

Cite this: *RSC Appl. Interfaces*, 2024,  
1, 173

## Highly efficient oil-fouling and foam removal achieved by surfactant mixed systems†

Zeyu Zhao,<sup>ad</sup> Tengda Wang,<sup>bc</sup> Jiling Yue,<sup>a</sup> Yaxun Fan <sup>\*abc</sup> and Yilin Wang <sup>\*abcd</sup>

Excessive usage of surfactants in daily life and industry and their undesirable high foamability have caused serious environmental pollution and economic loss. Improving cleaning efficiency and reducing foam stability concurrently is a delicate strategy but a challenging task. Herein, we mixed the most widely used surfactant sodium dodecyl sulfate (SDS) with cyclic amines ( $C_nN$ ,  $n = 6, 8, 12$ ), by which the self-assembly ability of SDS at the air/water interface and in bulk is significantly enhanced, while spherical micelles, vesicles and wormlike micelles are formed at appropriate total surfactant concentration ( $C_T$ ) and molar fraction of SDS ( $X_{SDS}$ ). Especially around  $X_{SDS} = 0.50$  and above critical micellar concentration (CMC), the stronger self-assembly ability leads to a higher contact angle of machine oil on stainless-steel plates and lower oil-water interfacial tension in  $C_nN/SDS$  solution, thus the oil-fouling removal efficiency of  $C_nN/SDS$  solutions is remarkably improved. Meanwhile, the foamability and foam stability dramatically decline at smaller  $X_{SDS}$  and slightly above CMC, attributed to the rapid molecular migration from liquid film of foams to the bulk between the films when the limited surfactant molecules in the films prefer to aggregate in bulk. As a result,  $C_6N/SDS$  exhibits the best oil cleaning and lowest foaming simultaneously at low  $X_{SDS}$  and just above the CMC. This study opens an efficient avenue to eliminate the contradiction between cleaning ability and foamability, thereby obtaining a high-efficiency and low-foam detergent.

Received 24th August 2023,  
Accepted 27th September 2023

DOI: 10.1039/d3if00145h

rsc.li/RSCApplInter

## Introduction

Amphiphilicity of surfactants endows them with unique surface activity and self-assembly ability in aqueous solution, thus they are widely applied in many fields, such as consumer household cleaning products,<sup>1–4</sup> industrial cleaning,<sup>5–7</sup> food industry,<sup>8,9</sup> agriculture,<sup>10–14</sup> drug delivery,<sup>15–18</sup> *etc.* Particularly as detergents, the global surfactant market turnover reached USD 42.1 billion in 2020 according to the data from *Markets and Markets*<sup>TM</sup>.<sup>19</sup> Moreover, the global cleaning products industry is projected to reach USD 61.6 billion by 2026.<sup>20</sup> Excessive consumption of surfactants causes environment chemical exposure and huge economic loss. With regard to this issue, many researchers have devoted their efforts in developing a wide range of novel surfactants by introducing more functional groups,<sup>21–24</sup> increasing the oligomerization degree,<sup>25–28</sup> and adjusting the

length of the spacer or alkyl chain<sup>29–31</sup> so as to optimize the cleaning performance of surfactants and reduce their dosage by altering the static/dynamic surface tension,<sup>32–35</sup> adsorption kinetics,<sup>36–39</sup> aggregation ability,<sup>40–42</sup> *etc.* In parallel, mixing surfactants with additives (inorganic/organic salts, other surfactants, polymers, *etc.*) is also an effective way to adjust the physicochemical properties of surfactants at the surface/interface and in solution,<sup>43–49</sup> while a large number of commercial additives offer much more optionality, convenience and practicability. Hence, introducing appropriate additives into commonly used surfactants is undoubtedly an economic and convenient approach to obtain highly efficient surfactant systems and achieve sustainable development.

The generation of liquid foams is at the heart of numerous natural, technical, or scientific processes related to surfactants. In many cases, they have very useful properties for practical applications, such as cleaning, foam flotation, food processing and firefighting. However, foams are not always desirable. The unwanted foams can obstruct gas transport and render the process of interest ineffective with significant cost implications. Kister *et al.*<sup>50,51</sup> made a survey on causes of malfunctions in industry, and they found that the existence of foam in surfactant solutions in distillation processes was a major reason for 900 investigated cases of column malfunctions. The accumulation of impurities that stabilize the foam on the sea also produces foams and destroys the normal ecological

<sup>a</sup> Beijing National Laboratory for Molecular Sciences and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.  
E-mail: yxfan@iccas.ac.cn, yilinwang@iccas.ac.cn

<sup>b</sup> Suzhou Institute for Advanced Research, University of Science and Technology of China, Suzhou, Jiangsu, 215123, P. R. China

<sup>c</sup> University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

<sup>d</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China

† Electronic supplementary information (ESI) available: Fig. S1–S7. See DOI: <https://doi.org/10.1039/d3if00145h>



environment.<sup>52–54</sup> Coincidentally, those aforementioned physicochemical properties facilitating the cleaning efficiency, such as low surface tension, strong aggregation ability and fast adsorption kinetics, often result in the strong foamability and foam stability in surfactant solution.<sup>55–58</sup> Therefore, the development of surfactant systems with high cleaning efficiency but adjustable foaming ability in different conditions encounters great technological hurdles although it is urgently desired in multiple fields.

The length and topological structure of alkyl chains play important roles in physicochemical properties of surfactants at surface/interface and in solution. Cyclic amines with bulky alkyl chains may form a larger hydrophobic domain in bulk but create looser arrangement at the air/water interface.<sup>59,60</sup> Their special structure makes it greatly possible for cyclic amine-containing systems to achieve high cleaning efficiency and low foam concurrently. Bearing in mind the structural advantages, we designed mixed systems composed of cyclic amines with various sizes of the cycloalkane ring ( $C_nN$ ,  $n = 6, 8, 12$ ) and widely used sodium dodecyl sulfate (SDS) at pH = 7.0. We found that the mixed solutions ( $C_nN/SDS$ ) show lower CMC and surface tension and form various assemblies at different molar fractions of SDS ( $X_{SDS}$ ) and total concentrations ( $C_T$ ), driven by the electrostatic and hydrophobic interactions between SDS and cyclic amines. With the balance of the self-assembly of surfactants at the liquid film of foam and in bulk between the films, the oil cleaning efficiency of  $C_8N/SDS$  is much higher than that of the other two systems, whereas its foamability and foam stability are remarkably weakened. This work offers a feasible method for effectively removing oil with low foamability and foam stability at low surfactant concentrations, thereby potentially reducing surfactant usage and promoting sustainable development of environments.

## Experimental section

### Materials

Cyclohexylamine ( $C_6N$ , >99.5%) was purchased from Energy Chemical, cyclooctylamine ( $C_8N$ , >97%) was purchased from Acros Organics, cyclododecylamine ( $C_{12}N$ , >99%) was purchased from Leyan Chemical, sodium dodecyl sulfate (SDS, >99%) was purchased from Sigma-Aldrich, and hydrochloric acid (HCl, 36%) was purchased from Beijing Chemical Works. 20<sup>#</sup> machine oil was purchased from Kunlun Lubricant Company. Deionized water (18.2 M $\Omega$  cm) from Milli-Q equipment was used in all the experiments.

### Surface tension measurement

The surface tension measurements of the  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixed systems at different molar fractions of SDS ( $X_{SDS}$ ) were carried out with a Wilhelmy plate method on the DCAT21 tensiometer (DataPhysics Co., Germany). The length and width of the plate were 19.90 and 0.20 mm, respectively. The standard error of surface tension is  $\sim 0.03$  mN m<sup>-1</sup>, and

the test temperature was  $25.00 \pm 0.01$  °C controlled by using a thermostat. Each measure was tested at least three times.

