

Effect of Bolaform Counterions on the Adsorption of Sodium Dodecyl Sulfonate at the Air/Water Interface

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Abstract The effect of quaternary ammonium-based bolaform counterions (Bolan-series where n is the number of carbon atoms between the heads) on the adsorption of sodium dodecyl sulfonate (SDDS) at the air/water interface has been studied using surface tension measurements. The results showed that the Bolan counterions strongly interacted with SDDS even at very low concentrations. This reduced the CMC and C_{20} in the presence of Bolan counterions. The SDDS packed more tightly at the interface under the inducement of Bolan counterions and thus the occupied area per surfactant molecule decreased. Another bolaform counterion series (Bolanph) with a benzene ring attached on each side of the quaternary ammonium heads could further enhance the interaction with SDDS. This is due to the fact that the attached aromatic rings penetrate into the gaps between the surfactant headgroups, which provide an additional association force besides the electrostatic attractions. The present results suggested an approach to construct gemini-like surfactants depending on the electrostatic attraction between the bolaform counterions and the conventional ionic surfactants or an additional hydrophobic force made by the attached aromatic rings.

Keywords Bolaform counterions · Electrostatic attractions · Gemini-type surfactants

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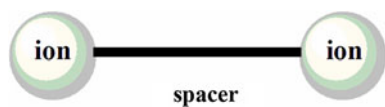
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Introduction

For the counterions, the bolaform molecular structure is rather unique which forms separately, charge controlled by a spacer as seen in Scheme 1. Early studies showed that the spacer length strongly influenced the interaction of the counterions with the oppositely charged ionic surfactants and thus their adsorption and aggregation [1–8]. For instance, Moroi et al. studied the effects of a series of cationic bolaform counterions, 1,1'-(1, ω -alkanediyl)bis-pyridinium, on the micellization and the solubility of alkane-1-sulfonates in aqueous solution. They found that the charge separation of up to six methylene groups did not make much difference in the critical micelle concentration (CMC) but of from 8 to 14 methylene groups considerably reduced the CMC [1, 5]. The micelle aggregation number monotonously decreased with increasing the methylene groups in the spacer and passed through a minimum around 8 CH₂ groups [3]. And the surface excess also monotonously decreased with increasing the methylene groups and produced a minimum around 8 CH₂ groups [3].

Recently, bolaform counterions have attracted much attention because they have perhaps the potential to construct gemini surfactants. A gemini surfactant has a dimeric molecular structure, i.e., it is made up of two monomer surfactants linked at the headgroups by a spacer [9]. Gemini surfactants have been extensively studied and are known to exhibit a very high surface activity. Up to now, the preparation of gemini surfactants still depends on chemical synthesis, in which the linking between the headgroup and the spacer is provided by a covalent bond. The chemical synthesis is always a troubling and time consuming process. Thus, another possible approach attracts our interest, i.e. testing the use of a bolaform counterion associating two conventional ionic surfactant



Scheme 1 Schematic representation of bolaform counterion

molecules through electrostatic attraction. Under the electrostatic force, a “pseudo molecule” with a gemini-type structure is expected to form. This approach is undoubtedly very convenient for “preparing” a gemini surfactant. Very recently, we observed that bolaform counterions in the aqueous subphase can indeed effectively control the monolayer behavior of sodium hexadecyl sulfate [10]. This seems to indicate the feasibility of this new approach. At present, however, the related knowledge is lacking and there is a great need for experimental results. For this purpose, we continue to report the effect of bolaform counterions on the adsorption behavior of sodium dodecyl sulfonate (SDDS) at the air/water interface in this paper.

Experimental

Materials

All compounds used in the present work, including their chemical structure and abbreviation, are listed in Scheme 2.

TMAB and BTMAB were purchased from Acros and used as received. SDDS was the product from TCI (Tokyo Chemical Industry Co., Ltd.) and was used after re-crystallization three times from ethanol. The others were synthesized in our laboratory, which we described in a previous paper [10] except Tetra6. All the solutions were prepared with Milli-Q water (resistivity = 18.2 MΩ cm⁻¹).

