Colloid Polym Sci (2015) 293:3177–3187
DOI 10.1007/s00396-015-3714-5

INVITED ARTICLE

Influence of SDS on the L_α-phases of siloxane surfactant swollen by glycerol

Yun Yan[1] · **Ying Zhao**[1] · **Jianbin Huang**[1]

Received: 1 April 2015 / Revised: 29 June 2015 / Accepted: 16 July 2015 / Published online: 20 August 2015

Abstract The interaction between SDS and the swollen lamellar phase of an A-B-A type nonionic siloxane surfactant IM-22 in 60 % glycerol has been investigated with macroscopic phase observation, FF-TEM, SAXS, conductivity, and rheology experiments. Without addition of SDS, 20 % IM-22 forms highly swollen planar lamellar phase stabilized by strong thermal undulations. Upon addition of 1 mM SDS, the lamellae were transformed into giant multilamellar vesicles. The size of the vesicles decreases with increasing the amount of SDS below 5 mM whereas the number density of the vesicles increases. Further increasing the concentration of SDS leads to break of the vesicles. In this self-assembly transition process, the viscosity of the system exhibits maximum at 5 mM SDS, where the system owns property of gels. Conductivity measurements suggest that SDS starts to bind IM-22 at a concentration below 2 mM, but SAXS results reveal that the interlamellar spacings were not affected up to 5 mM. This was explained by the special interactions in this system. On the one hand, the ionization degree of SDS in 60 % glycerol is very low due to the low dielectric constant, which results in lower charge density in the lamellae. Therefore, thermal undulations dominate the electrostatic forces at SDS concentration below 5 mM. On the other hand, the mutual phobic nature of SDS with IM-22 allows break of the lamellae at higher SDS concentrations.

Keywords Siloxane surfactant · Glycerol · Swollen · Lamellar structure

Introduction

Various vesicles are of high interest in biology, pharmaceutics, and material science owing to their application in a broad field including membrane mimic [1–4]], drug delivery [5–7], template synthesis [8–10], and hydrogels [11]. The research on lamellar structures [12–15], including planar lamellae and multilamellar vesicles (MLV), build up the theoretical understanding on these systems. The lamellar structures, which are usually called L_α-phases, were found with anionic [16], cationic [17], zwitteronic [18–20], and noininc surfactants [21]. The properties of the L_α-phases can be modified with additives, such as alcohols [22, 23], ionic charges [24–26], and inert electrolytes [27, 28]. For instance, charging the low viscous L_α-phases of 100 mM C_{14}DMAO/220 mM C_n-OH/water gives the system high viscoelastic properties [14]. Generally, the nonionic lamellae structures undergo strong thermally induced out-of-plane undulations which can be described with Helfrich equation [29, 30]. These nonionic lamellae can be conveniently charged up upon replacing about 10 % C_{14}DMAO by charged surfactant, such as SDS or TTAB [14]. Charging the lamellae brings up electrostatic repulsions to the system, and the undulation is suppressed. Thus, the lamellae are “stiffened,” and the system

---

✉ Yun Yan
yunyan@pku.edu.cn

✉ Jianbin Huang
jbhuang@pku.edu.cn

[1] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

possesses viscoelastic properties [31, 32]. It was shown by Hoffmann et al. that the shear modulus increases strongly at the beginning then levels off or slightly passes over a maximum with increasing the charge density [33]. They have repeated these measurements on many systems and always found more or less the same behavior.

In this paper, we describe experiments to study the influence of ionic charges on a swollen L_α-phases formed by an A-B-A type siloxane surfactant in 60 % glycerol. Owing to their surface active property both in aqueous and nonaqueous media [34, 35], siloxane surfactants find many commercial applications ranging from the manufacture of polyurethane foam to cosmetics, textile manufacture, wetting agent, agricultural adjuvant, and coating additives [36–38]. Like the interaction between hydrocarbon and fluorocarbon surfactants, siloxane surfactants are mutual phobic with hydrocarbon surfactants. In a previous research [39], we have reported the influence of SDS on the vesicles of the 1 % A-B-A type siloxane surfactant—poly (ethyleneoxide)-poly (dimethylsiloxane)-poly (ethyleneoxide), i.e., EO_{15}-$PDMS_{15}$-EO_{15}, which is commercially available under the name of IM-22. For the sake of convenience, we will use the name IM-22 as we have used before in the following text. We found that the vesicles in the 1 % IM-22 were already broken by addition of 0.4 mM SDS. With progressively increasing the SDS concentration, the vesicles and vesicle fragments finally vanish completely, and the system is full of mixed spherical micelles of SDS/IM-22. Meanwhile, the turbidity of the system decreases with increasing the concentration of SDS (1 % IM-22 aqueous solution is bluish turbid due to the presence of large vesicles), which is a consequence of the formation of small micelles.

Having the above knowledge in mind, we are curious about the influence of SDS on the L_α-phases of IM-22. As we have reported before, the IM-22-water binary system separates into L_1/L_α two phases at concentration lower than 80 % [40]. But, the volume of L_α-phases can be swollen by substitution of the solvent water gradually with glycerol owing to the refractive index matching between that of the lamellae and the solvent which brings up the disappearance of the attractive van der Waals interaction between the layers so that they have to swell [27]. In the case of 20 % IM-22 system, the whitish L_α-phase which is on the bottom of the investigated glass test tube gradually swells to the whole volume at 60 % glycerol and the system becomes a single L_α-phase which is colorlessly transparent. In such a swollen state, the thermal undulation of the layer is significant, and the layer is very soft. Such a swollen L_α-phase is of our interest in this study. We aim to find out (1) can ionic hydrocarbon surfactant SDS stiffen the layers of the siloxane surfactant IM-22? (2) How the mutual phobic interaction between SDS and IM-22 affect the swollen L_α-phase? Macroscopic phase observation, rheology, and SAXS measurements were employed to investigate the system.

Experimental section

Phase diagram The samples were prepared by vortex mixing IM-22-water-glycerol systems in 10-ml test tubes. Air bubbles were removed by centrifugation. The phases were allowed for equilibrium under temperature-controlled conditions for at least 3 days. The phases were characterized by visual inspection with and without polarizers. The concentration of IM-22 is expressed in weight percent (wt %), while the content of glycerol in glycerol-water mixed solvent refers to volume percent (v %) to keep the same volumes for all the samples.

Freeze-fracture transmission electron microscopy (FF-TEM) TEM observations on the replication of samples were performed by using a JEOL-100CX II electron microscope. For the preparation of replica, a small amount of sample was placed in a gold cup; then, the cup was swiftly plunged into melt of liquid nitrogen. The frozen samples were fractured and replicated in a freeze-fracture apparatus EE-FED.B freeze-fracture device equipped with a JEE-4X vacuum evaporator at ×140 °C. Pt/C was deposited at an angle of 45° and 90°, respectively.