### Turbidity measurement

The turbidity values of the  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixtures at different  $C_T$  and  $X_{SDS}$  values, reported as 100 - %  $T$ , were measured at 450 nm using a Shimadzu UV-vis spectrophotometer (model UV-2800) with a water-circulating thermostat at  $25.0 \pm 0.01$  °C. All the measured values were corrected by taking the turbidity of Milli-Q water as the controller.

### Dynamic light scattering (DLS)

The size distribution of  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixtures at  $C_T = 20$  mM with  $X_{SDS}$  from 0 to 1.00 was measured using a Malvern ZetaSizer Nano ZS Instrument (ZEN3600, Malvern Instruments, Worcestershire, UK) at a scattering angle of 173° equipped with a 4 mW He-Ne laser ( $\lambda = 632.8$  nm) and a thermostating chamber at  $25.0 \pm 0.1$  °C.

### Cryogenic transmission electron microscopy (cryo-TEM)

5  $\mu$ L  $C_6N/SDS$  solutions at  $X_{SDS} = 0.10$ ,  $C_8N/SDS$  solutions at  $X_{SDS} = 0.20, 0.60$  and  $C_{12}N/SDS$  solutions at  $X_{SDS} = 0.80$  ( $C_T = 20$  mM) were loaded onto a carbon-coated holey TEM grid. The excessive solution was sucked away by filter paper leaving a thin liquid film on the grid. After a few seconds, the grid was quickly vitrified by plunging into liquid ethane (cooled by liquid nitrogen) at  $-183$  °C. The vitrified sample was transferred to a cryogenic sample holder and examined with a Themis 300 TEM (Thermo Fisher Scientific, America) at about  $-174$  °C. The images were recorded on a Gatan charge-coupled device (CCD) camera in the minimal electron dose mode.

### Interfacial tension measurement

The interfacial tension between surfactant mixtures and machine oil was measured by a TX500<sup>TM</sup> Spinning Drop Interface Tensiometer (Model TX500C). 1 mL  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixtures at  $C_T = 5$  mM with  $X_{SDS}$  from 0 to 1.00 were injected into a quartz glass tube as an external phase and 10  $\mu$ L of machine oil was injected into liquid solution as an internal phase. Oil drop formations at different rotation rates were recorded by a CCD camera, and interfacial tension was calculated by measuring the length and width of the oil drop and using Vonnegut and Bashford-Adams fitting. All the measurements were tested at  $25.0 \pm 0.1$  °C.

### Contact angle measurement

$C_nN/SDS$  ( $n = 6, 8, 12$ ) mixture solutions at  $C_T = 5$  mM with  $X_{SDS}$  from 0 to 1.00 were poured into a cuboid glass case. The stainless-steel plate was stuck to the bottom of a floating foam broad on the liquid solution. The machine oil droplet was squeezed out through a crooked needle and floated to the plate. The contact angle was recorded by a digital camera



and fitted by Image J software. Each measure was tested at least three times.

### Cleaning measurement

Oil cleaning efficiency was determined by weighing the metage of the weight gap during cleaning progress. The weight of the stainless-steel plate was  $M_0$ . Each 50  $\mu\text{L}$  of machine oil was daubed onto stainless-steel plates evenly. Stainless-steel plates with oil were weighed as  $M_1$  and then soaked into 10 mL liquid solution at different ratios of SDS. After ultrasonic vibration in an ultrasonic cleaning tank with an ultrasonic power of 120 W at the temperature of 25  $^\circ\text{C}$  for 10 min, the oil on the stainless-steel plates was removed to different extent and weighed as  $M_2$ . All the measures were tested at least three times. The oil cleaning efficiency was calculated by using the following equation,

$$\text{Oil cleaning efficiency}\% = [(M_1 - M_2)/(M_1 - M_0)] \times 100$$

### Foaming and defoaming measurement

The foaming and defoaming ability of various surfactant mixtures were tested by two methods. One is the air blowing method using a dynamic foam analyzer DFA 100 (KRÜSS, Germany).  $\text{N}_2$  was continuously blown into 50 mL analyte liquor at the bottom of the container until the foam height did not increase, then the highest foam height was recorded as foaming ability. The state change of foams with time was recorded with a CCD camera, and bubble counts and half-time were recorded as defoaming ability. The other is the visual inspection method, *i.e.*, shaking 10 mL  $\text{C}_n\text{N}/\text{SDS}$  solutions of 5 mM at different  $X_{\text{SDS}}$  or fixed  $X_{\text{SDS}} = 0.10$  with various  $C_T$  for 30 s. Following that, we recorded the change in foam height with aging and obtained the equilibrium foam height after resting for 2 h. The relative foam height is termed as the ratio of the measured foam height to the vial height.

## Results and discussion

### Self-assembly of $\text{C}_n\text{N}/\text{SDS}$ mixtures at the air-water interface

The surface activity and the onset of micellization of SDS with a series of cyclic amines ( $\text{C}_n\text{N}$ ,  $n = 6, 8, 12$ , Fig. 1A<sub>1</sub>–A<sub>3</sub>) were determined by surface tension measurements. Fig. 1B<sub>1</sub>–B<sub>3</sub> show the surface tension curves for the  $\text{C}_n\text{N}/\text{SDS}$  mixtures as a function of the total concentration ( $C_T$ ) at a fixed  $\text{C}_n\text{N}/\text{SDS}$  molar fraction ( $X_{\text{SDS}} = C_{\text{SDS}}/(C_{\text{SDS}} + C_{\text{C}_n\text{N}})$ , from 0.00 to 1.00). For comparison, the surface tension curves of pure SDS and  $\text{C}_n\text{N}$  aqueous solution are also included. Correspondingly, all the CMC and the surface tension at CMC ( $\gamma_{\text{CMC}}$ ) of  $\text{C}_6\text{N}/\text{SDS}$ ,  $\text{C}_8\text{N}/\text{SDS}$  and  $\text{C}_{12}\text{N}/\text{SDS}$  are summarized in Fig. 1C<sub>1</sub>–C<sub>3</sub> to clearly show the influence of  $X_{\text{SDS}}$  on CMC and  $\gamma_{\text{CMC}}$ .

Obviously, the surface tension curves exhibit broadly similar profiles for all the  $\text{C}_n\text{N}/\text{SDS}$  mixtures regardless of the



Fig. 1 Chemical structures and self-assembly behaviors of  $\text{C}_n\text{N}/\text{SDS}$  mixtures at the air/water interface. (A<sub>1</sub>–A<sub>3</sub>) Chemical structures of  $\text{C}_n\text{N}$  ( $n = 6, 8, 12$ ). (B<sub>1</sub>–B<sub>3</sub>) Surface tension of (B<sub>1</sub>)  $\text{C}_6\text{N}/\text{SDS}$ , (B<sub>2</sub>)  $\text{C}_8\text{N}/\text{SDS}$  and (B<sub>3</sub>)  $\text{C}_{12}\text{N}/\text{SDS}$  mixtures at  $25.00 \pm 0.01$   $^\circ\text{C}$ . (C<sub>1</sub>–C<sub>3</sub>) The variation of CMC and  $\gamma_{\text{CMC}}$  values of (C<sub>1</sub>)  $\text{C}_6\text{N}/\text{SDS}$ , (C<sub>2</sub>)  $\text{C}_8\text{N}/\text{SDS}$  and (C<sub>3</sub>)  $\text{C}_{12}\text{N}/\text{SDS}$  mixtures as a function of  $X_{\text{SDS}}$ .

sizes of the cycloalkane ring and the  $X_{\text{SDS}}$  values. The CMC value of SDS without  $\text{C}_n\text{N}$  derived from the breakpoint is 8.0 mM and the surface tension at CMC ( $\gamma_{\text{CMC}}$ ) is  $38 \text{ mN m}^{-1}$ , which are consistent with previously reported values. For  $\text{C}_n\text{N}$  solution alone, the surface tension curves of  $\text{C}_6\text{N}$  and  $\text{C}_8\text{N}$  display no inflection point in the concentration range studied ( $< 50$  mM) and just show a slight decline to  $\sim 55 \text{ mN m}^{-1}$ , whereas the CMC and  $\gamma_{\text{CMC}}$  values of  $\text{C}_{12}\text{N}$  are 28 mM and  $47 \text{ mN m}^{-1}$ , indicating that the three cyclic amines possess a very weak surface activity. As expected, the molecular arrangement at the air/water interface of cyclic amines with a bulky alkyl chain is much looser than that of the alkyl amine with the same carbon number, *e.g.*, CMC and  $\gamma_{\text{CMC}}$  values of *N*-dodecylamine are 2.6 mM and  $30 \text{ mN m}^{-1}$  (Fig. S1†).