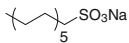
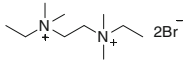
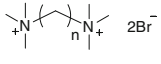

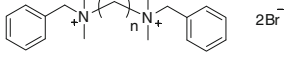
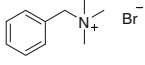
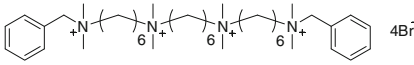
Synthesis of Tetra6

The synthesis route of Tetra6 is represented in Scheme 3 and the procedure is described as follows:

The materials for the synthesis: 1,6-dibromohexane, were purchased from TCI (Tokyo Chemical Industry Co., Ltd.) and the others were from SCR (Sinopharm Chemical Reagent Co., Ltd.) and used without further treatment. All the materials were of analytical grade.

N-benzyl-6-bromo-*N,N*-dimethylhexan-1-aminium bromide (1)

1,6-Dibromohexane (7.32 g, 30 mmol) and 10 mL acetone was put into a 100-mL three-necked flask and the mixture

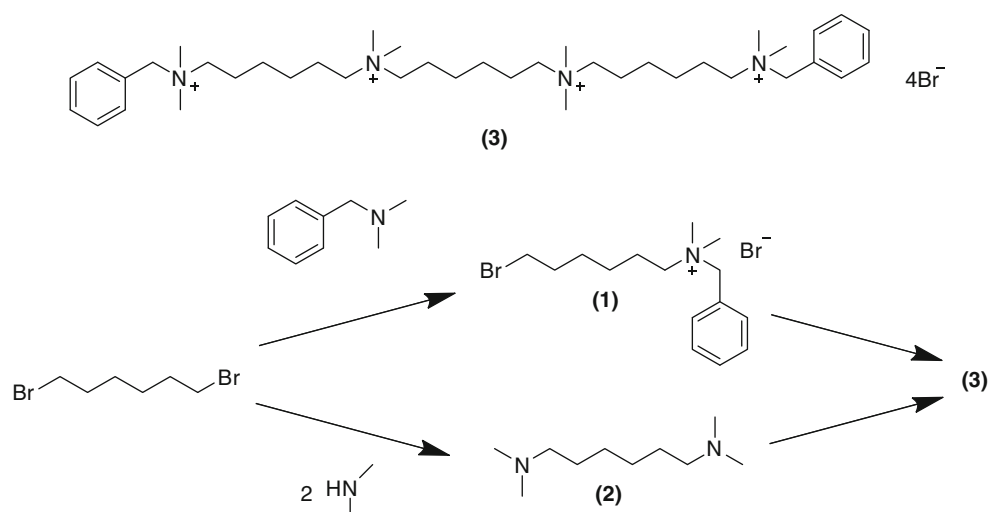
Compounds	Abbreviation
Sodium dodecyl sulfonate 	SDDS
Ethanediy- α,ω -bis(ethyl-dimethylammonium bromide) 	Bola2Et
Alkanediy- α,ω -bis(trimethylammonium bromide) 	Bolan ($n=4, 6, 12$)
Tetramethylammonium Bromide 	TMAB
Alkanediy- α,ω -bis(benzyl-dimethylammonium bromide) 	Bola n ph ($n=2, 4, 6$)
Benzyltrimethylammonium Bromide 	BTMAB
1,6-Hexanediaminium- N^1,N^6 -bis[6-[dimethyl(phenylmethyl)ammonio]hexyl]- N^1,N^6 -tetramethyl tetrabromide 	Tetra6

Scheme 2 Chemical structure, name and abbreviation

was heated to 50 °C, after which *N,N*-dimethyl-1-phenylmethanamine (1.35 g, 10 mmol) was dissolved in 10 mL acetone and added to the three-necked flask dropwise. The reaction lasted 24 h and the solid product was obtained by filtration. The crude product was washed with acetone. Yield: 1.8 g (47 %).

N,N,N',N'-tetramethylhexane-1,6-diamine (2)

1,6-Dibromohexane (12.1 g, 50 mmol) was dissolved in 100 mL ethanol, and then dimethylamine aqueous solution (33 %wt, 23.9 g, 250 mmol) and K₂CO₃ (6.9 g, 50 mmol) were added. After the reaction was complete at ambient temperature within 24 h, the mixture was acidified to pH = 1~2 using HCl. The mixture was extracted by petroleum ether twice, and the aqueous layer was reserved. A NaOH aqueous solution was added to the aqueous layer until pH = 12 ~ 13. This basic mixture was extracted by ether three times. The organic layer was combined and the ether was removed by rotary evaporation. The product (2) was collected by atmospheric distillation at 206 °C. Yield: 4.3 g (40 %).

