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Effects of sodium chloride on adsorption at different interfaces and aggregation behaviors of disulfonate gemini surfactants

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Abstract: Effects of NaCl on adsorption of dialkylated diphenyl ether disulfonate gemini surfactants (C_n-DADS, n=8, 10 and 12) at different interfaces were studied by equilibrium surface tension, dynamic surface tension, interfacial tension and wetting measurements. The results show that the critical micelle concentration (cmc) values of C_n-DADS aqueous solutions decrease with an increase in NaCl concentration. For C_8-DADS aqueous solution, the values of the surface tension at cmc (γ_{cmc}) keep almost invariable with the addition of NaCl. The monomer diffusion coefficient (D_{deff}) values of C_n-DADS increase with an increase in both alkyl chain length and inorganic salt concentration. The interfacial tensions (IFTs) between C_n-DADS solutions with various amount of NaCl added and dodecane slightly decrease with the increase of NaCl concentration. The equilibrium contact angle values decrease significantly firstly and then no further change with increasing the NaCl concentration. The vesicles are formed in both 0.5 mM C_8-DADS aqueous solution and 2 mM C_8-DADS solution with 0.1 M NaCl.

Key words: disulfonate gemini surfactants; salt effects; adsorption; different interfaces.

1. Introduction

Gemini surfactants are composed of two amphiphilic head groups and two hydrocarbon chains connected by a spacer moiety. Over the past decade, much attention has been focused in the investigation of gemini surfactants due to their lower CMC, better wetting and solubilizing properties, unusual rheological, biological activity and ultra-low oil/water interfacial tension compared with traditional monomeric surfactants [1-6].

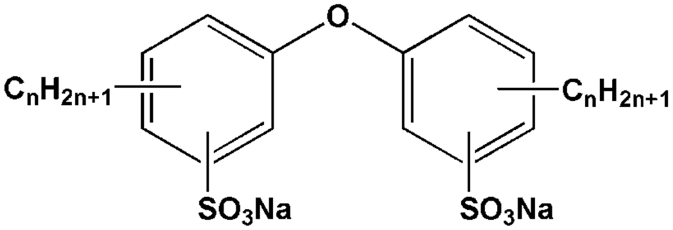
Effects of inorganic salts on adsorption behavior of ionic surfactants at different interface are vital to numerous applications for detergency, emulsification, and petrochemical systems in industry. The additive of inorganic salts in surfactant aqueous solutions often causes salting-out phenomenon which is the result of preferential movement of water molecules according to hydration theory [7].

Inorganic electrolytes have pronounced effects on the formation of micelles by surfactants in aqueous solution resulting in significant decrease of their cmc [8-9]. Moreover, the addition of inorganic salts can generally impact the formation and size of aggregates and decrease the γ_{cmc} of surfactants [9-11]. Yu et al [12] reported that the cmc values of cationic gemini surfactants have a significantly decrease with the addition of inorganic salts (NaCl and Na_2SO_4). Jiao et al [13] discovered that 1-butyl-3-methylimidazolium dodecylsulfate ($[C_4mim][C_{12}SO_4]$) shows higher minimum area per molecule (A_{min}) and lower surface excess concentration (Γ_{max}) in the presence of various electrolytes. This implies a lower tendency to be adsorbed at air-water interface upon addition of electrolytes. Inorganic salts have a tremendous impact on the adsorption of at oil/water interface. For a given surfactant, the greater concentration of surfactant molecules at the interface results in the lower surface tension. Cao et al [14] showed that the interfacial tension values of alkylbenzene sulfonate solutions pass through a minimum with increasing the NaCl concentration due to the variation of adsorption amounts at oil/water interface.

Most of the previous work focused on the effect of inorganic salts on the adsorption of surfactants at one interface individually, while the adsorption of surfactants on different interfaces influenced by inorganic salts, of which the process and mechanism could be supported and explained by each other, has been rarely investigated.