Upon mixing the two components, the CMC and  $\gamma_{\text{CMC}}$  values decrease significantly to lower than those of individual components, attributed to the strong electrostatic attraction between the cationic headgroup of protonated  $\text{C}_n\text{N}$  and the anionic sulfate of SDS and the hydrophobic interaction of the alkyl ring of amines with the alkyl chain of SDS. Even at  $X_{\text{SDS}} = 0.01$ , the CMC values have already reduced to 27.8, 11.6 and 1.1 mM for  $\text{C}_6\text{N}/\text{SDS}$ ,  $\text{C}_8\text{N}/\text{SDS}$  and  $\text{C}_{12}\text{N}/\text{SDS}$  mixtures, respectively, whereas the  $\gamma_{\text{CMC}}$  values declined to  $\sim 30 \text{ mN m}^{-1}$ , nearly  $8.0 \text{ mN m}^{-1}$  lower than that of the pure SDS solution. When  $X_{\text{SDS}}$  approaches 0.5 from 0 or 1.0, the CMC value is steadily decreased to the lowest one, *i.e.*, 4.0, 2.0 and 0.4 mM for  $\text{C}_6\text{N}/\text{SDS}$ ,  $\text{C}_8\text{N}/\text{SDS}$  and  $\text{C}_{12}\text{N}/\text{SDS}$ , respectively, while the  $\gamma_{\text{CMC}}$  values are maintained at low values ( $\sim 30 \text{ mN m}^{-1}$ ) and there is almost no further decrease with varying  $X_{\text{SDS}}$ . Thus, the variation of CMC and  $\gamma_{\text{CMC}}$  values displays similar trends to  $X_{\text{SDS}}$  changing from 0 to 1.0, *i.e.*, decreasing first and then reaching a plateau and increasing rapidly



again. It is worth noting that the surface tension curves of the mixed solutions at high  $X_{\text{SDS}}$  show an upward end with increasing  $C_{\text{T}}$ , which is attributed to the significant excess SDS, thus causing the increase in surface tension to reach the  $\gamma_{\text{CMC}}$  value of SDS itself. These results show that the binding affinity becomes stronger when the molar ratio of  $C_n\text{N}$  and SDS is close to 1:1, and the strong binding between the two components possibly induces the remarkable deformation or the transformation of the molecular configuration of  $C_n\text{N}$ ,<sup>60–62</sup> thereby the molecular packing is significantly compacted at the air/water interface. However, the surface tension curves of the  $C_{12}\text{N}/\text{SDS}$  mixtures at  $0.20 < X_{\text{SDS}} < 0.70$  are excluded because the precipitation takes place in such a wide range of  $X_{\text{SDS}}$ , which is different from the  $C_6\text{N}/\text{SDS}$  and  $C_8\text{N}/\text{SDS}$  mixtures with smaller cycloalkane rings. Despite these, we can still observe that the ability to reduce CMC is enhanced from  $C_6\text{N}/\text{SDS}$  to  $C_{12}\text{N}/\text{SDS}$ , demonstrating that the larger alkyl ring leads to the stronger hydrophobic interaction of the cyclic amines with SDS.

### Aggregation behavior of $C_n\text{N}/\text{SDS}$ mixtures in bulk

To further understand the impact of the cyclic amines with different sizes of the cycloalkane ring on the self-assembly of SDS in bulk, the aggregation behaviors of  $C_n\text{N}/\text{SDS}$  mixtures were studied by turbidity measurement (Fig. 2A<sub>1</sub>–A<sub>3</sub>), dynamic light scattering (DLS, Fig. 2C) and cryogenic transmission electron microscopy (cryo-TEM, Fig. 2D<sub>1</sub>–D<sub>3</sub>). The different aggregate structures were observed with

changing  $X_{\text{SDS}}$  and  $C_{\text{T}}$  as depicted in phase diagrams (Fig. 2B<sub>1</sub>–B<sub>3</sub>), which are derived from the turbidity curves of the  $C_n\text{N}/\text{SDS}$  aqueous solution as a function of  $C_{\text{T}}$  at various  $X_{\text{SDS}}$  values.

For  $C_6\text{N}/\text{SDS}$ , the turbidity value remains extremely low no matter which value  $X_{\text{SDS}}$  or  $C_{\text{T}}$  is. Taking the situation at  $C_{\text{T}} = 20$  mM as a representative, the mean particle size remains below 20 nm. The broadly invariable turbidity and size as well as the lower CMC values (Fig. 1B<sub>1</sub>) demonstrate that the addition of  $C_6\text{N}$  promotes the micellization of SDS, but only induces the formation of small spherical or rodlike micelles, which is confirmed by the cryo-TEM micrographs of  $C_6\text{N}/\text{SDS}$  aggregates at  $X_{\text{SDS}} = 0.20$  and  $C_{\text{T}} = 20$  mM (Fig. S2†).

In contrast, the self-assembly behavior of SDS is significantly affected by  $C_8\text{N}$  and  $C_{12}\text{N}$ , and undergoes different processes at various  $X_{\text{SDS}}$  and  $C_{\text{T}}$ . For the  $C_8\text{N}/\text{SDS}$  mixture, there is almost no change in the turbidity with  $C_{\text{T}}$  as  $X_{\text{SDS}} > 0.5$ , indicating that the small fraction of  $C_8\text{N}$  has a strong ability to accelerate the micellization of SDS but not enough to affect the molecular packing and the aggregate structures. At  $X_{\text{SDS}} > 0.5$ , the turbidity values increase with increasing  $C_{\text{T}}$ , and the largest value appears at  $X_{\text{SDS}} = 0.40$ . Fixing  $C_{\text{T}} = 20$  mM, a weakly bluish solution was observed, and the  $C_8\text{N}/\text{SDS}$  mixed solution forms vesicles of a few tens of nanometers at  $X_{\text{SDS}} = 0.20$ , while the solution becomes transparent and forms wormlike micelles with a few millimeters long at  $X_{\text{SDS}} = 0.60$ , as evidenced by the results of DLS (Fig. 2C) and cryo-TEM (Fig. 2D<sub>1</sub> and D<sub>2</sub>). Compared with the phase boundaries of  $C_8\text{N}/\text{SDS}$  and  $C_{12}\text{N}/\text{SDS}$  mixtures, they go through similar changing processes with increasing  $X_{\text{SDS}}$  at the same  $C_{\text{T}}$ , but the big differences take place at much lower  $X_{\text{SDS}}$  and  $C_{\text{T}}$  for the aggregate formation, the larger vesicles (>100 nm, Fig. 2D<sub>3</sub>) and the wider precipitate region over the  $C_{\text{T}}$  range in  $C_{12}\text{N}/\text{SDS}$ .

