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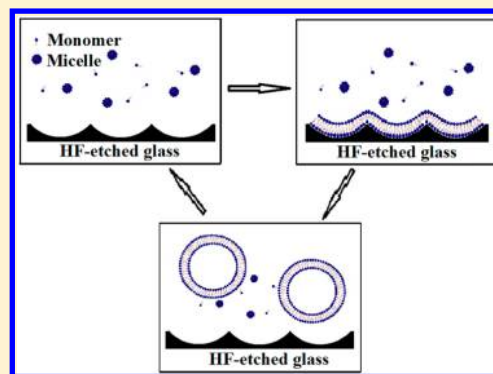
Rough Glass Surface-Mediated Transition of Micelle-to-Vesicle in Sodium Dodecylbenzenesulfonate Solutions

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Supporting Information

ABSTRACT: In this paper, we report a micelle-to-vesicle transition in aqueous solution of the anionic single-tailed surfactant (STS) sodium dodecylbenzenesulfonate (SDBS), with the mediation of a rough glass surface (RGS) in the absence of cosurfactants or additives. This transition produced a mixed solution of vesicles and micelles. Interestingly, the obtained SDBS vesicles in the solution displayed good stability during a long-term storage (at least 6 months at room temperature), exposure to high temperature (80 °C for 2 h), and freeze–thawing (−20 or −196 °C for 2 h to approximately 25 °C) after the RGS was removed. Our results confirmed that SDBS could adsorb on the RGS to form bilayers, in which the molecular packing parameter of SDBS was in the range of 1/2–1. The bilayer adsorption and the roughness of the solid surface played an important role in the vesicle formation. In addition, we propose a possible mechanism for the RGS-mediated transition of micelle-to-vesicle in SDBS solutions: SDBS micelles and molecules adsorb on the RGS to form curved bilayers; the curved bilayers detach from the RGS, and then close to form vesicles.



INTRODUCTION

Amphiphilic molecules in aqueous solutions can spontaneously assemble into organized structures such as micelles, liquid crystals, bilayers–lamellae, vesicles/liposomes, and micro-emulsions.¹ Among these self-assemblies, vesicles have attracted much interest over the past several decades because of their practical importance.^{2–6} A large number of vesicles in aqueous solutions of surfactants^{7–11} and amphiphilic polymers^{5,12–14} have been reported. For the surfactant vesicles, either surfactants with double tails⁷ or mixtures of two or more surfactants are typically used.^{8–11} To date, however, studies on vesicles consisting of one simple single-tailed surfactant (STS), such as sodium dodecylbenzenesulfonate (SDBS), in the absence of cosurfactants or additives have not been proposed yet, except for our recent reports on the vesicle formation (or micelle-to-vesicle transition) from dodecyltrimethylammonium bromide (DTAB)¹⁵ and lauryl sulfobetaine (LSB),¹⁶ respectively.

The self-assembly morphology of amphiphilic molecules in aqueous solutions is generally explained or predicted by the well-known concept of molecular packing parameter (P), introduced by Israelachvili et al.¹⁷ The P is determined by three geometric parameters of a surfactant molecule as

$$P = \nu/a_0l$$

where ν is the surfactant tail volume, l is the tail length, and a_0 is the occupied area per amphiphile at the aggregate surface. As a general rule,¹⁸ spherical micelles are favored with $P \leq 1/3$; cylindrical micelles are favored with $1/3 \leq P \leq 1/2$; curved

bilayers or vesicles are favored with $1/2 \leq P \leq 1$. Based on this concept, simple STSs alone are generally considered to be unable to form vesicles in water owing to their high experimental a_0 values (usually at gas–liquid interfaces) that reduce their P values to less than 1/2. The high a_0 values of surfactants arise from the electrostatic repulsion between adjacent surfactant head groups and their hydration. Therefore, a reduction of the electrostatic effect and hydration of the head groups may decrease the a_0 values of surfactants, resulting in higher P values. It has been reported that the pH,¹⁹ temperature,²⁰ salinity,²¹ and addition of organic additives²² or heavy metal ions²³ can alter the electrostatic effect and hydration of the head groups, and thus the self-assembly morphology. Zhai et al.²¹ reported the salt-induced vesicle formation from SDBS alone in water. More recently, we found that a rough glass surface (RGS) can mediate the micelle-to-vesicle transition in aqueous solutions of the cationic STS DTAB¹⁵ and the zwitterionic STS LSB,¹⁶ respectively, in the absence of cosurfactants and additives, producing the mixed solutions of micelles and vesicles. Surprisingly, the so-obtained DTAB and LSB vesicles in the mixed solutions displayed good stability during long-term storage, exposure to high temperatures, and freeze–thawing after removal of the RGS. This differs from the behavior of the SDBS vesicles formed under the inducement of salt, which displayed low long-term