Conductivity The conductivity measurements were performed on a Seven Multi type (S40) conductivity meter (Mettler Toledo, Switzerland) at 25 °C using the MI-900 series conductivity electrodes (Microelectrodes, USA).

Small-angle X-ray scattering (SAXS) SAXS measurements were performed on a Kratky compact small angle system equipped with a position-sensitive detector (OED 50M, Mbraun, Graz, Austria) consisting of 1024 channels of 53.0-μm width each. The camera volume was kept under vacuum during the measurements in order to minimize the background scattering from air. The temperature was controlled and kept at 25 °C by using a Peltier element. The sample holder was a 1-mm quartz capillary which was filled with the samples by using a syringe.

Rheological measurements The rheological measurements were performed by a Haake RS600 with a cone and plate sensor. Temperature in the measuring system was controlled to ±0.1 °C by a thermo-controller (Haake TC 81). The viscous properties were determined by steady-state shear rate ramping, and the viscoelastic properties by oscillatory measurements from 0.01 to 10 Hz, for which the deformation was controlled to be in the linear region.

Results and discussion

Macroscopic behaviors

In 60 % glycerol solution, the 20 % IM-22 (ca. 82 mM) forms highly swollen viscous L_α-phase which shows good fluidity but with large bright domains of stationary birefringence (Fig. 1). This is neither the same as that of classic lamellar phase ($L_{\alpha h}$) which shows dotted domain-like birefringence, nor alike that for typical multilamellar vesicle phases ($L_{\alpha l}$) which shows schleren birefringence [25, 31, 41]. Such a birefringent pattern is probably the feature for swollen lamellae that have strong thermal undulations. As have discussed in our previous paper [40], the attractive van der Waals interaction between the lamellae almost vanishes to zero in 60 % glycerol. With increasing the glycerol content in the mixed solvent, the refractive index of the solvent increases, and the difference between that of the IM-22 and the solvent decreases. At 60 % glycerol system, the refractive index of the solvent is almost the same as that of the IM-22 compound. Therefore, the Hamaker constant A, which depends on the difference between the refractive index of the particles and the medium, approaches zero, and the attractive force which is proportional to the Hamarker constant A, between the bilayers vanishes. As a result, the repulsive pressure drives the bilayers to swell, which leads to an increase of the interlayer spacing, d [40]. The increased interlayer spacing allows for strong thermal undulation of the lamellae. Addition of 1~2 mM SDS does not change the transparency of the phases but brings up strong birefringence with large colorful domains. The different colors represent different lamellae orientation, which indicates the existence of giant MLVs. The area of the colorful domains in 2 mM SDS system is smaller than that in the case of 1 mM SDS, demonstrating the presence of smaller MLVs in the 2 mM SDS system. With further addition of SDS, the system gradually loses its stationary birefringence, but the viscosity keeps increasing up to 5 mM SDS. Actually, the samples with 4 and 5 mM SDS lose their fluidity and become gels. Higher than 5 mM SDS results in the complete loss of the stationary birefringence. Instead, flow birefringence was observed for samples with up to 40 mM SDS, which is about half of the molar concentration of the IM-22. This means that although the phase behaviors of IM-22 are very sensitive to small amount of SDS, increasing the SDS concentration may lower this sensitivity. This is probably because of there are too many SDS binding sites in the polymer chain of IM-22. According to the EO_{15}-$[SiO(CH_3)_2]_{15}$-EO_{15} composition of IM-22, the total molar concentration of the subunits of EO and $[SiO(CH_3)_2]$ for the 20 % IM-22 system is about 3690 mM, which is a huge number compared with the added SDS. Therefore, it is understandable that the change of the phase behaviors is not sensitive to the SDS concentration after initial binding.

Direct imaging of FF-TEM

The macroscopic changes for the samples with addition of SDS observed in Fig. 1 reflect the changes in microstructures in these systems. Micrographs were therefore taken of samples with various amount of SDS for the 20 % IM-22 in 60 % glycerol mixtures. In Fig. 2, we show FF-TEM results of 20 % IM-22 in 60 % glycerol in the presence of 0, 1, 3, 5, and 8 mM SDS

It is clearly observed that before addition of SDS, the swollen IM-22 L_α-phase is composed of lamellar phases (Fig. 2a). These lamellae are very soft with strong thermal undulation (Fig. 2a, as indicated with the short arrow) due to the weak van der Waals attraction between the layers. The strong undulation results in the deformation of the planar lamellar structures into closed giant MLVs (Fig. 2a, indicated with long arrows). The coexistence of planar and giant MLVs brings up the uncharacteristic stationary birefringent pattern for the system as observed in Fig. 1.

After addition of 1 mM SDS to the system, no break of lamellae is observed, but the planar lamellae become much stiffer and most of them are changed into giant MLVs (Fig. 2b). Obviously, the thermal undulations of the shells have been greatly reduced upon addition of the small amount of SDS. The existence of predominant giant MLVs is in good agreement with the colorful birefringence pattern observed in Fig. 1, which is caused by the deformation of these giant multilamellar vesicles.

At 3 mM SDS, no planar lamellae can be observed, and the system is transformed into a vesicle phase (Fig. 2c). Most of the vesicles are multilamellar with diameters in the range of 100–300 nm, and some of them are deformed. The smaller vesicle size is in line with the smaller birefringence domains than that in the 1 mM SDS system. Further increasing the SDS concentration to 5 mM, the number of the 300 nm vesicles is greatly reduced, and the system is dominated by densely packed vesicles of 60–150 nm (Fig. 2d). At much higher SDS concentration of 8 mM, the size of the majority of vesicles is further reduced to 30–80 nm, although some larger ones around 300 nm are still observable. The decrease in the vesicular size is reflected in birefringence: the stationary birefringence disappears gradually, but flow birefringence still exists due to the presence of small fraction of deformable large vesicles.