In this presentation, effects of sodium chloride on the adsorption of dialkylated diphenyl ether disulfonate gemini surfactants (C_n-DADS, the chemical structures are shown in Scheme 1) at air/water, oil/water, and water/solid interfaces were investigated systematically. Equilibrium and dynamic surface tension of C_n-DADS aqueous solutions were measured to investigate effects of NaCl on adsorption efficiencies and kinetics at air/water interface. The adsorption of C_n-DADS molecules at oil/water interface was studied by the results of interfacial tension measurement. The contact angles of C_n-DADS at hydrophobic surface were used to analyze effects of NaCl adsorption of surfactant molecules at two interfaces (water/solid, and water/air) involved.

Scheme 1 Chemical structures of C_n-DADS (n=8, 10 and 12)



2. Experimental section

2.1 Materials

C_n-DADS (n=8, 10, and 12) were synthesized and purified according to the method of Yadav, G.D et al [15] and our previous article [16]. Sodium chloride (≥99.5%) and Dodecane (≥98.0%) were purchased from Kermel Chemical Reagent Co. (Tianjin, China). Triply distilled water was used as solvents in all experiments.

2.2 Methods

2.2.1 Salt tolerance measurement

The transmittance of C_n-DADS at different NaCl concentrations was measured at 500 nm using UV-1601 spectrophotometer. The temperature was kept at 25 °C.

2.2.2 Equilibrium surface tension measurement

Surface tension measurements were carried out using a KRUSS K12 Processor Tensiometer by the Wilhelmy plate method at 25 ± 0.1 °C. The length and thickness of the platinum plate was 19.9 mm and 0.2 mm, respectively. Surfactant solutions were prepared for one day before the determinations at room temperature. The surface tension of triply distilled water was measured to calibrate the tensiometer. Each surface tension value was determined until the average deviation of three successive readings was less than 0.2mN/m.

2.2.3 Dynamic surface tension measurement (DST)

The dynamic surface tension experiments were performed with KRUSS bubble pressure tensiometer BP 100 that involves measuring the maximum pressure necessary to blow a bubble in a liquid from the tip of a capillary. The measurements were conducted with effective surface ages from 0.01 to 250 s at 25 °C.

2.2.4 Interfacial tension measurement

The interfacial tension between dodecane and C_n-DADS aqueous solution was carried out at 25 °C using a model TX-500C interfacial tensiometer by spinning drop method which is based on a balance of centrifugal and interfacial tension forces.

2.2.5 Wetting measurement

The wettability properties of C_n-DADS on parafilm were measured using a KRŰSS DSA25 (KRŰSS, Germany) equipped with a CCD camera at 25 °C. The horizontal CCD cameras monitored dynamic contact angle individually. To ensure minimal relative error, each experiment was repeated at least three times until the reproducibility was satisfactory.

2.2.6 Transmission electron microscopy measurement (TEM)

The structures of surfactant aggregates were imaged under JEM-1011 electron microscope at 100 kV by negative staining. A droplet of the surfactant solution was placed on a carbon-coated grid and allowed to equilibrate for 2 min. excess liquid was removed by carefully touching one end of the grid with filter paper, and the grid was dried at room temperature.

3. Results and Discussion

3.1 Salting-out Phenomenon

The phenomenon of salting-out is of both fundamental and applied interest. Its study is vital to many applications. The related transmittance curves for 3 mM

C_n-DADS solutions with NaCl are shown in Figure 1. The critical concentrations of NaCl for salting-out of C_n-DADS are determined from the concentration ranges of the sharply decreasing transmittance in the transmittance curves. These results were listed in Table 1. The critical concentration values for C_n-DADS decrease with the increase of alkyl chain length, indicating that C_n-DADS with longer alkyl length prefer to salt out. The hydrophobicity increases with increasing the alkyl chain length and cause C_n-DADS with longer carbon chains to salt out more easily.

Table 1 Critical concentration values of NaCl for 3 mM C_n-DADS solutions at 25 °C

	C_8-DADS	C_{10}-DADS	C_{12}-DADS
NaCl (M)	1.50 ± 0.07	0.50 ± 0.03	0.15 ± 0.01

3.2 Sodium chloride effects on adsorption at air/water interfacial properties

The surface tension curves of C_n-DADS in aqueous solutions at different concentrations of NaCl are shown in Figure 2. It is observed that the surface tension values of C_n-DADS aqueous solution decrease with increasing the ionic strength. Table 2 lists the cmc and γ_{cmc} values of C_n-DADS aqueous solution with different NaCl concentrations determined from the surface tension curves.