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stability.²¹ In addition, the RGS-mediated strategy simplifies the preparation of vesicles and does not require the introduction of new components into the surfactant system.

In fact, alteration of solid surfaces on the self-assembly morphology has been revealed by previous studies.^{24–28} Hanczyc et al.²⁴ reported that negatively charged clay mineral particles can catalyze the formation of vesicles from fatty acids, yielding composites of clay particles encapsulated in vesicles. We found that positively charged layered double hydroxide (LDH) particles can induce the spontaneous formation of vesicles in mixtures of zwitterionic/anionic^{25,26} or cationic surfactants,²⁷ producing composites consisting of LDH particles encapsulated in vesicles. Morigaki and Walde²⁸ reported that glass surfaces can induce the formation of giant vesicles from oleic acid/sodium oleate systems. However, to date, the role of the solid surface has not been clarified.

In this paper, we report a micelle-to-vesicle transition in the anionic STS SDBS solution with the mediation of RGS, which produces a mixed solution of micelles and vesicles. The stability of the STS vesicles in the solution was investigated. The mechanism of the RGS-mediated transition of micelle-to-vesicle is discussed. The results of this work significantly contribute to the understanding of the formation and features of vesicle systems.

EXPERIMENTAL METHODS

Materials. All the chemicals used in this work were of analytical reagent grade. SDBS was purchased from TCI Development Co., Ltd., China and was recrystallized from methyl alcohol before use; the purity of the recrystallized SDBS was examined, no minimum was found in the surface tension curve, and no impurities were obviously detected by ¹³C NMR, but the isomerization of the SDBS was observed by ¹H NMR (Figures S1–S3, Supporting Information). HF was purchased from Tianjin FuYu Fine Chemical Co., Ltd., China. Nile red was purchased from Tokyo Chemical Industry Co., Ltd., China. Ultrapure water was obtained using a Hitech-Kflow water purification system (Hitech, China).

RGS-Mediated Micelle-to-Vesicle Transition. The RGS was obtained by etching a plate glass surface using HF. Glass microscope slides with length, width, and thickness of 5.5, 2.5, and 0.1 cm, respectively, were immersed in HF for 3 min. The resulting etched glass plates were washed thoroughly with ultrapure water and then ethanol, and then dried at 80 °C. The chemical elements on the RGS were measured by energy dispersive X-ray spectroscopy technique, indicating that the surface mainly consists of O (47.7%), Si (26.9%), Mn (10.9%), Na (9.0%), Ca (3.5%), and Mg (2.0%).

A SDBS micellar solution (20 mM) was prepared by dissolving the surfactant in ultrapure water. Three etched glass plates were immersed in 50 mL of the micellar solution, in a well-sealed plastic tube. The sample was shaken in a thermostatic water-bath shaker (Jiangsu Medical Instrument Factory, China) for a given mediation time (t_{sm}) at a temperature of 25 ± 0.5 °C. The vesicle formation in the aqueous solution was characterized before and after removal of the etched glass plate. The SDBS solution maintained its natural pH value of 6.6 ± 0.2 for the entire duration of the experiment.