It is noteworthy that the number density of the vesicles in the 5 mM SDS system is the highest. Further addition of SDS decreases not only the size of the vesicles, but also their numbers. This suggests that high amount of SDS could destroy vesicular structures, probably due to the mutual phobic interaction between SDS and IM-22 molecules. Actually, in the dilute IM-22 system of 1 %, 0.4 mM SDS was found to destroy the self-assembled IM-22 vesicles into membrane fragments with dangling rod-like micelles [39]. Therefore,

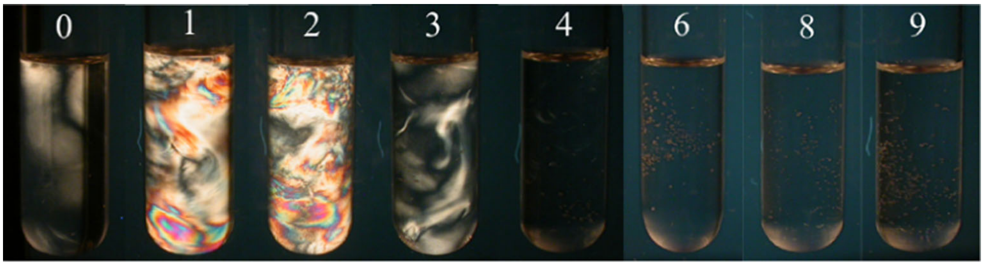

Fig. 1 Photos between crossed polarizers of 20 % IM-22 in 60 % glycerol with different SDS concentration. The digitals above the photos are the SDS concentration (mM)

the above experiments suggest that low amount of SDS charges the lamellar phase of siloxane surfactants, whereas it breaks the lamellar structure of siloxane surfactant, here vesicles, at higher concentrations. If we assume that break of vesicles occurs at the same IM-22/SDS ratio, in the present 20 % IM-SDS system, the amount of SDS that requires to have apparent effect of breaking should be 8 mM SDS. This is indeed the case, because we observed that at higher than 8 mM SDS, the system enters into a completely different state, as will be discussed in the rheology section. Anyway, it is very clear that that the effect of SDS on nonionic siloxane surfactant is different from that on the nonionic hydrocarbon surfactants, where no obvious break of vesicles was observed.

SAXS measurements

In order to have an insight on the effect of SDS on the swollen lamellar structures of IM-22 in 60 % glycerol, SAXS experiments were carried out to study the change in the interlamellar

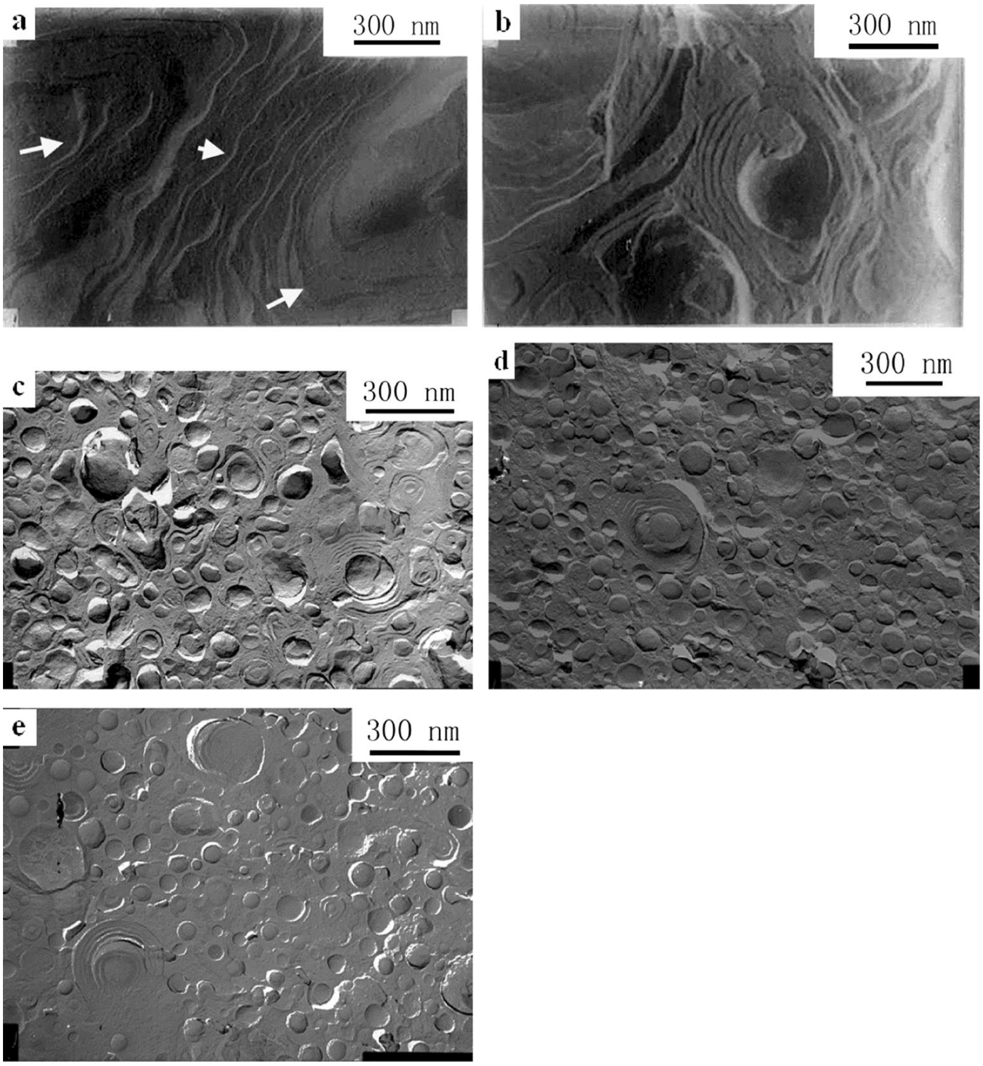

Fig. 2 Freeze-fracture TEM micrographs of the 20 % IM-22 in 60 % glycerol with different SDS concentration; **a** no SDS; **b** 1 mM SDS; **c** 3 mM SDS; **d** 5 mM SDS; **e** 8 mM SDS

spacing with increasing SDS concentration. As illustrated in Fig. 3, the scattering intensities for the 0 mM SDS system show one broad strong maximum. The lack of pronounced single peak is an indication that the L_{α}-phase is not highly ordered. This is in good agreement with the FF-TEM observations in Fig. 2a that the lamellae undergo strong undulations. Upon addition of 1 mM SDS, the scattering peak is very much sharpened indicating that the lamellae are much more ordered. This accords very well with the suppressed undulation of the lamellae observed by FF-TEM in Fig. 2b. With further increase of SDS concentration up to 5 mM, the strength of the sharp peak decreases gradually, but the position of the peak stays roughly constant. This result suggests that less than 5 mM does not affect the average interlamellar spacing, both for planar phase and for multilamellar vesicles, which is 34.5 nm according to Brag equation. Recalling the FF-TEM results, it can be inferred although the spacing between the lamellae did not change with SDS addition, the variation of the vesicle size distribution has decreased the overall order of the lamellae in the system. It is remarkable in Fig. 3 that higher than 5 mM SDS results in a shift of the peak position to higher *q* values, which accord with shrinking of the lamellae in the vesicles. The interlamallar distances for the 8 and 10 mM SDS systems were decreased to 29.9 and 25.3 nm, respectively.

