the \([\text{C12MOR(6)C12MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) and \([\text{C14MOR(6)C14MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) systems observed for the \(\text{H}_1\) phases at 25 °C. The lattice parameter \((\alpha)\) is calculated from the first peak position according to the formula \((4\pi/\sqrt{3})/ q_{100}\). \(\alpha\) signifies the distance between the centers of two neighboring cylinders and can be directly calculated from the first Bragg peak \((q_1)\). The lattice parameter gradually decreases with increasing the surfactant concentration from 70 to 90% for the \([\text{C12MOR(6)C12MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) system and from 60 to 90% for the \([\text{C14MOR(6)C14MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) system. This gradual decrease of distance between the centers of two neighboring cylinders with increasing surfactant concentration can be attributed to the overall decrease of water channels in between the cylinder because of the decreasing percentage of water in the sample.68

Gemini morpholinium surfactants demonstrated a quite different binary surfactant–water phase behavior compared to standard quaternary ammonium gemini surfactants and imidazolium gemini surfactants. The standard \(m\)−\(s\)−\(m\)-type quaternary ammonium gemini surfactant \(12\text{−}2\text{−}12\) with bromide counterion existed as micellar solution up to 39 wt % gemini surfactant in water at 25 °C.69 Similarly, hydroxyl-functionalized quaternary ammonium gemini surfactant \(12\text{−}3\text{(OH)}\text{−}12\) containing chloride counterion was able to exist as micellar phase up to 40 wt % at 25 °C.65 In contrast to quaternary ammonium gemini surfactants, the morpholinium gemini surfactants, \([\text{C12MOR(6)C12MOR}]_2\text{Br}\) and \([\text{C14MOR(6)C14MOR}]_2\text{Br}\), are able to exist as micellar solution up to 59 and 53 wt %, respectively, in water at 25 °C. The phase behavior of morpholinium geminis is also significantly different from those observed for imidazolium gemini surfactant \([\text{C12im−4−C14im}]_2\text{Br}_2\cdot\text{H}_2\text{O}\) as the latter exists as mixed micellar and hexagonal lyotropic phases up to 80 wt % at room temperature.70 With increasing surfactant concentration, the conventional quaternary ammonium gemini surfactant \(12\text{−}2\text{−}12\) is able to exist as hexagonal lyotropic phase up to 58 wt % and then as lamellar liquid crystalline phases up to 80 wt %. Above 80 wt %, the \(12\text{−}2\text{−}12\) exists as mixed solid and lamellar liquid crystalline phases.70 The hydroxyl group containing quaternary ammonium gemini surfactant \(12\text{−}3\text{(OH)}\text{−}12\) forms \(\text{H}_1\) phases between 41 and 59 wt % and then exists as mixed hydrated surfactant monoclinic crystals along with \(\text{L}_\alpha\) phase between 60 and

Figure 7. POM images of the morpholinium gemini surfactant at different wt % in water.

Figure 8. SAXS curves for (a) \([\text{C12MOR(6)C12MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) system and (b) \([\text{C14MOR(6)C14MOR}]_2\text{Br}\)−\(\text{H}_2\text{O}\) system observed at 25 °C at different concentrations. (c) Calculated lattice parameter \((\alpha)\) vs surfactant concentration plot for morpholinium gemini surfactants.
97 wt %.

In contrast to the quaternary ammonium gemini surfactants, the morpholinium gemini surfactants demonstrate the affinity to specifically exist as H₃ lyotropic liquid crystalline phase up to surfactant concentration as high as 96 wt % (for [C₁₂MOR(6)C₁₂MOR]₂Br) and 94 wt % (for [C₁₄MOR(6)-C₁₄MOR]₂Br). Imidazolium gemini surfactant [C₉im₄−C₈Zn]−[Br₂]⁻•••H₂O exists as mixed H₂ and hydrated solid above 80 wt % up to 95 wt %, and above this concentration, it simply exists as hydrated/nonhydrated solid.⁷⁰ The observed room-temperature phase behavior of morpholinium gemini surfactants is quite different from the other types of cationic gemini surfactants. Typically, all other types of gemini cationic surfactants exist as hydrated/nonhydrated solid. The observed room-temperature phase behavior of morpholinium gemini surfactants is quite different from the other types of cationic gemini surfactants. Typically, all other types of gemini cationic surfactants exist as solid or mixed solid system with other lyotropic phases at high surfactant concentration in a binary surfactant–water system. However, the morpholinium gemini surfactants exist as single homogeneous self-assembled H₃ liquid crystalline phases at relatively higher concentration.