Characterization. The morphology of solid surfaces was analyzed using a Nanoscope IIIa Multimode atomic force microscope (AFM, Digital Instruments, USA) and a JEOL JSM-6700F field emission scanning electron microscope (SEM,

JEOL, Japan). Observations of the vesicle morphology were performed using a JEM-1011 transmission electron microscopy (TEM, JEOL, Japan). Samples for TEM were prepared by freeze-fracture (FF) and negative staining (NS, with uranyl acetate ethanol solution). Fracturing and replication were carried out in a Balzers BAF-400D high-vacuum freeze-etching system (Leica, Germany). Confocal laser scanning microscopy (CLSM) imaging was performed with an Olympus IX81 fluorescence microscope (Japan). Optical excitation was carried out with a 488 nm argon laser beam; fluorescence emission was detected over a range of 560–630 nm. Nile red was used as the fluorescent dye to label the formed vesicles. 4.5 μL of the vesicle sample was mixed with 0.5 μL of 10 $\mu\text{g}\cdot\text{mL}^{-1}$ Nile red acetone solution prior to microscopic examination. Dynamic light scattering (DLS) measurements were performed using a BI-200SM DLS instrument (Brookhaven, England). The incident laser light had a wavelength of 532 nm, and the incident angle was 90°. The DLS data were analyzed using the Contin method, and size distribution information was obtained by measuring the light intensity $f(D_h) = \Gamma \cdot G(\Gamma)$ as a function of the hydrodynamic diameter (D_h). The water contact angles (θ_w) on the glass surfaces were measured using a DSA10 contact angle goniometer (Kruss, Germany). A droplet of water (~ 30 μL) was carefully placed on the surface of the glass substrate using a syringe. Photographs of the droplet were then recorded after equilibrium was reached (~ 2 min) to obtain the θ_w values; the θ_w values used in this study are the average of three measurements on different locations of the glass surface.

RESULTS AND DISCUSSION

RGS-Mediated Micelle-to-Vesicle Transition. The RGS obtained by etching a glass microscope slide using HF was characterized by SEM and AFM (Figure 1). A very rough surface with many “islands” with a height of approximately 12 nm was obtained, indicating that the RGS consists of curved surfaces.^{15,16}

After the etched glass plates were immersed in the SDBS micellar solution (20 mM), a significant formation of vesicles was observed. Figure 2a,b shows NS- and FF-TEM images of the SDBS solutions, recorded at a t_{sm} of 9 d. Our data clearly showed a large number of vesicles with an average size of

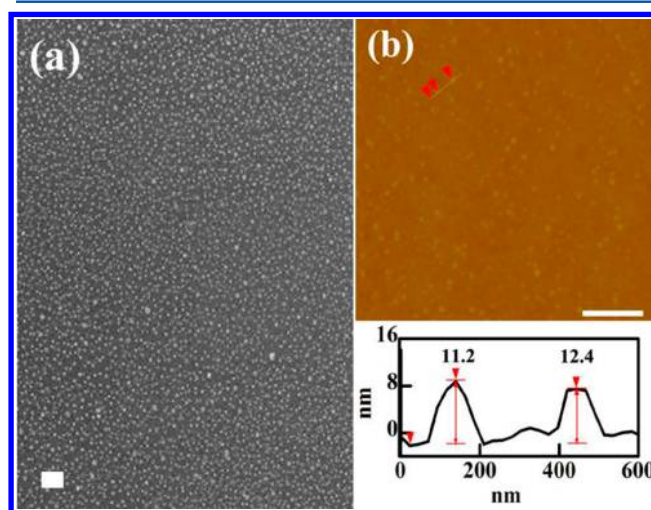


Figure 1. (a) SEM and (b) AFM height images and section analysis of the etched glass plate surface. Scale bar = 1 μm .