In summary, the addition of  $C_n\text{N}$  only promotes the micellization of SDS for  $C_6\text{N}$ , while leads to an aggregate transition from small micelles to vesicles and then to wormlike or spherical micelles at a fixed  $C_{\text{T}}$  for  $C_8\text{N}$  without precipitation and for  $C_{12}\text{N}$  with a large range of precipitation. In all the three  $C_n\text{N}/\text{SDS}$  mixtures, the electrostatic interaction between the protonated amine and sulfate groups and the hydrophobic interaction among the alkyl chains of  $C_n\text{N}$  and SDS are the main driving forces for their self-assembly. However, taking a variety of conformations of cycloalkylamine in aqueous solution into account,<sup>60–62</sup> we speculate that both the size and conformation of the cycloalkane ring of  $C_n\text{N}$  may play a decisive role in the different aggregate formation and transition. Fig. 3 summarizes a simplified schematic diagram of aggregation behavior for the  $C_n\text{N}/\text{SDS}$  mixture in bulk with changing in  $X_{\text{SDS}}$  at a fixed  $C_{\text{T}}$ .

The  $C_6\text{N}$  molecule has the smallest cycloalkane ring. It is not long enough to enlarge the hydrophobic area in the aggregate relative to the SDS itself, thereby the  $C_6\text{N}/\text{SDS}$



**Fig. 2** Self-assembly of  $C_n\text{N}/\text{SDS}$  mixtures in bulk solution. (A<sub>1</sub>–A<sub>3</sub>) Turbidimetric curves of (A<sub>1</sub>)  $C_6\text{N}/\text{SDS}$ , (A<sub>2</sub>)  $C_8\text{N}/\text{SDS}$  and (A<sub>3</sub>)  $C_{12}\text{N}/\text{SDS}$  at different  $X_{\text{SDS}}$  values measured by UV-vis spectroscopy. (B<sub>1</sub>–B<sub>3</sub>) Phase diagram of (B<sub>1</sub>)  $C_6\text{N}/\text{SDS}$ , (B<sub>2</sub>)  $C_8\text{N}/\text{SDS}$  and (B<sub>3</sub>)  $C_{12}\text{N}/\text{SDS}$  mixtures. (C) The size variation of  $C_n\text{N}/\text{SDS}$  aggregates at  $C_{\text{T}} = 20$  mM as a function of  $X_{\text{SDS}}$ . (D<sub>1</sub>–D<sub>3</sub>) Cryo-TEM images of the  $C_n\text{N}/\text{SDS}$  aggregates at  $C_{\text{T}} = 20$  mM: (D<sub>1</sub>)  $C_8\text{N}/\text{SDS}$  at  $X_{\text{SDS}} = 0.20$ , (D<sub>2</sub>)  $C_8\text{N}/\text{SDS}$  at  $X_{\text{SDS}} = 0.60$ , and (D<sub>3</sub>)  $C_{12}\text{N}/\text{SDS}$  at  $X_{\text{SDS}} = 0.80$ .





**Fig. 3** The schematic illustrations of the variation of the aggregate morphologies in the  $C_nN/SDS$  mixtures with increasing  $X_{SDS}$ . In  $C_6N/SDS$ , only spherical micelles are formed regardless of  $C_T$  and  $X_{SDS}$ . In  $C_8N/SDS$ , the aggregates transit from spherical micelles to vesicles, wormlike micelles and then to spherical micelles again by increasing  $X_{SDS}$  from 0 to 1.00. In  $C_{12}N/SDS$ , the precipitate is formed rich in  $C_{12}N$  because of the enhanced interaction between  $C_{12}N$  and SDS due to the distinctive molecular conformation of  $C_{12}N$ . With increasing  $X_{SDS}$ , the precipitate is redissolved and transfers to vesicles and spherical micelles.

mixture only forms small micelles. In comparison, the  $C_8N$  molecule with a larger cycloalkane ring can produce stronger hydrophobic interaction with SDS and form a larger hydrophobic area. As such, the spontaneous curvature of the  $C_8N/SDS$  aggregates becomes slightly smaller, forming the wormlike micelles rich in SDS ( $X_{SDS} > 0.5$ ) and vesicles rich in  $C_8N$  ( $X_{SDS} < 0.5$ ). As for  $C_{12}N$  with a much larger cycloalkane ring, it forms precipitate with SDS in a large range, which could be attributed to the remarkably enhanced hydrophobic interaction by the unique  $C_{12}N$  ring. It was reported that the conformers of cyclooctane can be classified into three families, including boat-chair, chair-chair or crown, and boat-boat, while cyclododecane shows a square topology and has at least 100 possible conformations.<sup>62</sup> Thus, the large hydrocarbon ring is flexible enough to optimize the molecular conformation and nest together, in which case the ion pairs formed by  $C_{12}N$  and SDS may be drawn closer with each other due to the tight entanglement between the  $C_{12}N$  rings, thereby the precipitate with compact microstructure is formed, especially with the excessive  $C_{12}N$ . For the same reason, a small amount of  $C_{12}N$  can lead to a significant change in the molecular packing of  $C_{12}N/SDS$  mixtures, thus the vesicles are formed at a large  $X_{SDS}$  (e.g.,  $0.65 < X_{SDS} < 0.85$  at  $C_T = 20$  mM). Hence, the cycloalkylamines with different sizes of rings lead to diverse aggregate structures, and the large chair conformation of  $C_{12}N$  displays the most obvious effect on the association with SDS.

### Oil-fouling removal efficiency of $C_nN/SDS$

Surfactants that form aggregates with a strengthened hydrophobic domain and show strong ability to enhance surface activity should be beneficial to strip and solubilize

the oil from substrates, so we selected  $C_nN/SDS$  with  $C_T = 5$  mM, which is higher than their CMC but as low as possible, to test the oil-fouling removal efficiency. Stainless-steel plates covered with machine oil-fouling were immersed into the  $C_nN/SDS$  solutions, and ultrasonically treated for 10 min, it was observed that the homogenous emulsion with machine oil was entrapped in the interior, or the machine oil was separated from the plate and suspended in the solution. After that, the stainless-steel plates were taken out from the solutions to evaluate the oil-fouling removal efficiency by inspection and weighting methods.

With the visual approach to observe the oil-fouling efficiency, we took the photos of residual oil on stainless-steel plates under ultraviolet light (UV) based on the blue light character of oil-fouling under UV light (Fig. 4A). For both the  $C_6N/SDS$  and  $C_8N/SDS$  mixtures, the area of blue light on plates becomes smaller first and then enlarges again with the increase of  $X_{SDS}$ , indicating that the optimum oil-fouling removal result appears around  $X_{SDS} = 0.5$ . The  $C_{12}N/SDS$  mixture follows the same changing pattern except for the precipitate region. In parallel, the quantitative evaluation by



**Fig. 4** Cleaning efficiency and mechanism of  $C_nN/SDS$  for removing machine oil contamination from stainless-steel plates. (A) Photos of stainless-steel plates contaminated with machine oil after ultrasonic cleaning by  $C_nN/SDS$  solutions at different  $X_{SDS}$  observed under the irradiation of UV light. The plates with machine oil contamination emit blue light under irradiation of UV light. (B) The oil-fouling cleaning efficiency of  $C_nN/SDS$  mixtures at different  $X_{SDS}$  by the weighting method. Oil cleaning efficiency% =  $[(M_1 - M_2)/(M_1 - M_0)] \times 100$ . (C) Solid/liquid contact angle of machine oil droplets on the stainless-steel plates under water with  $C_nN/SDS$ . (D) Oil/water interfacial tension values for machine oil in the  $C_nN/SDS$  solutions. In all the experiments,  $C_T$  was fixed at 5 mM. (E) The possible mechanism of oil-fouling cleaning efficiency for single SDS solution and  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixtures.



the weighting method is summarized in Fig. 4B, also indicating that the  $X_{\text{SDS}}$  value for the highest oil-fouling removal efficiency is nearly 0.5. In addition, the  $\text{C}_8\text{N}/\text{SDS}$  system shows the wider  $X_{\text{SDS}}$  region ( $0.1 < X_{\text{SDS}} < 0.5$ ) to reach high cleaning efficiency and the efficiency is better than that of  $\text{C}_6\text{N}/\text{SDS}$ . For  $\text{C}_{12}\text{N}/\text{SDS}$ , in the region without precipitation at larger  $X_{\text{SDS}}$ , it displays better cleaning performance than either  $\text{C}_6\text{N}/\text{SDS}$  or  $\text{C}_8\text{N}/\text{SDS}$ . That is, the  $\text{C}_n\text{N}/\text{SDS}$  mixture with a larger cycloalkylamine and stronger aggregation ability exhibits higher oil-fouling removal efficiency.