Table 2 The cmc and γ_{cmc} values of C_n-DADS with various concentrations of NaCl

Surfactants	NaCl (mol/L)	cmc (mol/L)	γ_{cmc} (mN/m)
C_8-DADS	0.01	1.80×10^{-4}	28.13
	0.05	1.14×10^{-4}	28.47
	0.1	8.49×10^{-5}	28.41
	0.2	6.33×10^{-5}	28.57
	0.4	4.22×10^{-5}	28.90
C_{10}-DADS	0.01	3.49×10^{-5}	31.67
	0.05	8.32×10^{-6}	30.70
	0.1	5.10×10^{-6}	29.84
	0.2	2.25×10^{-6}	29.38
	0.4	2.16×10^{-6}	29.01
C_{12}-DADS	0.01	2.13×10^{-5}	34.03
	0.05	6.64×10^{-6}	33.47
	0.1	3.70×10^{-6}	32.78

As presented in Table 2, the cmc values of C_n-DADS in aqueous solution decrease sharply at first and then decrease much more slowly. A possible explanation is that sodium ions are inserted into the stern layer around the aggregates and reduce the electrostatic repulsion between the intermolecular headgroups, leading to a decrease of the cmc values. Once the ionic strength is large enough, the electrostatic repulsion tends to invariable [12-13].

As for surface activity, NaCl at various concentrations almost do not affect the γ_{cmc} of C_8-DADS. The γ_{cmc} values of both C_{10}-DADS and C_{12}-DADS decrease with the increase of NaCl concentrations as shown in Table 2. This role can be attributed to the decreasing electrostatic repulsion, which leads to a close packing of sulfonate gemini surfactant molecules at air/water interface [12, 17].

The maximum surface excess concentration estimated at the cmc (Γ_{max}) and the surface areas A_{min} occupied by the surfactant molecules at the air-water interface were calculated using the Gibbs adsorption isotherm equations as follows [18]:

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{dlogC}\right)_T \qquad (1)$$

$$A_{min} = \frac{10^{16}}{N_A\Gamma_{max}} \qquad (2)$$

where R=8.314 $J\cdot mol^{-1}\cdot K^{-1}$, T=298.15 K, $(d\gamma/dlogC)_T$ is the slope of the surface tension γ vs logc below the CMC, N_A is Avogadro's number, n is the number of solute species and takes 1 in presence of excess NaCl additive[18, 19].

Adsorption efficiency (pC_{20}) is the negative logarithm of the surfactant concentration required to reduce the surface tension of the solvent by 20 mN m^{-1}. It was obtained according to the following equation [18].

$$pC_{20} = -logC_{20} = \frac{\pi_{cmc}-20}{2.303nRT\Gamma_{max}} - logcmc \qquad (3)$$

where π_{cmc} represents the surface pressure.

The surface active parameters of C_n-DADS in 0.1 M NaCl base solution were listed in Table 3. The surface area A_{min} reflects the packing densities of surfactants at the air-water interface. The A_{min} values of C_n-DADS with 0.1 M NaCl is lower than their corresponding salt-free systems as shown in Table 3, while the decrease of A_{min} value for C_8-DADS is the lowest, indicating that NaCl has a limited influence on the packing of C_8-DADS molecules air/water interface. This phenomenon is in agreement with the variation of γ_{cmc} values for C_n-DADS. As shown in Table 3, the A_{min} values of

C_n-DADS with 0.1 M NaCl remain almost constant with the increase of chain length, reflecting that the A_{min} values are mainly determined by the cross-sectional area of hydrophilic groups.

Table 3 Surface properties of C_n-DADS aqueous solutions at 25 °C

Surfactants	Media	Γ_{max} (μmol/m^2)	A_{min} (nm^2)	pC_{20}	CMC/C_{20}
C_8-DADS [16]	water	2.62	0.63	4.26	3.73
C_8-DADS	NaCl(0.1M)	3.02	0.55	5.65	3.85
C_{10}-DADS [16]	water	1.91	0.87	4.41	4.58
C_{10}-DADS	NaCl(0.1M)	2.98	0.56	6.00	5.10
C_{12}-DADS [16]	water	1.82	0.91	4.20	2.00
C_{12}-DADS	NaCl(0.1M)	2.92	0.58	6.23	6.28