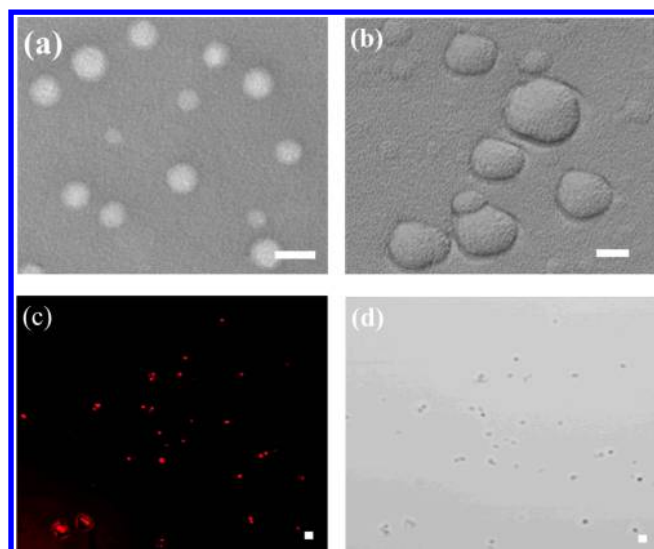


Figure 2. (a) Negative stain and (b) FF TEM images, and (c) CLSM and (d) its bright-field images of the SDBS vesicles at a RGS-mediation time of 9 days. Scale bar = 200 nm (a,b) and 1 μ m (c,d).

approximately 180 nm, indicating that the RGS induced micelle-to-vesicle transition occurred in the STS solution. After staining by a trace amount of the fluorescent dye Nile red, the sample was observed in a hydrated state by CLSM in fluorescence mode. This also proved the formation of vesicles, as shown in Figure 2c,d. In addition, similar tests were performed using 50, 100, 150, and 200 mM SDBS solutions, respectively, and similar results were obtained (Figure S4, Supporting Information).

In addition, the RGS-mediated formation of vesicles in the simple STS solution was confirmed by DLS measurements. The difference in the correlation function plots of between the micellar and vesicle solutions was clearly observed (Figure S5, Supporting Information), indicating that the structural transition of assemblies occurred under the RGS mediation. Typical D_h distribution results are shown in Figure 3. Before the addition of the etched glass plates, the D_h distribution of the STS solution exhibited a single peak at $D_h \sim 4$ nm; this is a typical value for a micellar system. After the RGS was added to the STS solution, the intensity of the micelle peak significantly decreased, and a new peak around $D_h = 170$ nm was observed, corresponding to the formation of vesicles. The most probable

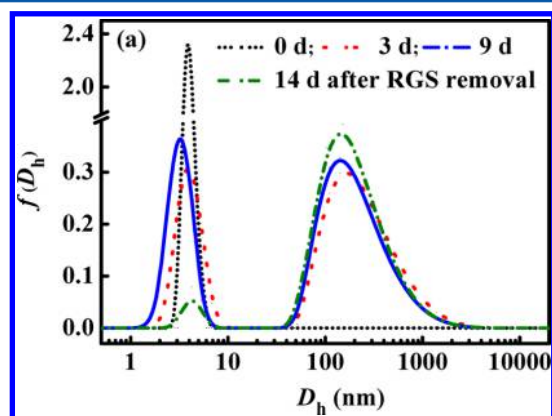


Figure 3. Hydrodynamic diameter distributions for the SDBS solution at different times with RGS mediation and after RGS removal.

vesicle diameter (approximately 170 nm) was consistent with the average size (~ 180 nm) obtained from the TEM images. In addition, the result of both micelle and vesicle peaks coappearing in the DLS plots of the SDBS solutions indicated that the micelles and vesicles coexisted in the solutions. That is, a micelle-to-vesicle transition occurred in the systems with the RGS mediation, but only partial micelles were converted to vesicles.

Similar tests using smooth (unetched) glass plates were performed under the same conditions. No vesicles were observed using either TEM or DLS; this demonstrated that the roughness of the solid surface plays a key role in the vesicle formation. In addition, to explore whether water-soluble substances from the etched glass plates may induce the vesicle formation, we prepared the surfactant solution using ultrapure water in which the etched glass plates had been soaked for 6 days; no vesicle aggregates were observed in this system using either TEM or DLS. The chemical composition of the SDBS vesicle solution obtained with RGS-mediation was identified by X-ray photoelectron spectroscopy technique, and no substances (such as Si, Mn, Ca, and Mg) dissolving from the RGS were detected in the system. Furthermore, we also examined whether surfactant-mediated soluble species from the etched glass plates may induce the vesicle formation. The RGS slides were soaked in 100 mM SDBS solution for about 3 h, and then thoroughly washed with ultrapure water; this treatment process was repeated 10 times. Such surfactant-treated RGS slides were used for vesicle formation tests in the SDBS micellar solution (20 mM), and the vesicles were clearly observed by TEM and DLS (Figure S6, Supporting Information), similar to the results of untreated RGS slides. These tests proved that the micelle-to-vesicle transition in the STS solution is induced solely by the RGS.

