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Synthesis and monolayer film of a series of new twin-tailed gemini cationic surfactants at the air/water interface

Research Article

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Abstract: A series of new dimeric surfactants, twin-tailed gemini surfactants, 2(12)-s-2(12), were successfully prepared and characterized, and their monolayer films investigated by the measurement of surface pressure-area (π-*A*) and surface pressure-time (π-*t*) isotherms at the air/water interface by a Langmuir film balance. Compared to their monomeric counterparts, their collapse pressure ($\gamma_{collapse}$) is smaller, whilst all the molecular area parameters are larger. The limited area ($A_{limited}$) and the initial area ($A_{initial}$) of these twin-tailed gemini surfactants change with increasing spacer length s, and the surface pressure decreases with increasing time. It was also found that the higher the initial surface pressure, the larger the attenuation.

Keywords: *Synthesis • Monolayer • LB films • Twin-tailed gemini surfactant • Isotherms*

1. Introduction

Gemini surfactants are a new family of amphiphiles made up of two hydrophobic tails connected by a spacer group at, or very close to the head groups by a spacer group [1]. Generally, quaternary ammonium gemini surfactants with linear alkyl chains are represented as m-s-m, where *m* and *s* refer to the number of carbon atoms in the alkyl tail and spacer group, respectively. Compared with their monomeric counterparts, gemini surfactants usually have favorable surface activities, lower critical micelle concentration (CMC), better wetting ability, enhanced dispersion, higher foaming stability, and unique rheological responses [1,2]. As a result of these desirable properties, gemini surfactants have attracted considerable attention in both academic research and practical applications [1-7].

Based to the nature of the hydrophilic head groups, gemini surfactants are classified into four categories: cationic, anionic, nonionic and zwitterionic. Within this series, cationic gemini surfactants have been most widely investigated due to their favorable physicochemical properties [1,2]. However, most of the published results concentrate on dimeric quaternary ammonium salts [2], and occasionally on trimeric and tetrameric surfactants [8-10] and multi-armed oligomeric cationic surfactants that have 4 or 6 quaternary ammonium sites [11]. To the best of our knowledge, however, the quaternary ammonium geminis that possess four hydrophobic tails, each two of which are attached to one of the two hydrophilic heads, have been less well documented [12,13]. As there are two identical hydrocarbon groups linked to each ionic site, we refer to this new type of quaternary ammonium geminis as “twin-tailed gemini surfactants” and classify them as 2m-s-2m.

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This paper describes the synthesis of a series of twin-tailed gemini surfactants, *s*(methylene)-1,s-*bis*(methyldidodecyl ammonium bromide), [2(12)-s-2(12) (s=3, 4, 6)], by the quaternization of *N*, *N*-didodecyl methyl amine with the corresponding alkyl dibromide. Their monolayer behaviors at the air/water interface have been examined using the Wilhelmy plate technique with a Langmuir film balance at 25°C. For comparison, the monolayer properties of their monomeric counterpart, *N*, *N*-didocdeyldimethylammonium bromide [2(12)], was also investigated under the same conditions.

2. Experimental Procedures

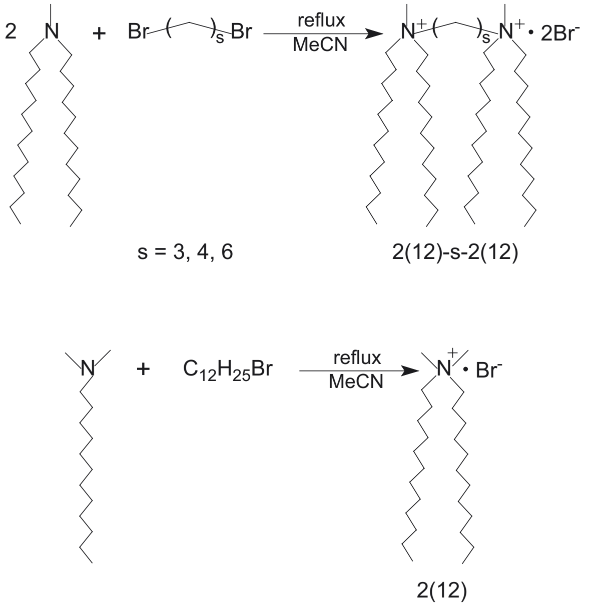
2.1. Materials

N,*N*-didodecylmethylamine (Feixiang Chemical Co., Ltd, Zhangjiagang, China), 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane (Alfa Aesar) and chloroform (Huizhou Chemical Co., Ltd, China) were all analytical grade and used without further purification. Water used in the experiment was doubly distilled.