pC_{20} is used to analyze the efficiency of surfactant to decrease the surface tension of water. The pC_{20} values of C_n-DADS in presence of 0.1 M NaCl are higher than their salt-free systems shown in Table 3. In other words, C_n-DADS aqueous solutions with NaCl have a higher surface efficiency than those of aqueous solutions without additive, with the reason that the additive of counterions would result in a smaller electrical repulsion between already adsorbed surfactant ions and oncoming surfactant ions at the interface. The pC_{20} values of C_n-DADS with 0.1 M NaCl increase as the length of alkyl chain increases, which is similar to traditional surfactants [18].

The CMC/C_{20} ratio is usually used to measure the relative effects of structural or microenviromental factors on micellization and on adsorption. It affords insights into the adsorption and micellization processes. The CMC/C_{20} ratio values of C_n-DADS with NaCl electrolytes are higher than those of salt-free solutions. This indicates that the additive of NaCl facilitates adsorption of the C_n-DADS molecules more than micellization.

The dynamic surface tension measurement method with a maximum bubble pressure technique can measure the surface tension in a few milliseconds and is suitable for investigating the kinetics of surfactant adsorption. Figure 3 shows the dynamic surface tension of C_n-DADS at air/water interface in the absence and presence of NaCl. Noticeably, the time required to attain the equilibrium surface tension in both systems decreases with an increase in the concentration of C_n-DADS surfactants.

The diffusion-controlled adsorption model is generally used to analyze the dynamic surface tension quantitatively using the Ward and Tordai equation [20].

$$\Gamma(t) = 2C_0\sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}}\int_0^{\sqrt{t}} C_s d(\sqrt{t-\tau}) \qquad (4)$$

where D represents the monomer diffusion coefficient, C_0 represents the bulk concentration, t represents the time, $C_S(t)$ represents the concentration at the subsurface, and τ represents a dummy timedelay variable. The Ward and Tordai equation at limiting cases of both short time, t→0, and long time, t→∞, was applied to analyze the monomer diffusion coefficient [21-24].

$$\text{at short time,} \quad \gamma(t)_{t\to 0} = \gamma_0 - 2nRTC_0\sqrt{\frac{Dt}{\pi}} \qquad (5)$$

$$\text{at long time,} \quad \gamma(t)_{t\to\infty} = \gamma_{eq} + \frac{nRT\Gamma_{eq}^2}{C_0}\sqrt{\frac{\pi}{4Dt}} \qquad (6)$$

where γ(t) is the surface tension measured at time t, γ_0 is the surface tension of the solvent, R is the gas constant, *T* is the absolute temperature, C_0 is the surfactant concentration, γ_{eq} is the equilibrium surface tension at infinite time, Γ_{eq} is the equilibrium surface excess concentration estimated with equilibrium surface tension data. The n values of gemini surfactants in absence and presence of excessive inorganic ions take 3 and 1, respectively. Figures 4 and 5 show the plots of the γ(t) decay versus $t^{1/2}$ and $t^{-1/2}$ for C_n-DADS aqueous solutions in absence and presence of NaCl, respectively. The plots of γ(t) versus $t^{1/2}$ shown in Figure 5 exhibit a good linear relationship with a short time scale, and the values of intercept are close to the surface tension of water when t equals zero. These results are consistent with the equation 5. Values of monomer diffusion coefficients (D_{eff}) obtained from the gradients of γ(t) decay versus $t^{-1/2}$ plots for C_n-DADS (Figure 5) are summarized in Table 4.

For salt-free system, The D_{eff} values of C_n-DADS are orders of magnitude lower than those of conventional hydrocarbon monomeric surfactants, indicating that the rates of adsorption at the air/water interface for C_n-DADS is very low because of their bulky structure. These deviations may be interpreted by a two step process: diffusion of the solute to the subsurface and adsorption of the solute from the subsurface to the surface. Similar roles were also observed for some gemini surfactants [25-26].