Stability of the SDBS Vesicles in the Micelle–Vesicle Solutions. The storage stability of the SDBS vesicles in the micelle-vesicle solutions, after the etched glass plates were removed, was examined using DLS and NS-TEM. Over a storage period of 20 d at room temperature, the DLS results showed no significant change in the vesicle peaks (Figure 3), and the TEM image (Figure 4a) confirmed that the vesicles in the systems remained stable. These findings demonstrate that the SDBS vesicle system has high storage stability. Notably, the obtained STS vesicle solution was still stable at room temperature approximately six months after the initial experiment.

The thermal and freeze–thaw stabilities of the SDBS micelle–vesicle system were also investigated. To examine its thermal stability, the STS micelle–vesicle system was placed in a thermostatic bath at 80 $^{\circ}$ C for 2 h. The NS-TEM and DLS experiments showed that the vesicles were still present in the system (Figures 4b and 5). To examine its freeze–thaw stability, the STS micelle–vesicle system was frozen at -20 $^{\circ}$ C and -196 $^{\circ}$ C (liquid nitrogen), respectively, for 2 h, and the frozen samples were then thawed at an ambient temperature of approximately 25 $^{\circ}$ C. After thawing, vesicles were clearly observed using NS-TEM and DLS (Figures 4c,d and 5).

According to these results, we concluded that the SDBS vesicles in the mixed solutions exhibit high stability, similar to those of the DTAB and LSB vesicle systems.^{15,16}

Possible Mechanism for RGS-Mediated Micelle-To-Vesicle Transition. Based on the concept of molecular packing parameter, simple STSs, such as SDBS, are generally considered to be unable to form vesicles in water in the absence

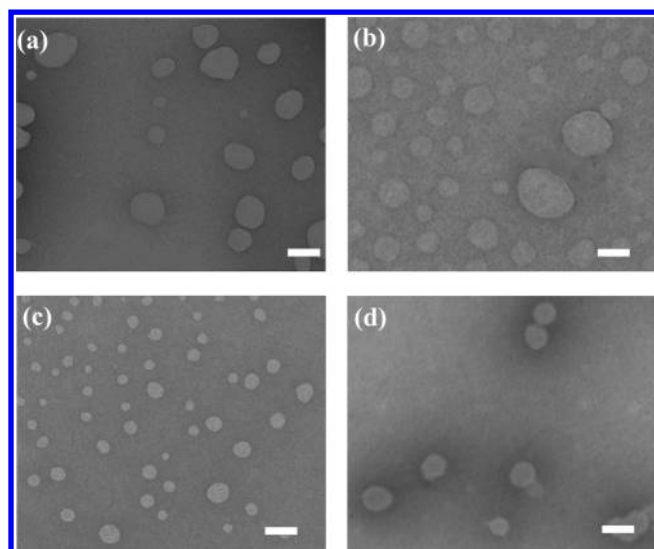


Figure 4. Negative stain TEM images of the SDBS micelle-vesicle solution after (a) standing 20 days at $\sim 25\text{ }^{\circ}\text{C}$, (b) thermal treatment at $80\text{ }^{\circ}\text{C}$ for 2 h, and (c) freezing at $-20\text{ }^{\circ}\text{C}$ for 2 h and (d) freezing at $-196\text{ }^{\circ}\text{C}$ for 2 h and then thawing, with the RGS being removed. Scale bar = 200 nm.

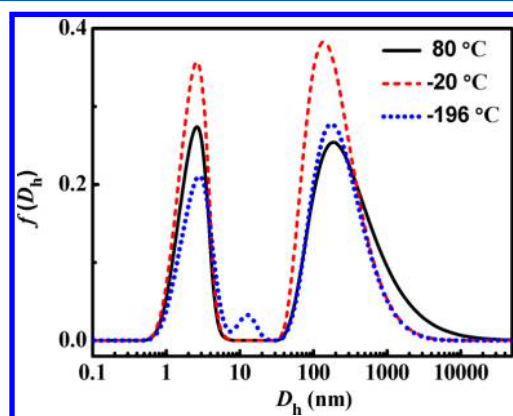


Figure 5. Hydrodynamic diameter distributions for the SDBS micelle-vesicle system after thermal treatment at $80\text{ }^{\circ}\text{C}$ for 2 h, and freezing at $-20\text{ }^{\circ}\text{C}$ and $-196\text{ }^{\circ}\text{C}$ for 2 h and subsequent thawing.