The above SAXS results suggest that at SDS concentrations below 5 mM, change of vesicle size is mainly caused by the increased charge density in the hydrophilic part of the lamellae, which favors the formation of structures with larger curvature. Therefore, the loss in vesicular size is compensated by an increase in the number density of the vesicles. This is in good agreement with our FF-TEM observations at SDS concentrations below 5 mM. However, at SDS concentration beyond 5 mM, two situations may occur: on the one hand, the charge density for the hydrophilic part keep increasing with more SDS binding so that the vesicles have to shrink in size; on the other hand, binding of SDS to the hydrophobic part of IM-22 molecules leads to the break of the lamellar skeleton due to the mutual phobic interaction between SDS and the dimethylsiloxane groups. Both effects bring up the decrease in the size and the number density of the vesicles.

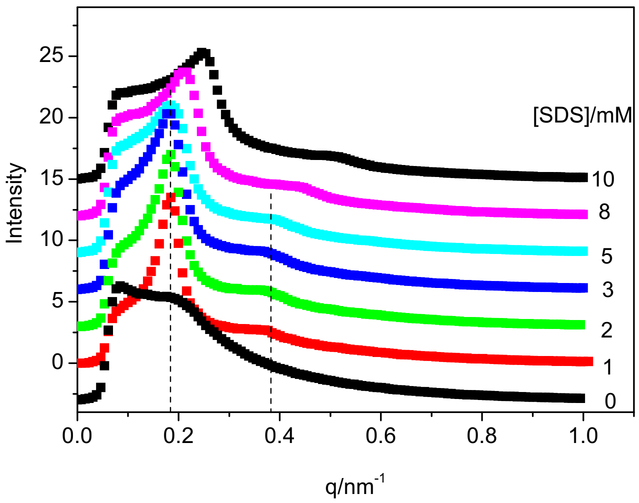

Fig. 3 Effect of SDS on the lamellar phase of 20 wt% IM-22 in 60 % glycerol

This effect of SDS on the interlayer distance is rather surprising. Other groups reported previously that addition of around 3.5 mM SDS (0.1 %) already resulted in more than two times swelling on the interlamellar distance [42]. This can be probably ascribed to the special interaction between SDS and IM-22. In hydrocarbon surfactant system, the added SDS molecules will mix up with the surfactants and participate the bilayer formation. In contrast, when interacting with IM-22 molecules, SDS molecules can either bind the EO groups or the siloxane groups of the IM-22 molecules. In the former case, the presence of SDS will mainly increase the area of the hydrophilic portion of the IM-22 molecules, which leads to the formation of structures with larger curvature but the hydrophobic skeleton of the lamellae is not very much affected. But, the charges on SDS can stiffen the lamellae slightly, so that the undulation is reduced to an extent that does not affect the interlayer spacing. However, in the latter case, SDS will trigger the break of the lamellae due to the mutual phobic interaction with the siloxane part. This means that SDS cannot effectively charge up the lamellae as it does for hydrocarbon surfactants.

Conductivity measurements

The binding of SDS with IM-22 molecules in 60 % glycerol should be reflected in the change in the conductivities. We therefore compared the conductivity of SDS in 60 % glycerol and that in the presence of 20 % IM-22.

As revealed in Fig. 4a, a break at 17 mM SDS is observed for the conductivity of SDS in 60 % glycerol, which characterizes the CMC of SDS in 60 % glycerol. This CMC value of SDS is much larger than that in water (8 mM) [39], demonstrating a weaker self-association ability of SDS in 60 % glycerol. In the presence of 20 % IM-22, the conductivity of SDS decreases considerably. Noticeably, no detectable inflection point was found in the conductivity as the concentration of SDS increases up to 100 mM. This suggests that the SDS keeps binding to IM-22 and no pure SDS micelles are formed even when the concentration of SDS is 100 mM. This is understandable since the concentration of IM-22 is 20 %, which is about 82 mM, where the overall concentration of the EO and $[SiO(CH_3)_2]$ unit is about 3690 mM. This concentration is much too high when compared with the highest concentration of SDS. Because SDS can bind to both the EO and $[SiO(CH_3)_2]$ unit, it is expected that SDS micelles can be formed only at cases all the IM-22 in the system are saturated with SDS.

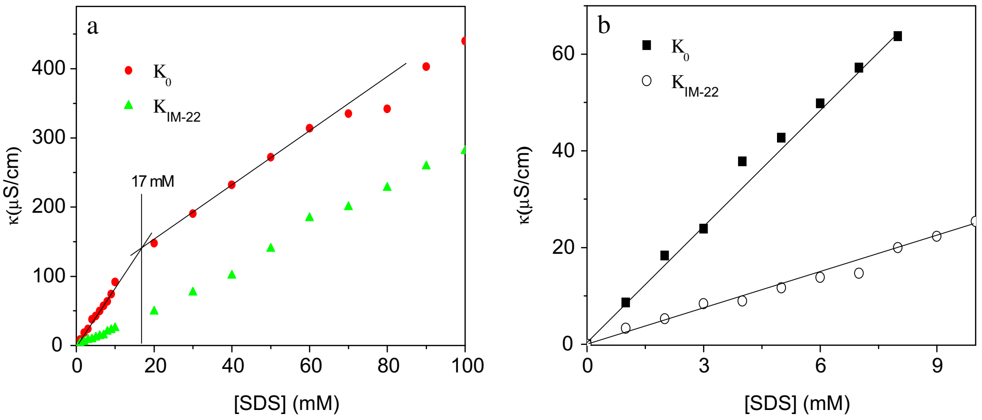

Fig. 4 **a** Conductivity measurements for SDS in 60 % glycerol without and with 20 % IM-22. **b** The enlarged plot of **a** for low SDS concentrations

Rheological behavior

The change in the microstructures was also reflected in the macrorheological behaviors. Before addition of SDS, the swollen lamellar phases of 20 % IM-22 in 60 % glycerin have good fluidity. With increasing the SDS concentration from 1 to 5 mM, the viscosity of the phases increases dramatically. The 4~5 mM SDS systems can support their own weight when the samples are allowed for up-side-down position. Further increase of SDS concentration results in again a decrease of the viscosity. In the following, we show the rheological results in detail.

In Fig. 5, rheograms of 20 % IM-22 in 60 % glycerol at various SDS concentrations are shown. The storage modulus G′, the loss modulus G″, and the magnitude of the complex viscosity η* are plotted against the oscillating frequency in a double log plot. The systems can be divided into two categories according to the rheogram pattern. Category I includes systems with SDS concentrations 0~5 mM, where the elastic (storage) moduli are roughly frequency independent (Fig. 5a–c), whereas category II contains those with higher SDS concentrations, where the elastic moduli depends on frequency (Fig. 5d–f).