To further understand the role of cycloalkylamine size in the oil-fouling removal efficiency of  $\text{C}_n\text{N}/\text{SDS}$ , the cleaning process is investigated by oil–water interfacial tension and contact angles ( $\theta$ ) of oil on plate under solution (Fig. 4C and D). Normally, cleaning by surfactants is realized through the de-wetting mechanism,<sup>63</sup> for which the contact angles of oil drops on substrates under surfactant solutions are very large. Herein, the contact angles of machine oil drops on the plates in the  $\text{C}_n\text{N}/\text{SDS}$  solutions at the representative  $X_{\text{SDS}}$  show a similar changing trend with the oil-fouling cleaning performance, *i.e.*, good cleaning performance corresponds to a large contact angle. The oil-fouling tends to separate from the stainless-steel substrates at the medium  $X_{\text{SDS}}$  (Fig. 4C). Therefore, the de-wetting occurs around  $X_{\text{SDS}} = 0.5$ . Meanwhile, the interface tension between the oil and  $\text{C}_n\text{N}/\text{SDS}$  solutions becomes smaller than that of either  $\text{C}_n\text{N}$  or SDS, which is beneficial to the formation of O/W emulsion (Fig. 4D). And the O/W interfacial tension curves as a function of  $X_{\text{SDS}}$  display a concave edge, showing a contrary changing trend of cleaning efficiency curves. It means that both the de-wetting and emulsion are enhanced at the medium  $X_{\text{SDS}}$ , which facilitates the oil-fouling removal and impedes the separated oil to stick back on the substrates. Moreover,  $\text{C}_8\text{N}/\text{SDS}$  shows  $0.5 \text{ mN m}^{-1}$  lower interfacial tension than  $\text{C}_6\text{N}/\text{SDS}$  at  $X_{\text{SDS}} < 0.50$ , whereas  $\text{C}_{12}\text{N}/\text{SDS}$  shows the minimum interfacial tension at  $X_{\text{SDS}} > 0.50$ . As a result, the oil-fouling is readily dispersed into the  $\text{C}_n\text{N}/\text{SDS}$  solutions due to de-wetting and emulsion, and the highly efficient cleaning performance is obtained for  $\text{C}_8\text{N}/\text{SDS}$  at  $X_{\text{SDS}} < 0.50$  and  $\text{C}_{12}\text{N}/\text{SDS}$  at  $X_{\text{SDS}} > 0.50$ .

Inspired by the Young's equation, we try to figure out the reasons for the various cleaning ability of  $\text{C}_n\text{N}/\text{SDS}$  solutions in the view of equilibrium of forces. Herein, the interfacial tensions of solid/water, oil/water and solid/oil are defined as  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_3$ , respectively. The three parameters fit the equation,  $\gamma_1 = \gamma_2 \cos \theta + \gamma_3$  (Fig. 4E). The contact angle of liquid on solid is proportional to the interfacial tension and energy, so according to the contact angles of  $\text{C}_n\text{N}/\text{SDS}$  ( $n = 6, 8, 12$ ) solutions on the stainless-steel plates (Fig. S3†), the  $\gamma_1$  values for pure SDS ( $\gamma_1^0$ ),  $\text{C}_6\text{N}/\text{SDS}$  ( $\gamma_1^a$ ) and  $\text{C}_8\text{N}/\text{SDS}$  ( $\gamma_1^b$ ) at  $X_{\text{SDS}} < 0.5$  are in order of  $\gamma_1^0 > \gamma_1^a \approx \gamma_1^b$ , while for  $\text{C}_6\text{N}/\text{SDS}$  ( $\gamma_1^A$ ),  $\text{C}_8\text{N}/\text{SDS}$  ( $\gamma_1^B$ ) and  $\text{C}_{12}\text{N}/\text{SDS}$  ( $\gamma_1^C$ ) when  $X_{\text{SDS}} > 0.5$ , the order is  $\gamma_1^A > \gamma_1^B > \gamma_1^C$ . Meanwhile,  $\gamma_2^0 > \gamma_2^a > \gamma_2^b$  at  $X_{\text{SDS}} < 0.5$  and  $\gamma_2^A > \gamma_2^B > \gamma_2^C$  at  $X_{\text{SDS}} > 0.5$  are obtained from Fig. 4D. Combining with the order of contact angle of

machine oil droplets on the plates in the  $\text{C}_n\text{N}/\text{SDS}$  solution (Fig. 4C), *i.e.*,  $\theta^0 < \theta^a < \theta^b$  at  $X_{\text{SDS}} < 0.5$  and  $\theta^A < \theta^B < \theta^C$  at  $X_{\text{SDS}} > 0.5$ , we can observe that  $\gamma_3^0 \leq \gamma_3^a < \gamma_3^b$  at  $X_{\text{SDS}} < 0.5$  and  $\gamma_3^A < \gamma_3^B < \gamma_3^C$  at  $X_{\text{SDS}} > 0.5$ . The results mean that the oil droplet has a stronger trend to retract inward and escape from the plate in  $\text{C}_8\text{N}/\text{SDS}$  at  $X_{\text{SDS}} < 0.5$  or in  $\text{C}_{12}\text{N}/\text{SDS}$  at  $X_{\text{SDS}} > 0.5$ . All the experimental results and theoretical derivations provide insights into the cleaning efficiency of  $\text{C}_n\text{N}/\text{SDS}$ , from which the oil-fouling removal performance could be predicted by the oil/water interfacial tension and solid/liquid contact angle of oil droplets in surfactant solutions.

### Foaming and defoaming test

For surfactant applications in cosmetics, detergents, food, *etc.*, strong foaming ability is normally needed. However, in industrial cleaning, petroleum refining and other large-scale applications, strong foamability and foam stability often lead to environmental hazards, wastewater treatment difficulty and economic loss. Therefore, surfactant systems with strong oil cleaning ability but weak foamability and foam stability are of importance in these fields.