Table 4 Parameters calculated from the dynamic surface tension for C_n-DADS with 0.1 M NaCl

material	Concentration mM	media	Gradient ($mNm^{-1}\,s^{1/2}$)	D_{eff} ($m^2\,s^{-1}$)
C_8-DADS	0.5	water	191.32	2.23×10^{-13}
	2	water	69.35	1.07×10^{-13}
	10	water	34.84	5.86×10^{-14}
	0.01	NaCl(0.1 M)	200.8	1.00×10^{-10}
	0.07	NaCl(0.1 M)	68.43	1.77×10^{-11}
	0.5	NaCl(0.1 M)	14.63	7.50×10^{-12}
C_{10}-DADS	0.5	water	112.97	1.81×10^{-13}
	2	water	60.97	3.88×10^{-14}
	10	water	54.00	1.92×10^{-15}
	0.01	NaCl(0.1 M)	165.26	1.40×10^{-10}
	0.07	NaCl(0.1 M)	31.69	7.72×10^{-11}
	0.5	NaCl(0.1 M)	18.68	4.36×10^{-12}
C_{12}-DADS	0.5	water	248.78	3.07×10^{-14}
	2	water	151.81	4.77×10^{-15}
	10	water	79.46	7.54×10^{-16}
	0.01	NaCl(0.1 M)	319.16	3.45×10^{-11}
	0.07	NaCl(0.1 M)	152.34	3.10×10^{-12}
	0.5	NaCl(0.1 M)	95.7	1.53×10^{-13}

As shown in Table 4, values of D_{eff} for C_n-DADS decrease obviously with increasing the surfactant concentration, which can be ascribed to the existence of activation barrier. These results indicate that the adsorption is a mixed kinetic-diffusion process [27].

The D_{eff} Values of C_n-DADS with 0.1 M NaCl is higher than their corresponding salt-free systems shown in Table 4. The addition of NaCl decreases the intermolecular electrostatic repulsion, leading to a lower adsorption energy barrier.

The D_{eff} values of C_n-DADS decrease with an increase in the length of alkyl chain. An interpretation for this phenomenon may be that C_n-DADS molecules with shorter carbon chain lengths diffuse faster and adsorb more effectively at the air interface.

3.3 Sodium chloride effects on adsorption at oil/water interface

The interfacial tension is one of the most commonly measured properties of surfactants in solution, which depends on the replacement of solvent molecules at the interface by surfactant molecules. The dynamic IFTs between between C_n-DADS solutions with various amount of NaCl added and dodecane are shown in Figure 6. Obviously, the IFTs reach equilibrium within 5 min. Figure 8 shows the effects of NaCl concentration on the equilibrium interfacial tension of C_n-DADS obtained from their corresponding dynamic IFT plots.

The IFTs between C_n-DADS aqueous solutions and dodecane decrease with an increase in NaCl concentration as shown in Figure 7. These results could be due to two aspects. One is that NaCl could deprive the water of hydration around the surfactant molecules and enhance the hydrophobicity of C_n-DADS, causing more surfactant molecules to transfer to the oil/water interface. The other one is that the increased NaCl concentration can reduce the electrostatic repulsion between the intermolecular headgroups which lead to a close packing of surfactant molecules at oil/water interface [28], which roles are similar to the NaCl effects on adsorption at air/water interface.

There is no intensive change for IFTs of C_n-DADS solutions with the increase of alkyl chain length, which demonstrates that the hydrophobic chains have little effect on the IFTs. The IFT values are on the order of 10^{-1} mN/m which is much higher than ultralow interfacial tension, indicating a looser arrangement of gemini surfactant molecules at the oil/water interface because of the rigid spacers of C_n-DADS molecules.

3.4 Sodium chloride effects on spreading behaviors at hydrophobic surface

Spreading of surfactant solution over the solid is an important property for practical applications such as herbicide, painting and coating [29-30]. The wetting equilibrium of a liquid droplet on a solid substrate is described by the Young equation:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta \qquad (7)$$

where γ_{sg}, γ_{sl}, and γ_{lg} are the solid/gas, solid/liquid and liquid/gas surface tensions, respectively, and θ is the contact angle.

Figure 8 shows the apparent dynamic contact angle of 0.5 mM C_8-DADS aqueous solutions on parafilm depending on the concentration of sodium chloride. Increasing the NaCl concentration decreases an intial (t=0) contact angle of droplets and enhances the spreading allowing reaching a final equilibrium contact angle much faster. A possible interpretation for this phenomenon can be attributed to the fast adsorption kinetics of molecules on the water/air interface [31] which is consistent with the dynamic surface tension results of C_n-DADS.