Scheme 3 Synthesis route of Tetra6

1,6-Hexanediaminium- N^1,N^6 -bis[6-(dimethyl(phenylmethyl)ammonio)hexyl]- N^1,N^6 -tetramethyl tetrabromide (3)

The compound (1) (9.47 g, 0.025 mol), (2) (1.72 g, 0.01 mol) and ethanol (30 mL) were put together in a 250-mL flask equipped with an Allihn condenser. The temperature was raised so as to dissolve the reactant, following which 40 mL acetone was poured into the flask. The reaction lasted 48 h and a precipitate was obtained. The crude precipitate product was washed with acetone and recrystallized three times from ethanol/acetone. Yield: 2.5 g (27 %).

$^1\text{H NMR}$ (D_2O , 400 MHz): δ 1.35 (12H, *m*, CH_2), δ 1.83 (12H, *m*, CH_2), δ 2.98 (24H, *s*, N- CH_3), δ 3.25 (12H, *m*, N- CH_2), δ 4.44 (4H, *s*, Ar- CH_2), δ 7.53 (10H, *m*, Ar-H). Anal. Calc. for: $\text{C}_{40}\text{H}_{74}\text{N}_4\text{Br}_4\cdot\text{H}_2\text{O}$: C, 50.64; H, 8.07; N, 5.91; Found: C, 50.40; H, 8.03; N, 5.83.

Method

Surface tension measurements were carried out with a CHAN DCA-315 tensiometer equipped with a Pt-Ir du Noüy ring. The circumference of the ring was 5.93 cm. The ratio of the outside radius to the radius of the ring cross section (R/r) was 53.1218. The error of surface tension measurements was within 0.1 mN m^{-1} .

Results and Discussion

Effect of the Spacer of Bolaform Counterions

Figure 1 shows the semilogarithmic plots of the surface tension (γ) against the concentration (C) of surfactant

(SDDS) in the bulk solution. Different from our previous study where 500 mmol L^{-1} counterions were contained in the subphase, only a small quantity of the bolaform counterions exits in the present system, i.e. always keeping a constant ratio of 2:1 for SDDS to bolaform counterion. From Fig. 1, one can obtain the critical micelle concentration (CMC) by the break point, the minimum surface tension (γ_{CMC}) at the CMC and the concentration (C_{20}) required to reducing 20 mN m^{-1} surface tension of water. Generally, the three parameters are used to characterize the ability to form micelles, the effectiveness and the efficiency in surface tension reduction, respectively [11]. The data are listed in Table 1.

For the Bola n -series, the characteristic parameters listed in Table 1 clearly show that the Bola n counterions can have a pronounced effect on the adsorption and aggregation of SDDS. For example, compared with the SDDS/TMAB (1:1), those parameters of the SDDS/Bola n (2:1), including CMC, γ_{CMC} and C_{20} , are different although the both have identical ionic strength. Moreover, from Bola2Et to Bola6, these parameters monotonously increase with increasing n (Fig. 2), which well reflects the control of the spacer length over the behavior of both adsorption and aggregation [10].

From the minimum area (0.80 nm^2) of SDDS occupied at the interface in the absence of salts (see Table 1), one can roughly estimate the radius ($r_{\text{sulfonate}}$) of sulfonate headgroup to be about 0.50 nm by the formula $\pi r_{\text{sulfonate}}^2 = A_{\text{min}}$. By this way the electrostatic equilibrium distance between the charge center of two sulfonate headgroups is $\sim 1\text{ nm}$ (i.e. $2r_{\text{sulfonate}}$). On the other hand, the stretched length of an alkanediyl spacer can be calculated by the formula $d_s(\text{nm}) = 0.127(n + 1)$, where n is the number of methylene groups in the spacer. [12] Thus the d_s is 0.381 nm for Bola2Et, 0.635 nm for Bola4 and 0.889 nm for Bola6, respectively. These lengths are shorter