Systems with 0~5 mM SDS

This group of samples all has an elastic modulus higher than viscous modulus in the examined frequency range. Before addition of SDS (Fig. 5a), the elastic modulus is independent of frequency below 5 Hz and has a constant value of about 8.5 Pa, whereas the loss modulus G″ is frequency independent below 0.2 Hz but depends very much on the frequency in the higher frequency range. This indicates that the phase behaves partly like soft solid material (gel) which is in-between the properties of planar lamellae and multilamellar vesicles. This rheological result is in very good agreement with the observation from FF-TEM micrographs, where we found the coexistence of undulated planar lamellae and giant multilamellar vesicles, and also agrees well with the observation of the birefringence in section 1 which gives an untypical pattern.

With addition of only 1 mM SDS, the elastic modulus G′ becomes constant in the range from 0.01~10 Hz, and the magnitude increases to about 14.5 Pa, which means that the layers have been stiffened by SDS. At 2–5 mM SDS, the rheogram looks similar to the case of 1 mM SDS system, but the storage modulus is increased steeply to 18.5, 61.6, 106.5, and 113.0 Pa, respectively. The increase of the shear modulus with addition of SDS to the 20 % IM-22 in 60 % glycerol aqueous system can be related with the change in microstructures. Recalling the FFR-TEM micrographs in Fig. 2 that the thermal undulations of the layers have been greatly reduced upon addition of SDS, and the system undergoes transition from planar lamellae -MLVs to ULVs. This demonstrates that systems with smaller vesicles are more robust in terms of against shear force. Although we do not have micrographs for all these samples, it is already very clear in Fig. 2 that vesicles in 5 mM SDS system are much smaller than those in the 2 mM SDS system. Hoffmann et al. have found that, under conditions of the same total material, the smaller the vesicles are, the larger the shear modulus would be [43]. Because the decrease in the vesicle size means the increase of their number density N, and the latter results in a higher storage modulus G′, which is proportional to the number density of the particles according to the following equation [44, 45]:

$$G' \approx NkT \qquad (1)$$

Equation (1) tells us that the number of vesicles increases with addition of SDS to the swollen lamellae phases up to 5 mM SDS. For an MLV system, increase of the number of vesicles is at the cost of their size. This is in very good agreement with our FFR-TEM observations that at 5 mM SDS, small vesicles become dominant. The decrease of the vesicle size also agrees well with the less stationary birefringence for the 3, 4, and 5 mM SDS systems. The more the shells in the multilamellar vesicles are, the stronger the birefringence is; the larger the vesicles, the bigger the colorful domains.

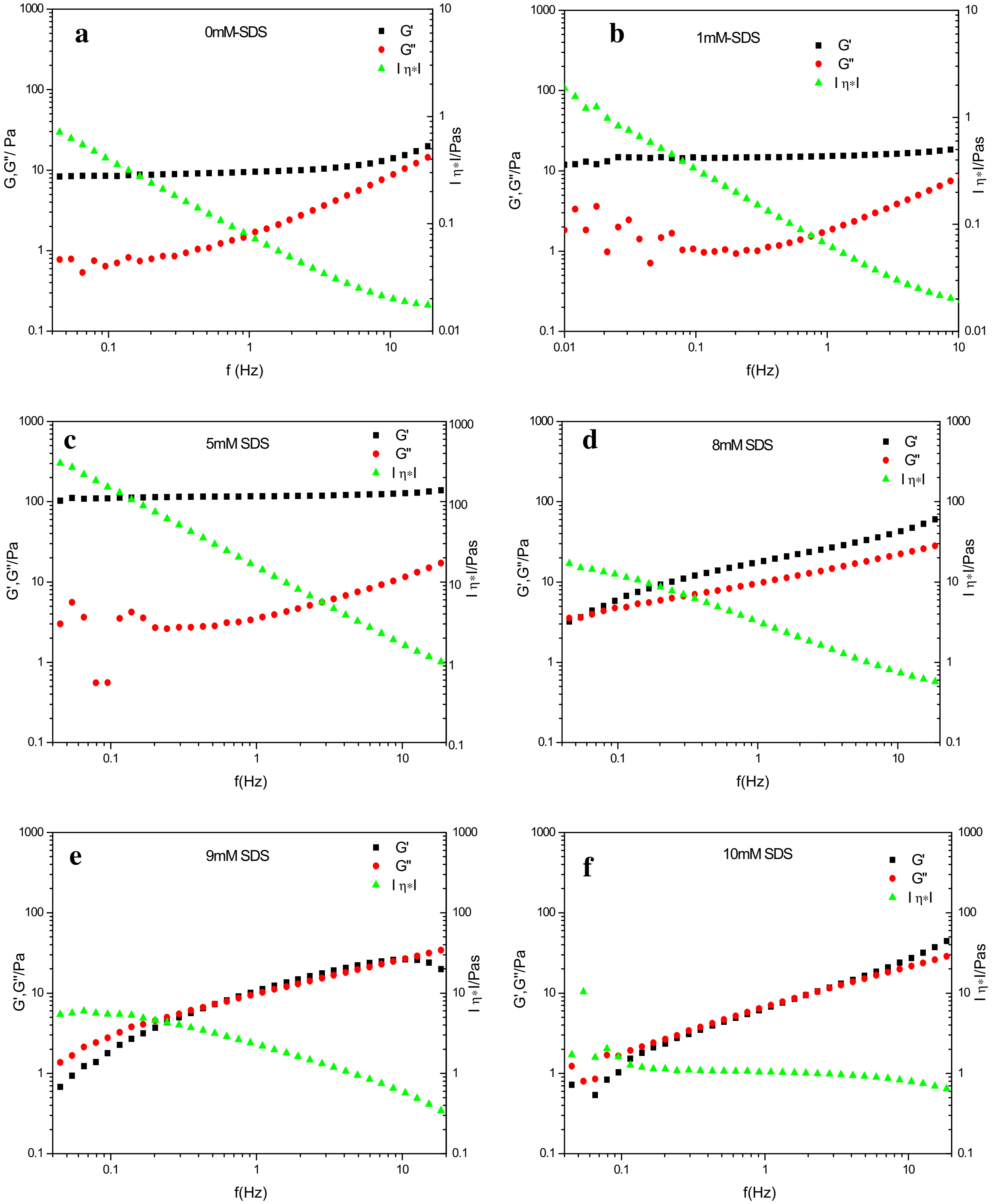

Fig. 5 Rheogram of 20 % IM-22 in 60 % glycrol with SDS concentration. **a** 0, **b** 1, **c** 5, **d** 8, **e** 9, **f** 10 (mM)

Therefore, the loss of the stationary birefringence in this system indicates that both the size and number of shells of the vesicles have been greatly decreased. It has to be pointed out that the magnitude of the shear modulus can also be affected by the interactions between the vesicles [46], but increasing the number of the vesicles will always bring up a stronger interaction due to the smaller distances between them.