2.2. Synthesis and characterization of twin-tailed gemini surfactants

The series of twin-tailed gemini surfactants were synthesized using the following procedure (Scheme 1): *N*,*N*-didodecylmethylamine was dissolved in acetontrile, and the solution added dropwise over 30 min to excess 1,3-dibromopropane [or 1, 6-dibromohexane for 2(12)-6-2(12) or 1, 4-dibromobutane for 2(12)-4-2(12)] at reflux under a nitrogen atmosphere. After appropximately 15 h heating at reflux, the solvent was removed by evaporation under reduced pressure, leaving a viscous solid, to which acetone was added. A white powder was subsequently obtained by filtrating and drying at 40°C under vacuum. The twin-tailed monomeric quaternary ammonium bromide, 2(12), was synthesized using the same procedure. The yields of both 2(12)-s-2(12) and 2(12) were above 95%. The purity of these compounds was determined by ^{1}H NMR spectroscopy (Bruker Advance 300 MHz) and high resolution mass spectrometry (HRMS, Bruker Bio TOF IIIQ, ESI).

The structures of 2(12)-s-2(12) and 2(12) were characterized by their ^{1}H NMR (BRUKER ADVANCE 300 MHz) and high resolution mass spectra (HRMS, Bruker Bio TOF IIIQ, ESI), using $CDCl_3$ and methanol, respectively, as solvents. **2(12), didodecyldimethyl ammonium bromide**, δ: 0.85-0.89 (*t*, 6H, CH_3C), 1.24-1.34 (*m*, 36H, $C(CH_2)_9C$), 1.68-1.71 (*d*, 4H, CCH_2CN^+), 3.40 (*s*, 6H, CH_3N^+), 3.47-3.52 (*t*, 4H, CH_2N^+). HRMS (m/z, 382.4407). **2(12)-3-2(12), 1,3-bis(didodecylmethyl ammonium)propane dibromide**, δ: 0.84-0.88 (*t*, 12H, CH_3C), 1.24-1.34 (*m*, 72H, $C(CH_2)_9C$), 1.70-1.71 (*d*, 8H, CCH_2CN^+), 2.71 (*s*, 2H, $N^+CCH_2CN^+$), 3.32 (*s*, 6H, CH_3N^+), 3.35-3.50 (*m*, 8H, CH_2N^+), 3.84-3.89 (*t*, 4H, $N^+CH_2CCH_2N^+$). HRMS (m/z, 388.4407). **2(12)-4-2(12), 1,4-bis(didodecylmethyl ammonium)butane dibromide,** δ: 0.83-0.85 (*t*, 12H, CH_3C), 1.21-1.31 (*m*, 72H, $C(CH_2)_9C$), 1.68 (*s*, 8H, CCH_2CN^+), 2.14 (*s*, 4H, $N^+CCH_2CH_2CN^+$), 3.18 (*s*, 6H, CH_3N^+), 3.23-3.29 (*t*, 8H, CH_2N^+), 3.83 (*s*, 4H, $N^+CH_2CCH_2N^+$). HRMS (m/z, 395.4486). **2(12)-6-2(12), 1,6-bis(didodecylmethyl ammonium)hexane dibromide**, δ: 0.83-0.87 (*t*, 12H, CH_3C), 1.24-1.34 (*m*, 72H, $C(CH_2)_9C$), 1.70-1.71 (*d*, 8H, CCH_2CN^+), 2.01 (*s*, 8H, $N^+CCH_2CH_2CH_2CH_2N^+$), 3.34 (*s*, 6H, CH_3N^+), 3.35-3.37 (*m*, 8H, CH_2N^+), 3.84-3.89 (*t*, 4H, $^+CH_2CCCCCH_2N^+$). HRMS (m/z, 409.4642).



Scheme 1. Synthetic routes to 2(12)-s-2(12) and 2(12).