of cosurfactants or additives.^{1,21,29} This is because their P values obtained from experimental a_0 values (usually at gas-liquid interfaces) are typically lower than $1/2$. Several studies have focused on the adsorption of SDBS at gas-liquid, liquid-liquid, and solid-liquid interfaces; the literature a_0 values for SDBS in the saturated adsorption layers at gas-liquid and liquid-liquid interfaces are approximately $0.45\text{--}0.59\text{ nm}^2$ and 0.60 nm^2 .^{30,31} The l and ν values of SDBS are 1.67 and 0.35 nm^3 ,³² respectively. Therefore, the P values for SDBS can be estimated to be approximately $0.36\text{--}0.47$ and 0.35 at gas-liquid and liquid-liquid interfaces, respectively. Thus, these P values suggest that micelles are favored for the surfactant. However, the intrinsic area of the headgroup (or the cross-sectional area of the nonhydrated headgroup) for SDBS is only 0.25 nm^2 , i.e., significantly lower than its experimental a_0 values at gas-liquid and liquid-liquid interfaces. The higher experimental a_0 values result from the hydration of the headgroup and the electrostatic repulsion between the head groups. Thus, available methods that can decrease the hydration and electrostatic effect of the head groups may be

used to prepare STS vesicles. It is well-known that the adsorption effect of solid surfaces toward surfactant molecules in aqueous solutions can decrease the hydration of the surfactant head groups and reduce the electrostatic repulsion between head groups, resulting in a lower a_0 value. Previous studies have reported that the a_0 values for SDBS in adsorption bilayers at some solid-liquid interfaces were $0.25\text{--}0.36\text{ nm}^2$,^{2,33–35} giving P values of $0.58\text{--}0.84$. We investigated the adsorption of SDBS on HF-etched glass particles in the 20 mM SDBS aqueous solution at $25\text{ }^{\circ}\text{C}$ and a solid dosage of $10\text{ g}\cdot\text{L}^{-1}$ (see the Supporting Information). The results showed that the equilibrium adsorption amount (Γ_e) for SDBS was $4.3 \times 10^{-2}\text{ mmol}\cdot\text{g}^{-1}$. The glass particles were obtained by milling glass microscope slides, and were then etched with HF prior to the adsorption measurements. The driving force of the SDBS adsorption on the glass particles can be attributed to the van der Waals force and hydrogen bonding interaction. By using the N_2 adsorption-desorption method, the specific surface area (A_s) of the HF-etched glass particles was measured to be $5.0\text{ m}^2\cdot\text{g}^{-1}$. The critical micelle concentration (cmc) of SDBS aqueous solution was measured to be about 1.21 mM , by surface tension measurements at $25\text{ }^{\circ}\text{C}$. Because the adsorptions of surfactants at solid-liquid interfaces typically form monolayers and bilayers when the surfactant concentrations (c) are below and above their cmc,³⁶ respectively, it is acceptable that, with $c = 20\text{ mM}$, the adsorption bilayers of SDBS formed on the HF-etched glass particles. Therefore, the a_0 value for the SDBS in the adsorbed bilayers can be estimated to be approximately 0.38 nm^2 from its Γ_e value and A_s of the HF-etched glass particles. This results in a P value of 0.55 for SDBS. This proves that the SDBS bilayers detached from solid surfaces may form vesicles based on the concept of molecular packing parameter.