3. CONCLUSIONS

New morpholinium gemini surfactants are synthesized and characterized using spectroscopic techniques. These gemini surfactants are able to self-aggregate at lower concentration and form nanosized micelles above their respective cmc values in dilute aqueous solution. The surface activities and the viscosities of the micellar solution of the morpholinium geminis are lower compared to the surfactants ideal for a wide range of application areas. The concentrated aqueous solution of the morpholinium geminis are lower compared to the conventional monomeric surfactants. Unlike the conventional cationic surfactants, these new gemini morpholinium surfactants are able to exist as micellar solution at surfactant concentration as high as 59 and 53 wt % for [C₁₂MOR(6)-C₁₂MOR]₂Br and [C₁₄MOR(6)C₁₄MOR]₂Br, respectively. The concentrated aqueous solution of the morpholinium geminis (10–50 wt %) demonstrated Newtonian fluidlike behavior, and the viscosities of the micellar solution increased with increase in surfactant concentration as well as hydrophobic tail length. At higher concentration, these gemini surfactants formed lyotropic liquid crystalline phases. [C₁₂MOR(6)-C₁₂MOR]₂Br formed lyotropic H₁ phase between 68 and 96 wt %, whereas [C₁₄MOR(6)C₁₄MOR]₂Br formed similar lyotropic liquid crystalline phases at relatively higher concentration. The ease of synthesis and the ability to form self-assembled phases over a wide range of concentrations make these new morpholinium gemini surfactants ideal for a wide range of application areas.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. Bromoacetic acid, dodecyl bromide, morpholine, and hexane-1,6-diol were purchased from TCI, Tokyo, Japan. Hexane-1,6-diybis(2-bromoacetaete) and 4-dodecylmorpholine were synthesized according to the previous reported synthetic methodology. ⁴⁶ ⁴⁷ ⁴-Tetradecylmorpholine was synthesized based on the synthetic procedure adopted for the synthesis of 4-dodecylmorpholine. ⁴⁶ ⁴⁷ MilliPore water was used in all experiments. The mass spectra of gemini surfactants were recorded on a JEOL JMS-T100CS instrument (JEOL Japan) using ESI as an ion source. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL-ECPS500 instrument (JEOL Japan) using CDCl₃ as a solvent and tetramethylsilane as an internal standard.

4.2. Synthesis of Morpholinium Gemini Surfactants. ¹Dodecylmorpholine (25.54 g, 0.1 mol) or 4-tetradecylmorpholine (28.35 g, 0.1 mol) was slowly added over a period of 30 min to the stirred solution of hexane-1,6-diybis(2-bromoacetaete) (18.00 g, 0.05 mol) dissolved in chloroform at 20 °C under a nitrogen atmosphere. After addition, the reaction mixture was stirred for 5 h at 60 °C. The chloroform was then removed from the crude reaction mixture under reduced pressure, subsequently washed twice with 100 mL of hexane, and cold-precipitated in ethyl acetate–diethyl ether mixture under inert nitrogen atmosphere. The precipitates after the removal of solvent upon drying in a rotary flash evaporator at 75 °C for 3 h gave pure morpholinium gemini surfactants: [C₁₂MOR(6)C₁₂MOR]₂Br and [C₁₄MOR(6)C₁₄MOR]₂Br.