2.3. Surface pressure-area (π-*A*) isotherm measurements

The surface pressure measurements were performed using the Wilhelmy plate technique on a computer-controlled Langmuir film balance (KSV 2000III, KSV Instrument Ltd., Finland) equipped with two rectangular Teflon troughs (700×120×10 mm). The troughs were previously filled with doubly-distilled water. Then, the surfactants, 2(12), 2(12)-3-2(12), 2(12)-4-2(12) and 2(12)-6-2(12), were dissolved in chloroform to give concentrations of 0.440, 0.416, 0.468 and 0.400 mg mL^{-1}, respectively. The chloroform solutions were carefully dispersed into the surface of the aqueous subphase. Since phase transitions in surface pressure-area (π-A) isotherms are strongly influenced by the subphase

Table 1. The surface pressure and molecular area parameters for twin-tailed geminis and twin-tailed monomeric surfactant.

Sample	2(12)	2(12)-3-2(12)	2(12)-4-2(12)	2(12)-6-2(12)
$\gamma_{collapse}$ (mN/m)	33.8	28.1	26.8	29.8
$A_{collapse}$ (nm^2/molecule)	0.788	1.456	1.564	1.490
$A_{limited}$ (nm^2/molecule)	0.921	1.042	1.049	1.091
$A_{initial}$ (nm^2/molecule)	1.573	2.269	2.595	2.810

temperature [14] , the temperature of the subphase was controlled at 25 ± 1°C with a circulative water bath. After evaporating chloroform for about 20 min, the movable barriers were compressed at a constant rate of 5 mm/min, and at the same time the surface pressure (π) and the area of the monolayer (A) at that time were automatically recorded by a computer connected to the balance.

2.4. Surface pressure-time (π-t) isotherm measurements

Using a method similar to that described in *2.3*, following evaporation of chloroform for about 20 min, the movable barriers were compressed at a constant rate of 5 mm/min. The surface pressure-time (π-t) isotherms of 2m-*s*-2m and 2(12) were registered when the movable barriers stopped at the first desired surface pressure value, 10 mN m^{-1}; then, after performing the first π-t isotherm for about 2 h, the movable barriers continued compressing to a second pressure value, 20 mN m^{-1}, and the corresponding π-t isotherms were recorded. The same procedure was used for the third π-t isotherm measurements at a pressure value of 30 mN m^{-1}.

3. Results and Discussion

3.1. The monolayer behavior of 2m-s-2m on the air/water interface

As Liu and his coworkers [15] stated, the conventional gemini surfactants 12-*s*-12 (s=3, 4, 6, 8, 10, 12) could not form stable monolayers on a plain water surface due to their inclination to dissolve in water. However, the water solubility of the twin-tailed gemini surfactants, 2(12)-*s*-2(12), is much reduced due to the incorporation of two additional hydrophobic groups. Therefore, the surface activities of these surfactants could not be measured using a surface tensiometer or conductometer in water. As a new class of amphiphilic molecules, the behaviours of twin-tailed gemini surfactants could be studied as monolayers resting upon the water surface. With the aid of a Langmuir film balance, surfactant monolayers were slowly compressed by a moveable barrier and the isotherms recorded. The resulting "surface pressure-molecular area isotherms" provide insight into the packing behavior of the surfactant molecules within the monolayers [16].

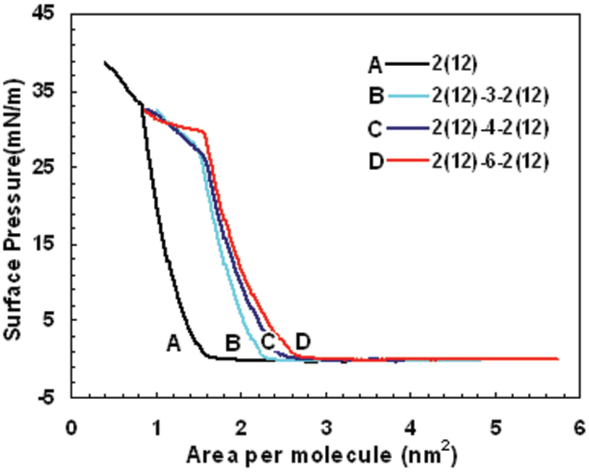


Figure 1. $\pi - A$ isotherms of twin-tailed gemini surfactants and monomeric counterpart at the air/water interface at 25°C.