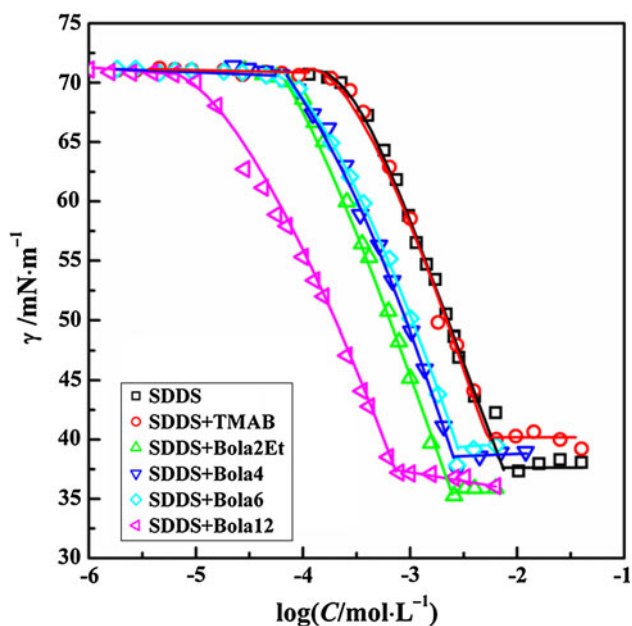


Fig. 1 Semilogarithmic plots of the surface tension against the surfactant concentration in aqueous bulk solution in the presence of Bola n (including Bola2Et) counterions, in which the ratio of surfactant to bolaform counterion is 2:1, while the ratio of SDDS to TMAB is 1:1

than the electrostatic equilibrium distance between the two sulfonate headgroups. This indicates that under the electrostatic attraction of the bolaform counterions, SDDS molecules can be pulled close together. This explains the reduction in CMC and C_{20} for these systems compared with that of SDDS-alone.

Bola12 has a spacer (1.65 nm) much longer than the electrostatic equilibrium distance between the headgroups of SDDS. The long and flexible alkanediyl spacer has been known generally to bend toward the alkyl tails [10, 13–15], which increases the density of hydrophobic moieties and hence strengthens the attraction between alkyl tails. This

should be the reason that its CMC and C_{20} reduce rather than rise compared with Bola n ($n \leq 6$).

As mentioned above, the added amount of Bola n counterions is very small in the present systems. Even so, the effect of the bolaform counterions is still very pronounced. This is an important result because it confirms that even a small amount of the Bola n is already sufficient to effectively affect the adsorption and aggregation of ionic surfactants. This must mean that Bola n counterions can associate strongly with SDDS. However, its monomer salt (tetramethylammonium bromide, TMAB) cannot do it. The data in Table 1 shows that for the system of SDDS/TMAB (1:1), the CMC and C_{20} are close and even identical to that of SDDS-alone. The strong interaction between the bolaform counterions and the ionic surfactants is the prerequisite for constructing the gemini-like surfactants. How to further enhance the interactions will be discussed in the following section.

In addition to the active parameters mentioned above, the surface excess and the corresponding area per molecule occupied at the interface are also important parameters reflecting the structure of the adsorption layer and the ability of the controlling spacer. It is known that the maximum surface excess of surfactant Γ_{\max} at the CMC can be obtained by the Gibbs equation

$$\Gamma = -\frac{1}{2.303nRT} \frac{d\gamma}{d \log C} \quad (1)$$

where n is a constant depending on the number of surfactant species. For conventional single-chain surfactant, the value of n is 2. From Eq. (1), the minimum area per molecule at the interface A_{\min} can be calculated by following formula