4.2.1. 4,4′-(Hexane-1,6-diylbis(oxy))bis(2-oxoethane-1,2-diyibis(4-dodecylmorpholin-4-ium) Dibromide. White solid, yield 59.2%. ¹H NMR (500 MHz, CDCl₃): 5.33 (s, 4H, 2×–COOCH₂N⁺), 4.48–4.46 (m, 4H, 2×–CH₂H₃–CH₂N⁺), 4.36–4.34 (m, 4H, 2×–CH₂H₃O–CH₂N⁺), 4.26 (t, J = 5.7, 4H, 2×–CH₂–COO), 4.02–3.98 (m, 4H, 2×–CH₂H₃O–CH₂N⁺), 3.82 (m, 8H, 2×–CH₂H₃N⁺–CH₂–), 1.86 (m, 4H, 2×–COOCH₂CH₂), 1.52 (m, 4H, –COO(CH₂)₃(CH₂–), 1.35–1.24 (m, 36H, 2×–(CH₃)₂–), 0.88 (t, J = 6.8, 6H, 2×–CH₃). ¹³C NMR (126 MHz, CDCl₃): 164.38, 66.28, 60.43, 60.06, 58.68, 56.61, 31.45, 29.17, 29.05, 28.99, 28.89, 28.58, 27.57, 25.87, 25.13, 22.23, 21.72, 13.70. ESI HRMS (positive ions) calculated m/z: 789.5351 and 791.5330 for [M − Br]⁺; found, 789.5361 and 791.5345 for [M − Br]⁻. Elemental analysis: calc (%) for C₄₆H₉₀Br₂N₂O₆: C, 59.71; H, 9.86; N, 3.05. Found: C, 59.71; H, 9.86; N, 3.05.

4.2.2. 4,4′-(Hexane-1,6-diylbis(oxy))bis(2-oxoethane-1,2-diyibis(4-dodecylmorpholin-4-ium) Dibromide. White solid, yield 41.5%. ¹H NMR (500 MHz, CDCl₃): 5.38 (s, 4H, 2×–COOCH₂N⁺), 4.53–4.49 (m, 4H, 2×–CH₂H₃–CH₂N⁺), 4.36 (m, 4H, 2×–CH₂H₃O–CH₂N⁺), 4.26 (t, J = 5.7, 4H, 2×–CH₂–COO), 4.01–3.97 (m, 4H, 2×–CH₂H₃O–CH₂N⁺), 3.82–3.81 (m, 8H, 2×–CH₂–CH₂N⁺), 1.87 (m, 4H, 2×–COOCH₂CH₂), 1.53 (m, 4H, –COO(CH₂)₃(CH₂–), 1.35–1.25 (m, 44H, 2×–(CH₃)₂–), 0.88 (t, J = 6.8, 6H, 2×–CH₃). ¹³C NMR (126 MHz, CDCl₃): 164.31, 66.18, 60.36, 59.99, 58.60, 56.53, 31.40, 29.14, 28.99, 28.93, 28.84, 28.52, 27.51, 25.81, 25.06, 22.17, 21.67, 13.63. ESI HRMS (positive ions) calculated m/z: 845.5977 and 847.5956 for [M − Br]⁺; found, 845.5976 and 847.5970 for [M − Br]⁻. Elemental analysis: calc (%) for C₆₅H₁₇₂Br₂N₂O₆C: 59.60; H, 9.49; N, 3.02; found: C, 59.71; H, 9.86; N, 3.05.

4.3. Surface Tension Measurements. The surface tension at the water–air interface was investigated using a Krüss K10 tensiometer (Krus, Germany) with a Wilhelmy plate at 25 °C. The tensiometer was calibrated using MilliPore water. The experimental runs chosen were based on the time required for the surfactant solution to attain equilibrium, and hence, a set of 10 consecutive readings with standard deviation less than 0.1 mN/m were taken into account. The surface parameters, that is, surface excess concentration (Γₓₓ), surface area occupied by molecule at the air–water interface (Aₓₓ), the effectiveness of surface tension reduction (γₓₓ), and the cmc values, were calculated from the slope of decrease in surface tension with increasing concentration of the surfactant solution.⁷¹