It is also remarkable that at 4 and 5 mM SDS, both the storage and loss modulus are frequency independent, with the latter approximately 10 times smaller than the former; meanwhile, the complex viscosity decreases double-logarithmically in the shown frequency region, i.e., a throughout shear thinning behavior is observed. Namely, at SDS concentrations around 4~5 mM, one reaches a system with rheological properties that are typical of a weak gel. This is the signature of a Binham fluid with a yield stress. Indeed, a typical yield stress for the samples with 4 and 5 mM SDS has been found (Fig. 6). The yield stress should come from the dense packing of the ULVs.

The system with 6~20 mM SDS

At much higher SDS concentration than 5 mM, the pattern of the rheogram has been completely changed. Both elastic and viscous moduli become frequency dependent in the whole experimental range, and the system recovers its fluidity with flow birefringence. For example, at 0.1 Hz, the shear modulus drops from 113 Pa sharply to 58.8 Pa for the 6 mM SDS system. This demonstrates that the number of vesicles is decreased when compared with the 5 mM SDS system. According to our previous report on the influence of SDS on the vesicle structures in aqueous solution [39], the vesicular structures of siloxane surfactant IM-22 can be destroyed by addition of SDS. It is, therefore, conceivable that more vesicles are broken at higher SDS concentration. As discussed in previous text, it is estimated that it requires at leat 8 mM SDS to break these vesicles. In this way, the system becomes a mixture of vesicles and the fragments of membranes with dangling rod-like micelles [39]. As a result, the dense packing of vesicles vanishes, and the system shows weak flow birefringence mainly due to the alignment the fragments under shear force. The higher the SDS concentration, the weaker the flow birefringence is. As shown in Fig. 5d, the storage and the loss modulus for the 8 mM SDS system cross at the frequency of 0.05. This means that the system has a structural relaxation time of $1/\omega=1/2\pi f=3.18$ s. At shorter times or higher frequencies, the elastic properties dominate. The rheological properties of the phases are thus very much like the properties of a viscous L_1-phase, which is an indication that unsymmetrical membrane fragments become dominant. According to our previous study [39], these unsymmetrical membrane fragments may have some rod-like micelles attached. With increasing the concentration of SDS to 9 and 10 mM, the population of such membrane fragments may further increase, which brings the system with completely different rheological behavior, as demonstrated in Fig. 5e, f. Now, both moduli are practically the same over a large frequency range. Such a rheogram is reminiscent of a phase that is at the sol-gel transition. This is in line with the dramatic break of vesicles by the addition of more SDS. At SDS concentration up to 40 mM, the storage modulus becomes undetectable, and the system becomes a viscous solution, indicating that no big membrane fragments present any more.

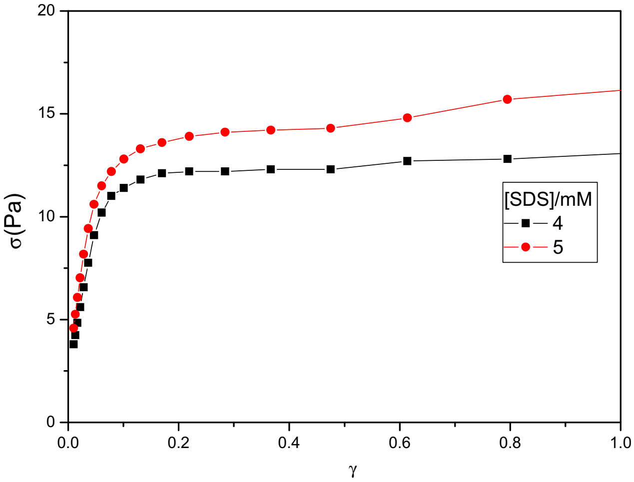

Fig. 6 Variation of stress versus deformation for systems with different SDS concentration

Apparent viscosities

Because the viscosities of the system vary significantly with increasing SDS, we therefore are very interested to investigate the shear viscosities of the systems with increasing SDS concentration. Although the viscosities of many viscoelastic solutions follow the Cox-Merz rule, namely, the shear viscosities as a function of the shear rate and the magnitude of the complex viscosities as a function of the angular frequency have the same value in the shear thinning region [47], most vesicle solutions do not show this simple behavior [48]. We therefore carry out the shear rate ramping viscosity measurement.

Figure 7 shows two plots of the apparent viscosity under shear versus the shear rate for different contents of SDS. The viscosity increases as SDS concentration varies from 0~5 mM, but all show shear-thinning behavior with many complicated details in these shear flow curves. This means that the phases are very fragile so that the phase structure is easily affected by shear, which is in line with our SXAS results that SDS does not affect the phases dramatically so that the phases are not ‘stiff’ enough against shear. Similar flow curves are found up to SDS concentration of 7 mM, but the viscosity exhibit a maximum around 5 mM SDS, then decreases with increasing SDS concentration.

Surprisingly, further addition of SDS to 8~12 mM, a total different pattern on the viscosity curve is found. The phases behave shear-thickening at low shear rate and become shear-thinning again after pass over a viscosity maximum. This is in

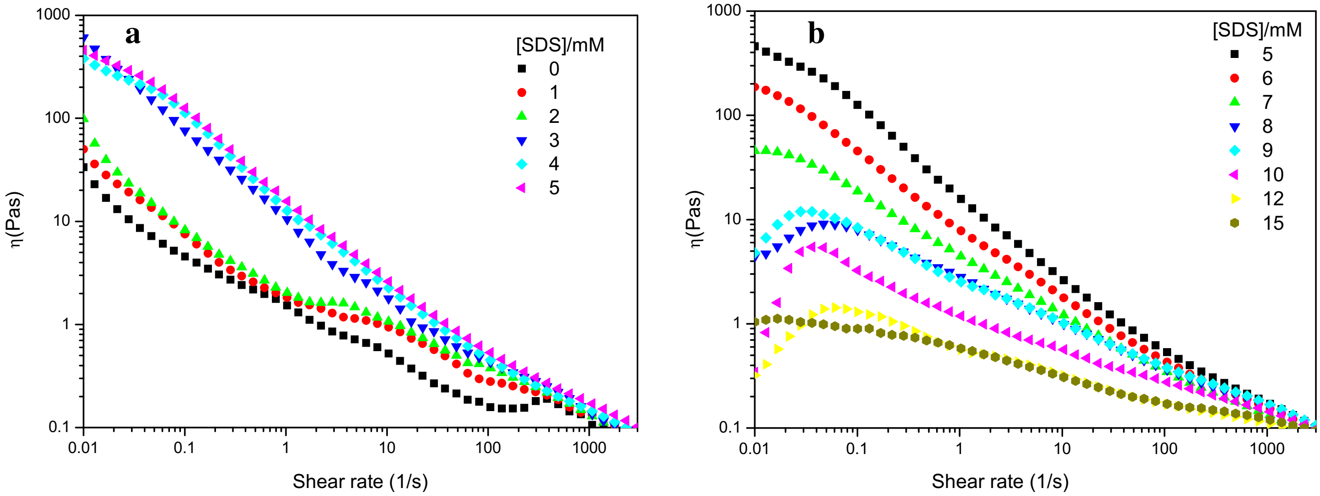

Fig. 7 Double log plot of the apparent shear viscosity versus the shear rate for 20 % IM-22 with different SDS concentrations