Fig. 1 details the lateral pressure (π) – area per molecule (A) isotherms for all four surfactants on aqueous subphases at 25°C. From these π-A isotherms, the initial area ($A_{initial}$) at which the isotherms depart from the baseline owing to intermolecular interactions, and the collapse pressure ($\gamma_{collapse}$) and collapse area ($A_{collapse}$) at which the monolayer ultimately "breaks", ,could be determined. The limited area ($A_{limited}$) was calculated from extrapolation of the steepest regions (close to collapse) of the isotherms to zero surface pressure, with the results summarized in Table 1.

As shown in Fig. 1, the surface pressure of 2(12) monolayer starts to rise at ca. 1.573 nm^2/molecule, and its limited molecular area ($A_{limited}$) is 0.921 nm^2/molecule. The monolayer collapsed at a surface pressure of around 33.8 mN m^{-1}, at which time the molecular area, $A_{collapse}$, decreases to 0.788 nm^2/molecule.

As seen in Table 1, all the molecular parameters of the twin-tailed gemini surfactants are larger than the monomeric surfactant 2(12). In particular, the collapse molecular area of the twin-tailed gemini surfactants is around two times that of 2(12). This is probably due to the two additional hydrocarbon chains in the twin-tailed gemini surfactants. Generally, two main factors govern the monolayer characteristics: the affinitive interaction between head groups of the surfactant and the subphase, and the cohesive interaction between

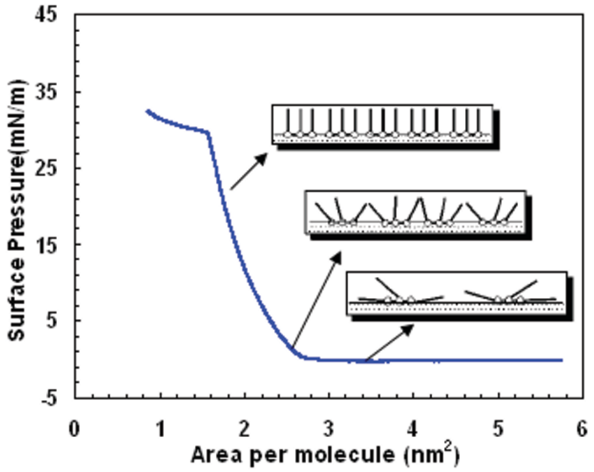


Figure 2. A schematic illustration showing the spread twin-tailed gemini monolayler at the air/water interface when compressing at 25°C.

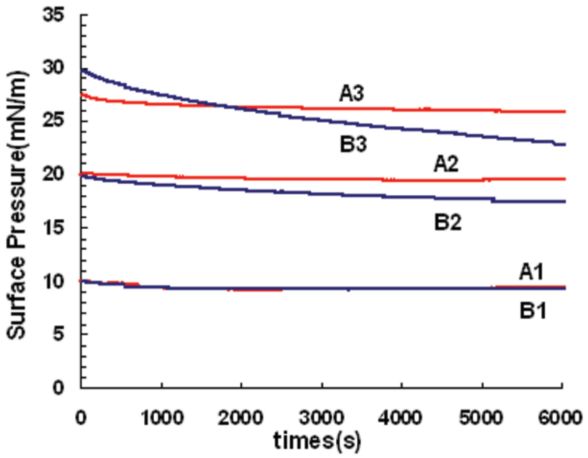


Figure 3. (π-t) isotherms of 2(12) and 2(12)-3-2(12) at various initial surface pressures at 25°C: A1, 2(12)-3-2(12) at 10; A2, 2(12)-3-2(12) at 20; A3, 2(12)-3-2(12) at 28; B1, 2(12) at 10; B2, 2(12) at 20; B3, 2(12) at 30 $mN\ m^{-1}$, respectively.

surfactant molecules. The affinitive interaction of the polar quaternary ammonium group with the subphase provides a driving force for the spreading of molecules on the subphase. On the other hand, the cohesive interaction, namely the van der Waals forces between hydrophobic chains, causes aggregation of the molecules, resulting in closely packed domains. The competition between these two forces determines the characteristic of the monolayer and may be the reason why different isotherms were found for the twin-tailed gemini surfactants versus their monomeric analogues. Interestingly, the pressure required to break the monolayer film for 2(12) is much stronger than those for 2(12)-*s*-2(12).