Herein, to intuitively observe the foaming and defoaming ability of  $\text{C}_n\text{N}/\text{SDS}$  systems with great oil cleaning ability, we firstly shake 10 mL  $\text{C}_n\text{N}/\text{SDS}$  solutions of 5 mM for 30 s and record the change in foam height with aging (Fig. S4†). In parallel, we gain the variation of foam volume ( $V_{\text{foam max}}$ ), foam state, foam height, and bubble counts with aging by using a dynamic foam analyzer (Fig. 5 and S5†). We compare foam state against aging for the  $\text{C}_6\text{N}/\text{SDS}$  and  $\text{C}_8\text{N}/\text{SDS}$  mixtures at fixed  $X_{\text{SDS}} = 0.10 \text{ mM}$  and  $C_{\text{T}} = 5.0 \text{ mM}$  with the visual inspection method (inset) and air blowing method using a dynamic foam analyzer (Fig. S6†), and apparently the visual and quantitative results are consistent with each other.  $\text{C}_n\text{N}$  ( $n = 6, 8, 12$ ) alone almost has no ability to form liquid foams. With the addition of  $\text{C}_n\text{N}$ , the foamability characterized by the maximum foam volume ( $V_{\text{foam max}}$ , Fig. 5B) gradually becomes weaker with decreasing  $X_{\text{SDS}}$ , and the  $\text{C}_8\text{N}/\text{SDS}$  system displays the smallest foam volume when  $X_{\text{SDS}} < 0.50$ , especially at  $X_{\text{SDS}} = 0.10$ . Although the values of the maximum foam volume do not show significant differences, the differences in the foamability and foam stability are manifested in the changes of the bubble size, the foam heights and bubble count with time. Obviously, the low foamability of  $\text{C}_8\text{N}/\text{SDS}$  is further verified by the bigger bubbles formed at  $X_{\text{SDS}} = 0.10$  and 30 s (Fig. 5A and S5†), following which the bubbles begin to break at 1500 s when the foams in pure SDS,  $\text{C}_6\text{N}/\text{SDS}$  ( $X_{\text{SDS}} = 0.10, 0.40, 0.50, 0.80$ ),  $\text{C}_8\text{N}/\text{SDS}$  ( $X_{\text{SDS}} = 0.30, 0.40, 0.80$ ) and  $\text{C}_{12}\text{N}/\text{SDS}$  ( $\text{C}_{12}\text{N}/\text{SDS} = 0.80$ ) are still very stable. Correspondingly, the  $\text{C}_6\text{N}/\text{SDS}$  system shows the similar changing speed in foam height against aging compared with SDS, the  $\text{C}_{12}\text{N}/\text{SDS}$  system defoams also quite slowly, but the foam height of  $\text{C}_8\text{N}/\text{SDS}$  decreases 3–5 times faster than that of SDS itself (Fig. 5C). The bubble count of  $\text{C}_n\text{N}/\text{SDS}$  also confirms that the  $\text{C}_8\text{N}/\text{SDS}$





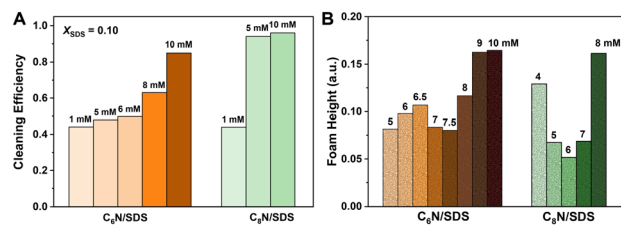
**Fig. 5** Foamability and foam stability of  $C_nN/SDS$  ( $n = 6, 8, 12$ ). (A) Images of foam state with aging recorded by a CCD camera for 5 mM SDS, 5 mM  $C_6N/SDS$  at  $X_{SDS} = 0.10$ , 5 mM  $C_8N/SDS$  at  $X_{SDS} = 0.10$ , and 5 mM  $C_{12}N/SDS$  at  $X_{SDS} = 0.80$ . The maximum foam volume after gas admission (B), the variation of foam height against aging (C) and the change of bubble count against aging (D) for  $C_nN/SDS$  mixtures at different  $X_{SDS}$ . (E) The possible mechanism of the decay process for foams in single SDS solution and  $C_nN/SDS$  ( $n = 6, 8, 12$ ) mixtures.

system shows the fastest defoaming speed (Fig. 5D). All the above results demonstrate that the  $C_8N/SDS$  mixture at  $X_{SDS} < 0.50$  can effectively reduce the foamability and enhance the defoam ability, perfectly corresponding to the condition for the high oil-fouling removal efficiency.

We speculate that there are two factors affecting the foam stability and defoaming ability of  $C_nN/SDS$  mixed systems: surface tension and dynamic molecular exchange between the bulk phase and air/water interface. The low surface tension manifests that the surfactant molecules prefer packing at the air/water interface, which contributes to the formation and stabilization of foams. However, all the  $C_nN/SDS$  systems reduce the surface tension of SDS from  $38 \text{ mN m}^{-1}$  to  $30 \text{ mN m}^{-1}$ , thus the foamability and foam stability should be improved in principle. Actually, only the  $C_{12}N/SDS$  system obeys this prediction, while the  $C_6N/SDS$  and  $C_8N/SDS$  systems exhibit similar or even weaker foamability and foaming stability than SDS. We turn back to analyze the  $C_T$  value we selected. In order to compare the foams, we selected the same  $C_T$  (5 mM), which is below the CMC of SDS ( $\sim 8.0 \text{ mM}$ ) and  $C_6N/SDS$  ( $\sim 6.0 \text{ mM}$ ), or much larger than that of  $C_{12}N/SDS$  ( $\sim 0.40 \text{ mM}$ ), but only slightly higher than the CMC value of  $C_8N/SDS$  ( $\sim 3.0 \text{ mM}$ ). In general, there are three

different mechanisms governing the lifetime of foam: (i) foam drainage caused by gravity, (ii) coarsening caused by the transfer of gas between bubbles generated by the capillary pressure differences, and (iii) bubble coalescence caused by the rupture of liquid films between neighbouring bubbles.<sup>64</sup> For the present systems, it is proposed that the dynamic molecular exchange between the bulk phase and air/water interface can accelerate the enlargement and destruction of bubbles, which can perfectly explain the anomalous phenomenon in the foam (Fig. 5E). Given that the selected  $C_T$  is close to but below the CMC for SDS and  $C_6N/SDS$ , the surfactant molecules are enough to promote the adsorption saturation at the air/water interface but still have no ability to form micelles, in which case the molecules locating in the liquid film are relatively stable, resulting in the low defoaming ability. However, this  $C_T$  is much higher than the CMC of  $C_{12}N/SDS$ , which indicates that the absorption saturation has been completely reached at the air/water interface, and the number of molecules in the  $C_{12}N/SDS$  aqueous solution is large enough to form stable micelles, thereby the molecules at the air/water interface do not exhibit the tendency to enter the bulk solution, leading to the stronger foam stability. In comparison, the  $C_T$  is slightly higher than the CMC value of  $C_8N/SDS$ . In the foaming process of  $C_8N/SDS$ , more surfactant molecules join the air/water interface, while the real surfactant concentration in bulk is just high enough for micellization. The unstable bubble films promote the fusion of neighbour bubbles, and the surfactant molecules prefer to return to the micelles in bulk solution from the bubble films, *i.e.*, the air/water interface, leading to the enlargement and destruction of bubbles under this condition.

In brief, it is concluded that high oil cleaning efficiency and low foam stability of surfactant mixtures are achieved at an appropriate concentration, *i.e.*, above CMC, but not too large at a proper  $X_{SDS}$ . Inspired by the present results, we tested oil-fouling removal efficiency and foam height with the  $C_6N/SDS$  and  $C_8N/SDS$  mixtures after vortexing for 30 s and resting for 2 h at  $X_{SDS} = 0.10$  and various  $C_T$ . For the given  $X_{SDS}$  at 0.10, we found that the cleaning efficiency becomes higher with the increase of  $C_T$  and is significantly enhanced especially above CMC. However, there is a



**Fig. 6** The cleaning and foaming performance of  $C_nN/SDS$  ( $n = 6, 8$ ) at  $X_{SDS} = 0.10$  and different  $C_T$ . (A) The oil-fouling cleaning efficiency by the weighting method and (B) foam height after vortexing for 30 s and standing for 2 h for  $C_nN/SDS$  ( $n = 6, 8$ ) at  $X_{SDS} = 0.10$  and different  $C_T$  as marked in the plots.



minimum foam height just above CMC, after which the height becomes larger again (Fig. 6A and B, S7 and S8†). The CMC of C<sub>6</sub>N/SDS is larger than that of C<sub>8</sub>N/SDS, so the minimum appears at the larger concentration for C<sub>6</sub>N/SDS, *i.e.*, at ~7.5 mM for C<sub>6</sub>N/SDS and ~6.0 mM for C<sub>8</sub>N/SDS. Combining with the continuous enhancement of cleaning efficiency and the minimum foam height above CMC, it can be speculated that selecting the concentration slightly above CMC at low X<sub>SDS</sub> should be beneficial to obtain a high-efficiency and low-foam cleaning system. Therefore, the concentration of 5 mM used above meets the requirements for C<sub>8</sub>N/SDS, resulting in good cleaning and deforming performance at X<sub>SDS</sub> < 0.50. Due to the weaker self-assembly ability of C<sub>6</sub>N/SDS at the air/water interface and in bulk, its performance in cleaning and defoaming efficiency cannot be better than that of C<sub>8</sub>N/SDS.