line with the rheological behaviors of rod-like micelles of several tens nanometer long [49]. These micelles undergo free Brownian motions at equilibrium state under slow shear rates. When the applied shear rate is above a critical value, however, they tend to rearrange and form larger aggregates. As a result, shear-thickening occurs [49]. We infer that it is likely most of the vesicle membranes that have been destroyed by increasing amount of SDS into rod-like micelles as a result of the mutual phobic effect between hydrocarbons and the silicones [39]. Although these rod-like micelles may still dangling from some membrane fragments [39], they already show unnegligible influence in the shear behavior. Especially, these rod-like micelles were induced to aggregate at critical shear rates, and this aggregation allows the rod-like micelles grow into long worm-like micelles at higher shear rates. Different from rod-like micelles or several tens nanometer long, a few hundred nanometer-long worm-like micelles may align under shear, so that shear-thinning occurs. The position of the shear-thickening peaks shifts to higher shear rate as SDS concentration increases from 8 to 12 mM which is probably due to the increase of the fraction of the rod-like micelles at higher SDS concentrations.

We have known that sufficient amount of SDS will finally destroy the vesicles in aqueous solution. Following this clue, we could expect that the shear-thickening behavior will become less pronounced with further addition of SDS. This is again proved by our experimental results. The shear-thickening peak becomes very small at 15 mM SDS, and the position shifts back to lower frequency. These two characters are signs that the number and size of the rod-like micelles are dramatically decreased, so that little energy is requited and the viscosity decreases. However, according to our conductivity results, completely break of the SDS-IM-22 mixed structures require a SDS concentration around 80 mM.

Conclusions

We have reported the effect of SDS on the swollen lamellar phase of siloxane surfactant IM-22 in 60 % glycerol solution. Although SDS progressively binds to the lamellae structure of 20 % IM-22 in 60 % glycerol from lower than 2 mM, they do not affect the interlamellae spacing up to 5 mM, which is attributed to the low ionization degree of the SDS in 60 % glycerol. In this stage, thermal undulations dominate over electrostatic forces. But, this small electrostatic force is big enough to intrigue transformation from planar lammellae into multilamellar vesicles, and the number density of the vesicles increases with increasing the amount of SDS which is at the cost of the size. When the electrostatic forces supreme the undulations, SDS leads to contract of the interlamellar spacings. Much more SDS breaks the vesicles due to the mutual phobic interaction with the siloxane portion of IM-22 molecules.

Acknowledgments The authors greatly acknowledge financial support from the natural science foundation of China (NSFC, project number 21173011). We also sincerely thank Professor Heinz Hoffmann for the helpful suggestions, and Dr. Aihua Zou for the SAXS experiments.

References

1. Lipowsky R, Sackmann E (eds) (1995) Handbook of Biological Physics, vol 1. Elsevier, Amsterdam
2. Rosoff M (1996) Ed.; Vesicles. Marcel Dekker, Inc., New York
3. Zhao Q, Wang Y, Yan Y, Huang JB (2014) Smart Nanocarrier: Self-Assembly of Bacteria-like Vesicles with Photoswitchable Cilia. ACS Nano 8(11):11341–11349
4. Layali I, Tahmasbpour E, Joulaei M, Gholam S, Jorsaraei A, Farzanegi P (2015) Total Antioxidant Capacity and Lipid Peroxidation in Semen of Patient with Hyperviscosity. Cell J 16(4):554–559