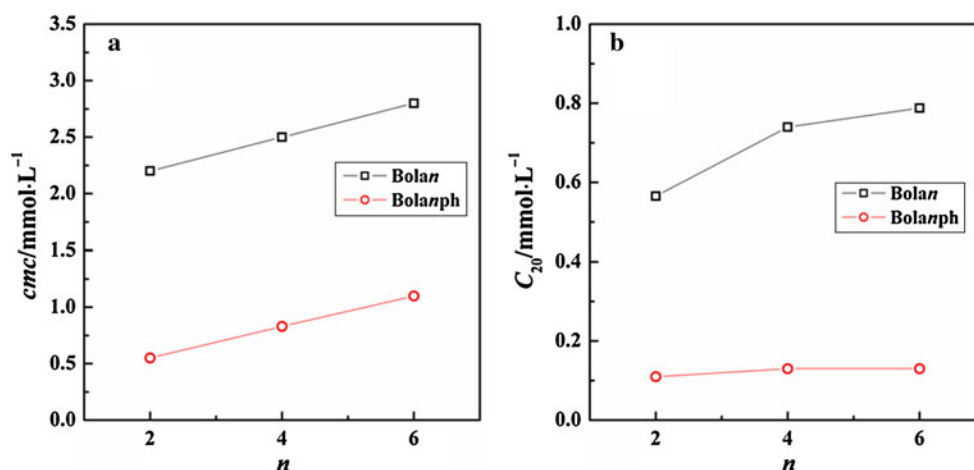
$$A_{\min} = 1/N_A \Gamma_{\max} \quad (2)$$

where N_A is the Avogadro constant.

Table 1 Characteristic parameters derived from the surface tension plots of SDDS and SDDS/bolaform counterions

System	CMC (mmol L ⁻¹)	γ_{CMC} (mN m ⁻¹)	C_{20} (mmol L ⁻¹)	Γ_{\max} ($\mu\text{mol m}^{-2}$)	A_{\min} (nm ²)	$\Delta G_{\text{mic}}^{\ominus}$ (kJ mol ⁻¹)	$\Delta G_{\text{ads}}^{\ominus}$ (kJ mol ⁻¹)
SDDS	7.4	37.6	1.86	2.08	0.80	-2.0	-18.1
SDDS/TMAB (1:1)	5.7	40.2	1.86	2.02	0.82	-2.3	-18.3
SDDS/Bola2Et (2:1)	2.2	35.9	0.57	2.15	0.77	-3.3	-20.6
SDDS/Bola4 (2:1)	2.5	38.9	0.74	2.10	0.79	-3.2	-20.2
SDDS/Bola6 (2:1)	2.8	39.2	0.79	2.08	0.80	-3.0	-20.2
SDDS/Bola12 (2:1)	0.76	37.1	0.15	1.64	1.0	-4.4	-26.7
SDDS/BTMAB (1:1)	2.1	39.2	0.88	2.90	0.58	-3.3	-17.3
SDDS/Bola2ph (2:1)	0.55	32.1	0.11	2.56	0.64	-4.7	-23.1
SDDS/Bola4ph (2:1)	0.83	32.5	0.13	2.07	0.80	-4.3	-24.7
SDDS/Bola6ph (2:1)	1.1	34.1	0.13	2.03	0.82	-4.0	-24.9
SDDS/Tetra6 (4:1)	0.28	34.5	0.037	1.66	1.0	-5.4	-30.2

Fig. 2 The CMC and C_{20} as a function of the number of methylene groups in the spacer of bolaform counterions: *Bolan* and *Bolanph* ($n \leq 6$)



From Table 1, the A_{\min} values for *Bolan* ($n \leq 6$) are smaller than that of SDDS-alone and that in the presence of TMAB, show more close packing of SDDS molecules at the interface. As discussed above, this benefits from the inducement of the bolaform counterions with a spacer shorter than the electrostatic equilibrium distance between the sulfonate headgroups. Reasonably, the A_{\min} for *Bola12* has a relatively large value (1.0 nm^2) since it has a quite long spacer even though the spacer can bend toward the alkyl tails.