In addition, the adsorption of SDBS on the smooth (unetched) glass surface (SGS) and RGS was investigated via θ_w measurements. The SGS and RGS were immersed in the SDBS solutions with different c for 24 h to reach the adsorption equilibrium. The resulting SDBS-adsorbed SGS and RGS were dried by airing and used for the θ_w measurements. Figure 6 shows the θ_w variation of the SDBS-adsorbed SGS and RGS versus c . The θ_w values of SGS and RGS without adsorbed SDBS were approximately 42° and 21° , respectively. For the RGS, as c increased, θ_w initially increased and then decreased, with a maximum θ_w value at $c \approx 1.0\text{ mM}$; this is near the cmc

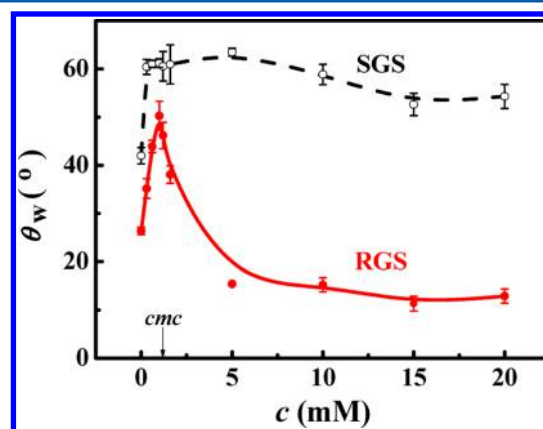


Figure 6. Variation of water contact angles of SDBS-adsorbed SGS and RGS versus SDBS concentration.

value of the SDBS solution, and in line with previous studies.³⁷ The initial increase and subsequent decrease in θ_w can be attributed to the formation of a monolayer and a bilayer of SDBS, respectively.^{36,37} This means that, with $c = 20$ mM, the SDBS molecules form a bilayer on the RGS. However, a different trend was observed for the SGS, i.e., after an initial increase, no significant changes in θ_w were observed when c was larger than the cmc of SDBS. This result suggests that, with $c = 20$ mM, SDBS only forms an adsorbed monolayer on the SGS.

Considering the adsorption and θ_w results, we can conclude that a bilayer of SDBS formed on the RGS in the 20 mM SDBS solution. Perhaps some aggregates are also contained in the adsorption bilayer. Notably, the bilayer adsorption played an important role in the micelle-to-vesicle transition. We suppose that, under the forces imposed by shaking, the curved bilayers (perhaps together with some aggregates) detach from the RGS, and then close to form vesicles to decrease the interfacial energy of the aggregates.¹⁵ With repetition of this adsorption-detachment process, partial micelles are gradually transformed into vesicles, until an equilibrium between the two phases is reached. In the curved bilayers, the P value of SDBS is in the range of $1/2-1$. Therefore, the formation of the STS vesicles under RGS-mediation is consistent with the concept of molecular packing parameter. Interestingly, the obtained STS vesicles are stable. Perhaps, these vesicles just are a metastable phase; this needs to be verified. Therefore, there are many essential questions concerning the nature of STS vesicles that need to be answered.

CONCLUSIONS

A RGS-mediated micelle-to-vesicle transition was observed in SDBS (a simple anionic STS) solution in the absence of cosurfactants or any additives. The resultant vesicles coexisted in the solution with micelles. Interestingly, the obtained SDBS vesicles in the solution show good stability during long-term storage (at least 6 months at room temperature), exposure to high temperature (80 °C for 2 h), and freeze-thawing (−20 or −196 °C for 2 h to approximately 25 °C) after the RGS was removed. Our results confirmed that SDBS can adsorb on the RGS to form curved bilayers, and the curved bilayer adsorption and the roughness of the solid surface play an important role in the micelle-to-vesicle transition. The P value of SDBS in the curved bilayers was found to be in the range of $1/2-1$. Therefore, we supposed that the curved bilayers detached from the RGS and then closed to form vesicles. This RGS-mediated strategy simplifies the formation of vesicles, and does not require the introduction of new components into the surfactant system. Further research is needed to fully understand this phenomenon, as many essential questions concerning the nature of STS vesicles need to be addressed.

ASSOCIATED CONTENT

Supporting Information

Adsorption experiments of SDBS on HF-etched glass particles. Surface tension curves of SDBS solutions. ¹³C NMR and ¹H NMR spectra of purified SDBS. Correlation function plots of micellar and vesicle solutions. NS-TEM images and hydrodynamic diameter distributions of SDBS vesicle solutions obtained under different conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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