5. Lasic DD (1994) Sterically Stabilized Vesicles. Angew Chem Int Ed Engl 33(17):1685–1698
6. Abdelkader H, Alani AWG, Alany RG (2014) Recent advances in non-ionic surfactant vesicles (niosomes): self-assembly, fabrication, characterization, drug delivery applications and limitations. Drug Delivery 21(2):87–100
7. Salim M, Minamikawa H, Sugimura A, Hashim R (2014) Amphiphilic designer nano-carriers for controlled release: from drug delivery to diagnostics. Medchemcomm 5(11):1602–1618
8. Christiansen SC, Zhao DY, Janicke MT, Landry CC, Stucky GD, Chmelka BF (2001) Molecularly ordered inorganic frameworks in layered silicate surfactant mesophases. J Am Chem Soc 123(19): 4519–4529
9. Junker K, Luginbuhl S, Schuttel M, Bertschi L, Kissner R, Schuler LD, Rakvin B, Walde P (2014) Efficient Polymerization of the Aniline Dimer p-Aminodiphenylamine (PADPA) with Trametes versicolor Laccase/O-2 as Catalyst and Oxidant and AOT Vesicles as Templates. ACS Catal 4(10):3421–3434
10. Zhang XL, Niu CY, Wang YQ, Zhou SM, Liu J (2014) Gel-limited synthesis of dumbbell-like Fe3O4-Ag composite microspheres and their SERS applications. Nanoscale 6(21):12618–12625
11. Grabner D, Hoffmann H, Forster S, Rosenfeldt S, Linders J, Mayer C, Talmon Y, Schmidt J (2014) Hydrogels from phospholipid vesicles. Adv Colloid Interface Sci 208:252–263
12. Helfrich W (1978) Z Naturforsch Teil A 33:305
13. Schomacker RSR (1994) J Phys Chem 98:3908
14. Hoffmann H, Thunig C, Schmiedel P, Munkert U (1994) Surfactant Systems with Charged Multilamellar Vesicles and Their Rheological Properties. Langmuir 10(11):3972–3981
15. Hoffmann HT (1995) C.; Schmiedel, P.; Munkert, U. Faraday Discuss 101:319
16. Roux D, Safinya CR (1988) J Phys Fr 49:307
17. Bassereau P, Marignan J, Porte G (1987) J Phys Fr 48:673
18. Thunig C, Hoffman H, Platz G (1989) Prog Colloid Polym Sci 79:297
19. Thunig C, Hoffman H (1990) Prog Colloid Polym Sci 83:167
20. Escalante JI, Hoffmann H (2000) Non-linear rheology and flow-induced transition of a lamellar-to-vesicle phase in ternary systems of alkyldimethyl oxide/alcohol/water. Rheol Acta 39(3):209–214
21. Strey R, Schomacker R, Roux D, Nallet F, Olsson U (1990) J ChemSoc, Faraday Trans 86:2253
22. Escalante JI, Gradzielski M, Hoffmann H, Mortensen K (2000) Shear-induced transition of originally undisturbed lamellar phase to vesicle phase. Langmuir 16(23):8653–8663
23. Jonstromer M, Strey R (1992) J Phys Chem 96:5993
24. Yamashita Y, Hoffmann H, Maeda H, Li L, Ballauff M (2007) Aggregation and phase behavior of a double-chain surfactant, N-dodecyl-N-octyl-N-methylamine oxide, as a function of the protonation degree. Langmuir 23(3):1073–1080
25. Bergmeier M, Hoffmann H, Thunig C (1997) Preparation and properties of ionically charged lamellar phases that are produced without shearing. J Phys Chem B 101(30):5767–5771
26. Dvir T, Fink L, Schilt Y, Raviv U (2014) Charging and Softening, Collapse, and Crystallization of Dipolar Phospholipid Membranes by Aqueous Ionic Liquid Solutions. Langmuir 30(49):14725–14733
27. Muir BW, Zhen GL, Gunatillake P, Hartley PG (2012) Salt Induced Lamellar to Bicontinuous Cubic Phase Transitions in Cationic Nanoparticles. J Phys Chem B 116(11):3551–3556
28. Dawin UC, Osipov MA, Giesselmann F (2010) Electrolyte Effects on the Chiral Induction and on Its Temperature Dependence in a Chiral Nematic Lyotropic Liquid Crystal. J Phys Chem B 114(32): 10327–10336
29. Helfrich W (1978) Steric Interaction of Fluid Membranes in Multilayer Systems. Z Fur Naturforschung Section J Phys Sci 33(3):305–315
30. Schomacker R, Strey R (1994) Effect of Ionic Surfactants on Nonionic Bilayers - Bending Elasticity of Weakly Charged Membranes. J Phys Chem 98(14):3908–3912
31. Bergmeier M, Gradzielski M, Hoffmann H, Mortensen K (1999) Behavior of ionically charged lamellar systems under the influence of a shear field. J Phys Chem B 103(9):1605–1617
32. Hoffmann H, Ulbricht W (1996) Surfactant gels. Curr Opin Colloid Interface Sci 1(6):726–739
33. Hoffmann H, Thunig C, Schmiedel P, Munkert U (1995) Gels from surfactant solutions with densely packed multilamellar vesicles. Faraday Discuss 101:319–333
34. Svitova T, Hoffman H, Hill RM (1996) Langmuir 12:1712
35. Nagatan N, Fukuda K, Suzuki T (2001) J Colloid Interface Sci 234:337
36. Schaefer D (1990) Tenside, Surfactants, Deterg 27:154
37. Schmidt G (1990) Tenside, Surfactants, Deterg 27:324
38. Hill RM (1999) Silicone Surfactants, vol 8. Marcel Dekker, New York
39. Yan Y, Hoffmann H, Drechsler M, Talmon Y, Makarsky E (2006) Influence of hydrocarbon surfactant on the aggregation behavior of silicone surfactant: Observation of intermediate structures in the vesicle-micelle transition. J Phys Chem B 110(11):5621–5626
40. Yan Y, Hoffmann H, Makarsky A, Richter W, Talmon Y (2007) Swelling of L-alpha-phases by matching the refractive index of the water-glycerol mixed solvent and that of the bilayers in the block copolymer system of (EO)(15)-(PDMS)(15)-(EO)(15). J Phys Chem B 111(23):6374–6382
41. Hoffmann H, Horbaschek K, Witte F (2001) Vesicle phases with semipolar additives. J Colloid Interface Sci 235(1):33–45
42. Fogden A, Daicic J, Mitchell DJ, Ninham BW (1996) Electrostatic rigidity of charged membranes in systems without added salt. Phys A 234(1-2):167–188
43. Gradzielski M, Muller M, Bergmeier M, Hoffmann H, Hoinkis E (1999) Structural and macroscopic characterization of a gel phase of densely packed monodisperse, unilamellar vesicles. J Phys Chem B 103(9):1416–1424
44. Thurn H, Lobl M, Hoffmann H (1985) Viscoelastic Detergent Solutions - a Quantitative Comparison between Theory and Experiment. J Phys Chem 89(3):517–522
45. Graessly WW (1974) Advances in Polymer Science, vol 6. Springer, New York
46. Li HG, Hao JC (2008) Phase Behavior and rheological properties of a salt-free catanionic surfactant TTAOH/LA/H2O system. J Phys Chem B 112(34):10497–10508
47. Cox WP, Merz EH (1958) J Polym Sci 28:619
48. Rehage H, Hoffman H (1991) Mol Phys 74:933
49. Hoffmann H (1994) Fascinating Phenomena in Surfactant Chemistry. Adv Mater 6(2):116–129

Professor Yun Yan earned her bachelor degree at Northeast Normal University (1997) and the PhD degree at Peking University (2003), China. After two postdoctoral studies in Bayreuth University (Germany, with professor Hoffmann) and Wageningen University (the Netherlands, with professor Martien A. Cohen Stuart) in colloid science, she joined Peking University as an associate professor in 2008. She was selected into the New Century Training Program for the Talents by the State Education Commission of China in 2009, and was awarded as "Outstanding Young Professor of Colloid Science of China" in 2013, Teaching Award of Peking University (2013), winner of Outstanding Youth Science Foundation, Natural Science Foundation of China (NSFC, 2014), Excellent doctoral thesis instructor of Peking University (2014). Her current interest is solution based molecular self-assembly, and the application of molecular self-assembly in various advanced materials.

Dr. Ying Zhao obtained her bachelor degree at China Agricultural University in 2006 and obtained the PhD degree at Peking University in 2011. Her PhD study focuses on self-assembly of surfactants in water-glycerol mixed solvents. After obtaining her phD degree from Peking University, she joined industry as a research scientist in the research institute of Shenhua company, which is one of the largest companies for coal chemistry. She is now leading a group focusing the fabrication of nanoparticles in Shenhua research institute.

Professor Jianbin Huang obtained his bachelor (1987), master (1990), and PhD (1993) degree all at Peking University, China. After a postdoctoral study at the same university, he was nominated as an associate professor in 1995, as a full professor in 2001, and was awarded "Outstanding Young Scientist of China" in 2004. His main research interests include soft self-assembly of amphiphiles and one dimension nanomaterials that are synthesized using soft templates. He is currently the senior editor of Soft Matter.