The standard free energy of micellization, $\Delta G_{\text{mic}}^{\ominus}$, is related to the CMC by the following formula [11]:

$$\Delta G_{\text{mic}}^{\ominus} = RTK_0 \ln(\text{CMC}/\omega) \quad (3)$$

where K_0 is the degree of counterion association and 0.41 for SDDS as measured by conductivity method (the plot is not shown), ω is the number of moles of H_2O per cubic decimeter for pure water at the absolute temperature T ($\omega = 55.5 \text{ mmol dm}^{-3}$ at $25 \text{ }^\circ\text{C}$). In addition, the standard free energy of adsorption at the surface pressure π , $\Delta G_{\text{ads}}^{\ominus}$, follows the formula:

$$\Delta G_{\text{ads}}^{\ominus} = RT \ln(C_{w,\pi}/\omega) - \pi N_A A_{\min} \quad (4)$$

At $\pi = 52 \text{ mN m}^{-1}$ (corresponding surfactant concentration is C_{20}), $\Delta G_{\text{ads}}^{\ominus}$ can relate to the pC_{20} ($= -\log C_{20}$) and the A_{\min} :

$$\Delta G_{\text{ads}}^{\ominus} = -2.303RT(pC_{20,w} + \log \omega) - 20N_A A_{\min} \quad (5)$$

The calculated thermodynamic parameters are also listed in Table 1.

Enhancing Associating Force

As pointed out above, in the process of constructing gemini-like molecules, the electrostatic attraction between bolaform counterions and ionic surfactants is of utmost

importance and hence needs to be strengthened as far as possible. At first sight, this seems very simple but it is really rather complicated in the field of colloid, polymer, and interface science. The most typical finding is the so-called ‘Hofmeister series’ of the salt-effects as revealed more than a century ago, which was found to relate to many factors such as ionic hydration, size, polarity and quantum electronic level, etc [16, 17]. By different influences of ions on the water structure, water-structure-making or water-structure-breaking, the ions can be classified into two types: cosmotropic (salting-out) ions and chaotropic (salting-in) ions [17]. The interaction between the identical types of ions is expected to be strong, for example, the interaction between cosmotropic/cosmotropic ions or chaotropic/chaotropic ions [18]. In the present work, the alkyl sulfonate and alkyl quaternary ammonium all belong to chaotropic ions [16, 18], which favors exhibiting a strong interaction. Moreover, compared with alkyl sulfate ions used in the previous work [10] the alkyl sulfonate ions can interact more strongly with the alkyl quaternary ammonium ions according to the Hofmeister series [16]. These choices result in a pronounced effect of the bolaform counterions in the present systems.

Even so, we still hope to further strengthen their interactions using other approaches. In a previous paper, we reported another series of bolaform counterions, i.e. alkanediyl- α,ω -bis(benzyltrimethylammonium bromide) (abbreviated as *Bolanph*) which all contain the aromatic ring on the each side of the quaternary ammonium groups (see Experimental). When this series of the counterions interact with the anionic surfactants in the adsorption layer or the aggregate, the attached aromatic rings can penetrate into the palisade layers of surfactants, which were also confirmed by NMR measurements in our previous work [10]. This behavior is analogous to sodium salicylate as promoter in the cationic micellar growth [19–21] and can

provide an additional force to associate the bolaform counterions with the surfactants besides the electrostatic attraction. Compared with the *Bolan*-series, the *Bolanph* with identical space length leads to smaller CMC and C_{20} (Fig. 2; Table 1). This again indicates that a strong interaction between the bolaform counterions and the ionic surfactants favors to better achieve the dimerization of active molecules (Fig. 3).

Oligomerization Test

Besides the effort made for the construction of gemini-like (dimeric) surfactants utilizing the electrostatic attractions, the preparation of oligomeric active-units is also interesting. For this purpose we synthesized a tetrameric counterion (abbreviated as Tetra6), whose chemical structure is described in the Experimental section, intended to play the role of one Tetra6 attracting four SDDS ions. Figure 4 is its surface tension plot, in which the ratio of SDDS to Tetra6 is kept at 4:1. The characteristic parameters concluded in Table 1 show that in the presence of Tetra6, the activity of the system is greatly enhanced. The CMC and C_{20} of SDDS/Tetra6 are one order of magnitude smaller than that of SDDS/Bola6 or SDDS/Bola6ph, for which the spacer of all the counterions are the same hexanedyl.