Although their isotherms are very similar, differences between the 2(12) monolayer and the series of twin-tailed gemini surfactants could be distinguished by analyzing their turning points in the curves. The initial area provides an insight into the molecular orientation at the onset of intermolecular contact. Thus, A_{initial} increases with increasing spacer length, indicating that a twin-tailed gemini possessing longer spacer length has difficulty packing at an air/water interface. The longer spacer separating the two parts in 2(m)-*s*-2(m) has a dramatic effect on the molecule's inclination to organize at the air/water interface. Compared with 2(12)-3-2(12), for example, repulsions between the quaternary ammonium ions of 2(12)-6-2(12) are smaller due to the longer distance between the two head groups, leading to a higher A_{initial}. On the contrary, A_{limited} of all the twin-tailed gemini surfactants remains constant at around 1.0 nm^2/molecule, regardless the spacer length s. Apparently, the major contribution to the geometric requirements of the film comes from the hydrophobic alkyl tail groups, rather than the bridging spacer connecting both ionic head groups. The collapse pressure γ_{collapse} (*i.e.,* the pressure at which the monomolecular films ultimately "break") of 2(12)-s-2(12) (where s = 3,4,6) are, respectively, 28.1, 26.8 and 29.8mN/m. This collapse area, A_{collapse}, is nearly double that of the single-head counterpart, 2(12), 0.788 nm^2/molecule (Table 1). However, compared with A_{initial}, A_{collapse} is much reduced, showing that with sufficient film pressure, it is possible to reorient both horizontal chains into a vertical arrangement. A schematic illustration of the orientation of molecules in different phases is shown in Fig. 2.

3.2. Surface pressure-time (π-*t*) isotherms of 2m-s-2m and 2(12) on the air/water interface

Fig. 3 describes surface pressure (π) - time (t) isotherms of 2(12) and 2(12)-3-2(12) with a constant whole area of monolayer at different initial surface pressures. Similar data for 2(12)-4-2(12) and 2(12)-6-2(12) are given in Fig. 1 of the supplemental materials. As shown in Fig. 3, the surface pressure decreased gradually with time. The variation of surface pressure was not obvious at low initial surface pressure (the two lines A1 and B1 are almost uniform at 10 $mN\ m^{-1}$). The higher the initial surface pressure, the more visible the variation. When approaching the collapse pressure (A3, B3), the the most noticeable decrease in surface pressure with time was for 2(12). One possible reason for this is the slow reorganization taking place in the monolayer on the time scale of the experiments. Another reason is monolayer loss, or multilayer formation [17-18], owing to good water solubility [19] at the air/water interface. The π-*t* isotherms of 2(12)-3-2(12), A1 and A3 are rarely changed at 10 $mN\ m^{-1}$ or close to the collapse pressure.

4. Conclusions

The monolayer properties of twin-tailed gemini surfactants and their monomeric analogue have been investigated by using a Langmuir film balance at the air/water interface at 25°C. It was demonstrated that twin-tailed gemini surfactants could form stable monolayers at the air/water interface. Moreover, the surface pressure-time (π-*t*) isotherms proved that the attenuations in monolayers of these surfactants were subtle at low initial surface pressure, whilst at high initial surface pressure (close to collapse pressure) the isotherms varied clearly. The surface pressure-area (π-*A*) isotherms show that the spacer length of the gemini surfactants plays an important role in determining the properties of the monolayers. The A_{limited} and A_{initial} increase with increasing spacer group length. Compared with the monomeric surfactant 2(12), all molecular area parameters, A_{collapse}, A_{limited}, and A_{initial} of twin-tailed gemini surfactants 2(12)-s-2(12) are larger, but their monolayers are less stable. The films might be very stiff, judging from the lower collapse pressure, because of the special molecular structure. These properties should prove an important foundation for their potential applications such as molecule self-assembly.

Acknowledgments

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