## Conclusions

In this work, we designed mixed surfactant systems composed of SDS and C<sub>*n*</sub>N (*n* = 6, 8, 12) and studied their oil-fouling and foam removal ability. With addition of C<sub>*n*</sub>N, the surface activity and aggregation ability of SDS are significantly enhanced, and the degree of enhancement is increased with the larger size of the cycloalkane ring because the hydrophobic interaction becomes stronger. As a result, only spherical micelles form in C<sub>6</sub>N/SDS mixtures, while vesicles, spherical micelles and wormlike micelles form in the C<sub>8</sub>N/SDS and C<sub>12</sub>N/SDS mixtures. However, the flexible and adjustable cycloalkane ring of C<sub>12</sub>N leads to the changeable conformation transformation and facilitates entanglement with each other tightly, thereby precipitation takes place in a large concentration range in C<sub>12</sub>N/SDS. Except for the region of precipitate, the oil cleaning efficiency of C<sub>*n*</sub>N/SDS shows a similar changing trend against X<sub>SDS</sub> at a fixed C<sub>T</sub> and the optimum condition mainly appears around X<sub>SDS</sub> = 0.50. Meanwhile, the stronger aggregation ability induces the higher cleaning efficiency with increasing cycloalkane ring size and C<sub>T</sub>. As a result, the best cleaning performance is achieved by C<sub>8</sub>N/SDS in a broader X<sub>SDS</sub> region, especially at low X<sub>SDS</sub>. In parallel, the changing trend of foam stability is broadly consistent with cleaning efficiency against X<sub>SDS</sub> for a given C<sub>T</sub>, *i.e.*, the strong defoaming ability appears at X<sub>SDS</sub> < 0.5, which is attributed to the low surface activity of C<sub>*n*</sub>N. But it is totally different with changing C<sub>T</sub> for a fixed X<sub>SDS</sub>, *i.e.*, there is an obvious decline of foam ability slightly above CMC, which is driven by the migration of the limited molecules from the liquid film of foams to bulk between films for micellization. Due to the stronger self-assembly ability of C<sub>8</sub>N/SDS than C<sub>6</sub>N/SDS, the highly efficient foam removal is realized by C<sub>8</sub>N/SDS at smaller C<sub>T</sub>. It can be concluded that the highly efficient oil-fouling and foam removal can be achieved concurrently in a surfactant system mixing with an additive of relatively high solubilization and low surface activity like cyclic amines as we expected, which may form a larger hydrophobic domain

in bulk through molecular conformation transition but create looser arrangement at the air/water interface because of bulky alkyl rings. This could also be realized in a single surfactant solution with such properties like star-shaped oligomeric surfactants. As such, the paradoxical self-assembly ability in bulk and at the air/water interface could induce a different changing tendency of cleaning and foaming performance against molar fraction or total concentration, providing a possible condition to achieve such a pair of contradictory properties. Thus, this work offers a simple approach obtain a high-efficiency and low-foam detergent with a low usage, meeting the requirements of some applications and supporting the sustainable development of the environment.

## Author contributions

Z. Z., Y. F., and Y. W. designed the research. Y. F. and Y. W. supervised the experimental work. Z. Z. performed most of the experiments. J. Y. performed cryo-TEM experiments on the C<sub>*n*</sub>N/SDS aggregates. T. W. and Z. Z. performed the experiments on cleaning measurements together. All authors discussed and contributed to the interpretation of the data. Z. Z. wrote the original manuscript, and Y. F. and Y. W. edited the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We are grateful for the financial support from the National Key R&D Program of China (2021YFA0716700), National Natural Science Foundation of China (21972149 and 21988102) and the Beijing National Laboratory for Molecular Sciences (BNLMS).

## Notes and references

- 1 J. J. Scheibel, *J. Surfactants Deterg.*, 2004, 7, 319–328.
- 2 J. J. Mueller and H. H. Wenk, *Chimia*, 2021, 75, 752–756.
- 3 L. Golsteijn, R. Menkveld, H. King, C. Schneider, D. Schowanek and S. Nissen, *Environ. Sci. Eur.*, 2015, 27, 1–12.
- 4 M. Bernat, C. Pey, M. J. Bermejo, B. Nogues, J. Vilaret and N. Siscart, *Riv. Ital. Sostanze Grasse*, 2007, 84, 246–252.
- 5 H. Lee, G. Amy, J. W. Cho, Y. M. Yoon, S. H. Moon and I. S. Kim, *Water Res.*, 2001, 35, 3301–3308.
- 6 J. A. Howarter, K. L. Genson and J. P. Youngblood, *ACS Appl. Mater. Interfaces*, 2011, 3, 2022–2030.
- 7 T. Wang, Y. Si, S. Luo, Z. Dong and L. Jiang, *Mater. Horiz.*, 2019, 6, 294–301.
- 8 J. Weiss, E. A. Decker, D. J. McClements, K. Kristbergsson, T. Helgason and T. Awad, *Food Biophys.*, 2008, 3, 146–154.
- 9 I. Kralova and J. Sjoblom, *J. Dispersion Sci. Technol.*, 2009, 30, 1363–1383.