The analysis for the minimum area of SDDS occupied at the interface can help us to understand the interaction

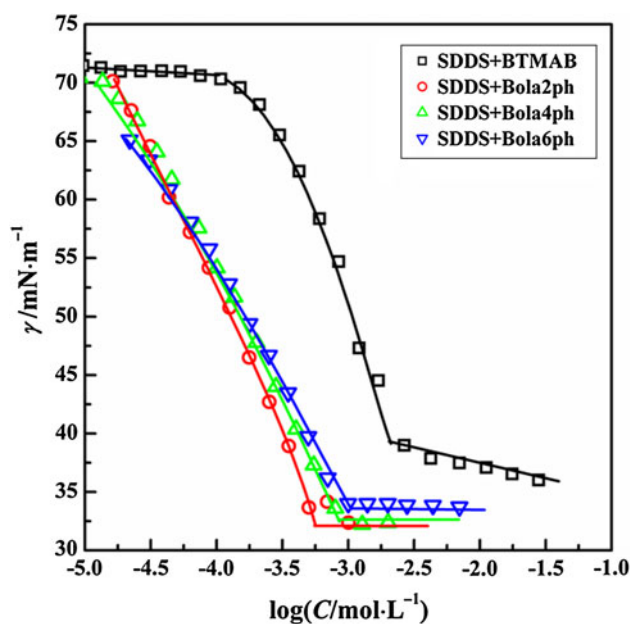


Fig. 3 Semilogarithmic plots of surface tension against surfactant concentration in aqueous bulk solution in the presence of *Bolanph* counterions, in which the ratio of surfactant to bolaform counterion is 2:1, while the ratio of SDDS to BTMAB is 1:1

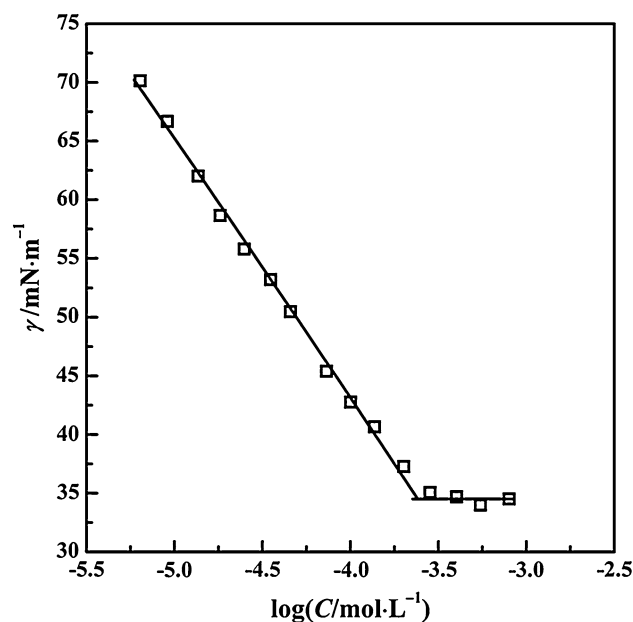


Fig. 4 Surface tension plot of mixed SDDS/Tetra6 (4:1) aqueous solution

between the bolaform counterions and the ionic surfactants. In the presence of simple salt TMAB (keeping the ratio of 1:1 for SDDS to TMAB), the A_{\min} (0.82 nm^2) reflects the electrostatic equilibrium result between the SDDS molecules at the interface. For SDDS/BTMAB (1:1), the A_{\min} is only 0.58 nm^2 , which even includes the benzene rings penetrating into the palisade layers. This result strongly suggests that under the inducement of BTMAB, SDDS molecules pack at the interface very tightly. For SDDS/Bola6 and SDDS/Bola6ph (the ratio of SDDS to bola is 2:1, having the same ionic strength with the above systems), however, the A_{\min} s are almost identical, i.e. 0.80 nm^2 with Bola6 and 0.82 nm^2 with Bola6ph. This fact indicates that the spacer of the bolaform counterion can effectively control the behavior of SDDS adsorption at the air/water interface. Comparatively, the A_{\min} (1.0 nm^2) of SDDS/Tetra6 (4:1) is slightly larger than that of both SDDS/Bola6 and SDDS/Bola6ph. This indicates that the control of oligomeric counterions over ionic surfactants is weaker than dimeric ones. It is perhaps due to more molecular disturbance when the length of bolaform counterion is increased, which must weakens its associating with ionic surfactants. Therefore, it may be more difficult for the construction of an oligomeric active-molecule than of a dimeric molecule when mainly depending on the electrostatic attractions.

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