4.4. Conductivity Measurements. The conductivity of the surfactant solution was measured using a conductivity meter CM-25R (DKK-TOA Corporation) equipped with a
conductivity cell having a cell constant of 1. The solutions were thermostated at 25 °C in a thermostated vessel controlled by a temperature controller. The cmc value was determined by adding an adequate quantity of a concentrated surfactant solution in water to change the surfactant concentration below the cmc to at least 2–3 times the cmc value.28

4.5. Viscosity Measurements. The viscosities of the aqueous surfactant solutions were measured using a stress-controlled rheometer, AR-G2 (TA Instruments) using cone-plate geometries (diameter 40 mm with a cone angle of 2° 0’ 4”) attached to a temperature controller. The samples were prepared in screw-capped glass tubes by weighing appropriate surfactant and Millipore water. The tubes were sealed and kept at 80 °C for 1 h, then vortexed for 10 min, and centrifuged at 3500 rpm for 30 min. The procedure was repeated, and the samples were kept for 24 h to attain equilibrium. The steady shear rheological measurements (viscosity vs shear rate) were performed at 25 °C. The zero shear viscosity of the solutions was determined from steady shear rate measurements by extrapolating the viscosity in shear rate curves to zero shear rate.28

4.6. DLS Measurements. The size of micelles formed by morpholinium gemini surfactants was measured with a DLS measuring particle analyzer (Litesizer 500, Anton Paar) at 25.0 °C. The surfactant solutions of 10 mM concentration were passed through a PVDA membrane filter with a pore size of 0.22 μm. The samples were equilibrated for 60 min before measurement, and an average of five measurement runs were considered for getting the size of micelles.74

4.7. Polarized Optical Microscopy. An appropriate amount of samples was mounted on the glass slides with a coverslip placed on the top. The slides were observed under an Olympus microscope through crossed polarizers at room temperature. The textures observed were transferred to a computer with the help of a Moticam 2000 digital camera fitted on the eyepiece. The images were used to characterize the lyotropic phases inherent in the mixtures.5

4.8. SAXS Measurements. The samples were prepared in the screw-capped glass tubes by weighing appropriate surfactant and water. The tubes were sealed and kept at 80 °C for 1 h, then vortexed for 10 min, and centrifuged at 3500 rpm for 30 min. The procedure was repeated thrice, and the samples were kept for 1 week to attain equilibrium. Measurements were performed using a SAXSess camera (Anton Paar, PANalytical) attached to a PW3830 laboratory X-ray generator with a long fine-focus sealed-glass X-ray tube (KR wavelength of 0.154 nm; PANalytical). The apparatus was operated at 40 kV and 50 mA. The SAXSess camera was equipped with focusing multilayer optics and a block collimator for an intense and monochromatic primary beam with low background, and a translucent beam stop was used for the measurement of an attenuated primary beam at zero scattering vector (q = 0). The samples were enclosed in a vacuum-tight thin quartz capillary with an outer diameter of 1 mm and a thickness of 10 μm. The sample temperature was controlled with a thermostated sample holder unit (TCS 120, Anton Paar). The 2D scattering pattern was collected on an image plate detection system Cyclone (PerkinElmer) and was finally integrated into one-dimensional scattering curves as a function of the magnitude of the scattering vector q = (4π/λ) sin(θ/2) using SAXSquant software (Anton Paar), where θ is the total scattering angle and λ is the wavelength of the X-ray. All data were normalized to the same incident primary beam intensity for the transmission calibration and were corrected for background scattering from the capillary and the solvent.70

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00428.

1H and 13C NMR spectra of morpholinium gemini surfactants, plot of molar conductivity versus C0.5 of morpholinium gemini surfactants, and plot of specific conductivity versus concentration for [C14MOR(6)-C14MOR]2Br (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: abhadani@rs.tus.ac.jp (A.B.).
*E-mail: abemasa@rs.noda.tus.ac.jp (M.A.).

ORCID

Avinash Bhadani: 0000-0002-4981-3083

Notes

The authors declare no competing financial interest.

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