- 10 J. Wang, Y. Fan, H. Wang, J. Yin, W. Tan, X. Li, Y. Shen and Y. L. Wang, *Chem. Eng. J.*, 2022, **430**, 132920.
- 11 D. P. Sachdev and S. S. Cameotra, *Appl. Microbiol. Biotechnol.*, 2013, **97**, 1005–1016.
- 12 P. Hu, J. An, M. M. Faulkner, H. Wu, Z. Li, X. Tian and J. P. Giraldo, *ACS Nano*, 2020, **14**, 7970–7986.
- 13 I. S. Curtis and H. G. Nam, *Transgenic Res.*, 2001, **10**, 363–371.
- 14 B. Liu, Y. Fan, H. Li, W. Zhao, S. Luo, H. Wang, B. Guan, Q. Li, J. Yue, Z. Dong, Y. L. Wang and L. Jiang, *Adv. Funct. Mater.*, 2021, **31**, 2006606.
- 15 Y. Luo, Z. Teng, Y. Li and Q. Wang, *Carbohydr. Polym.*, 2015, **122**, 221–229.
- 16 Y. Singh, J. G. Meher, K. Raval, F. A. Khan, M. Chaurasia, N. K. Jain and M. K. Chourasia, *J. Controlled Release*, 2017, **252**, 28–49.
- 17 C. H. Tsai, J. L. Vivero-Escoto, I. I. Slowing, I. Fang, B. G. Trewyn and V. S. Y. Lin, *Biomaterials*, 2011, **32**, 6234–6244.
- 18 R. Guagliardo, J. Perez-Gil, S. De Smedt and K. Raemdonck, *J. Controlled Release*, 2018, **291**, 116–126.
- 19 Surfactants market by type (anionic, non-ionic, cationic, and amphoteric), application (home care, personal care, industrial & institutional cleaning, textile, elastomers & plastics, agrochemicals, and food & beverage), region - global forecast to 2028, MARKETSDMARKETS, 2023, <https://www.marketsandmarkets.com/Market-Reports/biosurfactants-market-493.html>.
- 20 Industrial cleaning chemicals market by ingredient type (surfactants, solvents, chelating agents), product (gereneral & medical cleaning), application (manufacturing & commerical offices, healthcare, retail & food service), and region - global forecast to 2028, MARKETSDMARKETS, 2023, <https://www.marketsandmarkets.com/Market-Reports/industrial-institutional-cleaning-chemicals-market-52902227.html>.
- 21 T. Wang, Y. Han, S. Dai, J. Wang, B. Liu, M. Cao, B. Guan and Y. L. Wang, *Nano Res.*, 2023, **16**, 2551–2562.
- 22 B. O. Okesola and A. Mata, *Chem. Soc. Rev.*, 2018, **47**, 3721–3736.
- 23 G. Ren, M. Wang, L. Wang, Z. Wang, Q. Chen, Z. Xu and D. Sun, *Langmuir*, 2018, **34**, 5798–5806.
- 24 Q. Zeng, Q. Li, Y. Huang, Y. Lv, X. Liao and Q. Yang, *J. Macromol. Sci., Part B: Phys.*, 2015, **54**, 329–347.
- 25 Y. Fan, Y. Hou, J. Xiang, D. Yu, C. Wu, M. Tian, Y. Han and Y. L. Wang, *Langmuir*, 2011, **27**, 10570–10579.
- 26 D. Yu, Y. Wang, J. Zhang, M. Tian, Y. Han and Y. L. Wang, *J. Colloid Interface Sci.*, 2012, **381**, 83–88.
- 27 L. Zhu, Y. Tang and Y. L. Wang, *J. Surfactants Deterg.*, 2016, **19**, 237–247.
- 28 R. Zana, *Adv. Colloid Interface Sci.*, 2002, **97**, 205–253.
- 29 D. Shao, G. Liu, H. Chen, C. Xu and J. Du, *J. Surfactants Deterg.*, 2021, **24**, 357–364.
- 30 M. Wang, Y. Wang, D. Yu, Y. Han and Y. L. Wang, *Colloid Polym. Sci.*, 2013, **291**, 1613–1621.
- 31 R. Zana, *J. Colloid Interface Sci.*, 2002, **248**, 203–220.
- 32 S. A. Onaizi, *Eur. Biophys. J.*, 2018, **47**, 631–640.
- 33 F. G. Valeeva, E. A. Vasilieva, G. A. Gaynanova, R. R. Kashapov, S. V. Zakharov, D. A. Kuryashov, S. S. Lukashenko, N. Y. Bashkirtseva and L. Y. Zakharova, *J. Mol. Liq.*, 2015, **203**, 104–110.
- 34 A. Bera, K. Ojha and A. Mandal, *J. Surfactants Deterg.*, 2013, **16**, 621–630.
- 35 J. Eastoe and J. S. Dalton, *Adv. Colloid Interface Sci.*, 2000, **85**, 103–144.
- 36 N. Genc, E. Durna and O. Kilicoglu, *J. Water Chem. Technol.*, 2019, **41**, 236–241.
- 37 B. Riechers, F. Maes, E. Akoury, B. Semin, P. Gruner and J. C. Baret, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 11465–11470.
- 38 A. Bera, T. Kumar, K. Ojha and A. Mandal, *Appl. Surf. Sci.*, 2013, **284**, 87–99.
- 39 S. Paria and K. C. Khilar, *Adv. Colloid Interface Sci.*, 2004, **110**, 75–95.
- 40 D. Yu, Q. Zhang, C. Wu, Y. Wang, L. Peng, D. Zhang, Z. Li and Y. L. Wang, *J. Phys. Chem. B*, 2010, **114**, 8934–8940.
- 41 M. Deng, M. Cao and Y. L. Wang, *J. Phys. Chem. B*, 2009, **113**, 9436–9440.
- 42 M. L. Free, *Corros. Sci.*, 2002, **44**, 2865–2870.
- 43 Y. Chen, F. Qiao, Y. Fan, Y. Han and Y. L. Wang, *Langmuir*, 2017, **33**, 2760–2769.
- 44 S. Luo, Y. Wang, M. Wang and Y. L. Wang, *J. Surfactants Deterg.*, 2018, **21**, 899–908.
- 45 Z. Chen, J. Penfold, P. Li, J. Douch, Y. Fan and Y. L. Wang, *Soft Matter*, 2017, **13**, 8980–8989.
- 46 C. Zhou, D. Wang, M. Cao, Y. Chen, Z. Liu, C. Wu, H. Xu, S. Wang and Y. L. Wang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 30811–30823.
- 47 J. Larsson, A. E. Leung, C. Lang, B. Wu, M. Wahlgren, T. Nylander, S. Ulvenlund and A. Sanchez-Fernandez, *J. Colloid Interface Sci.*, 2021, **585**, 178–183.
- 48 Q. Cui, J. Z. Liu, L. Yu, M. Z. Gao, L. T. Wang, W. Wang, X. H. Zhao, Y. J. Fu and J. C. Jiang, *J. Cleaner Prod.*, 2020, **274**, 122652.
- 49 A. Bhadani, A. Kafle, T. Ogura, M. Akamatsu, K. Sakai, H. Sakai and M. Abe, *Curr. Opin. Colloid Interface Sci.*, 2020, **45**, 124–135.
- 50 H. Z. Kister, *Chem. Eng. Res. Des.*, 1997, **75**, 563–589.
- 51 H. Z. Kister, *Chem. Eng. Res. Des.*, 2003, **81**, 5–26.
- 52 W. Dou, Z. Zhang, W. Huang, X. Wang, R. Zhang, Y. Wu, A. Sun, X. Shi and J. Chen, *Chemosphere*, 2022, **303**, 135032.
- 53 L. Polasek, J. Bering, H. Kim, P. Neitlich, B. Pister, M. Terwilliger, K. Nicolato, C. Turner and T. Jones, *Mar. Pollut. Bull.*, 2017, **117**, 371–379.
- 54 K. Schilling and M. Zessner, *Water Res.*, 2011, **45**, 4355–4366.
- 55 D. Shao, G. Liu, H. Chen, C. Xu and J. Du, *J. Surfactants Deterg.*, 2021, **24**, 357–364.
- 56 P. Pal, I. Shittu, J. Oladunni and F. Banat, *J. Nat. Gas Sci. Eng.*, 2020, **81**, 103478.
- 57 Y. Sheng, X. Wu, S. Lu and C. Li, *J. Surfactants Deterg.*, 2016, **19**, 823–831.
- 58 Q. Liu, S. Zhang, D. Sun and J. Xu, *Colloids Surf., A*, 2010, **355**, 151–157.
- 59 P. W. Pakes, T. C. Rounds and H. L. Strauss, *J. Phys. Chem.*, 1981, **85**, 2469–2475.



- 60 I. Kolossvary and W. C. Guida, *J. Am. Chem. Soc.*, 1993, **115**, 2107–2119.
- 61 Y. Wang, P. Kirsch, T. Lebl, A. M. Z. Slawin and D. O'Hagan, *Beilstein J. Org. Chem.*, 2012, **8**, 1271–1278.
- 62 E. J. Saavedra, S. A. Andujar, F. D. Suvire, M. A. Zamora, M. L. Freile and R. D. Enriz, *Int. J. Quantum Chem.*, 2012, **112**, 2382–2391.
- 63 B. Liu, T. Li, W. Y. Wang, L. M. C. Sagis, Q. P. Yuan, X. G. Lei, M. A. C. Stuart, D. Li, C. Bao and J. Bai, *et al.*, *Nat. Sustain.*, 2020, **3**, 448–458.
- 64 I. Cantat, S. Cohen-Addad, F. Elias, F. Graner, R. Hohler, O. Pitois, F. Rouyer and A. Saint-Jalmes, *Foams: structure and dynamics*, Croydon: CPI Group (U.K.) Ltd, 2013.