Dependence of the final equilibrium contact angle on the NaCl concentration is shown in Figure 9 and images of 2 mM C_8-DADS aqueous drops in equilibrium with various NaCl concentrations are presented in Figure 10. The contact angle values decrease significantly firstly and then no further change with the increase of NaCl concentration. These results may be interpreted as follows: The higher the NaCl concentration, the closer packing at the liquid/solid interface, causing a decrease of γ_{sl} values. In addition, as can be seen in Table 2, the γ_{lg} values of both C_{10}-DADS and C_{12}-DADS decrease in additive of NaCl concentration, which leads to the decrease of contact angle values. Once the NaCl concentration is large enough, the electrostatic repulsion between intermolecular headgroups may become invariable which leads to the equilibrium of both γ_{lg} and γ_{sl} values, which represent the constant of adsorption quantities at air/water and water/solid interface, respectively.

3.5 Sodium chloride effects on aggregation

Negative-straining TEM is a reliable and versatile method to investigate the morphology of aggregates for C_8-DADS aqueous solutions above cmc. Both 0.5 M and 2 M C_8-DADS solutions in absence and presence of 0.1 M NaCl were imaged, respectively. For 2 M C_8-DADS solution, vesicles with a dark outer ring can be observed in 2 M C_8-DADS aqueous solution (Figure 11a), while the vesicle disappears after the additive of 0.1 M NaCl. However, vesicles were formed in 0.5 M C_8-DADS solution after the additive of inorganic salt (Figure 11b). This is an interesting property of C_8-DADS as well as an excellent characteristic which may be used as carries for drug delivery.

4. Conclusion

Effects of sodium chloride on adsorption of C_n-DADS molecules at different interfaces were investigated systematically. The following conclusions are made.

(i) The C_n-DADS surfactants have an salting-out phenomenon with the addition of NaCl concentration. The salt tolerance properties decrease in the order: C_8-DADS > C_{10}-DADS > C_{12}-DADS.

(ii) The cmc values of C_n-DADS aqueous solution increase with increasing the concentration of NaCl. The D_{deff} values of C_n-DADS at air/water interface increase with an increase in both NaCl concentration and carbon chain length.

(iii) The addition of NaCl has no significantly effect on adsorption of C_n-DADS molecules at oil/water interface.

(iv) From the contact angles data, the adsorption rates and amounts of C_n-DADS molecules at different interface (air/water and water/solid) increase with an increase of NaCl concentration.

(v) The vesicles formed in 2 M C_8-DADS solutions disappeared with the addition of 0.1 M NaCl, while the formation of vesicles occured in 0.5 M C_8-DADS solution with the addition of 0.1 M NaCl.

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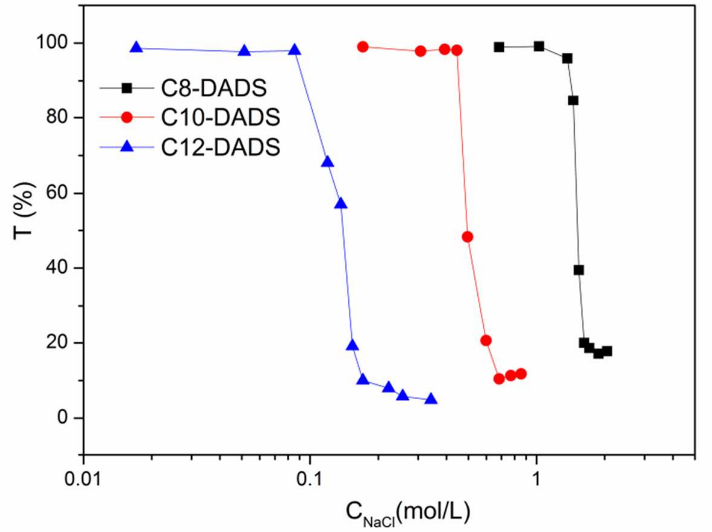


Fig. 1 Transmittance curves of curves of 3 mM C$_n$-DADS solutions plotted against the NaCl concentration at 25 °C.

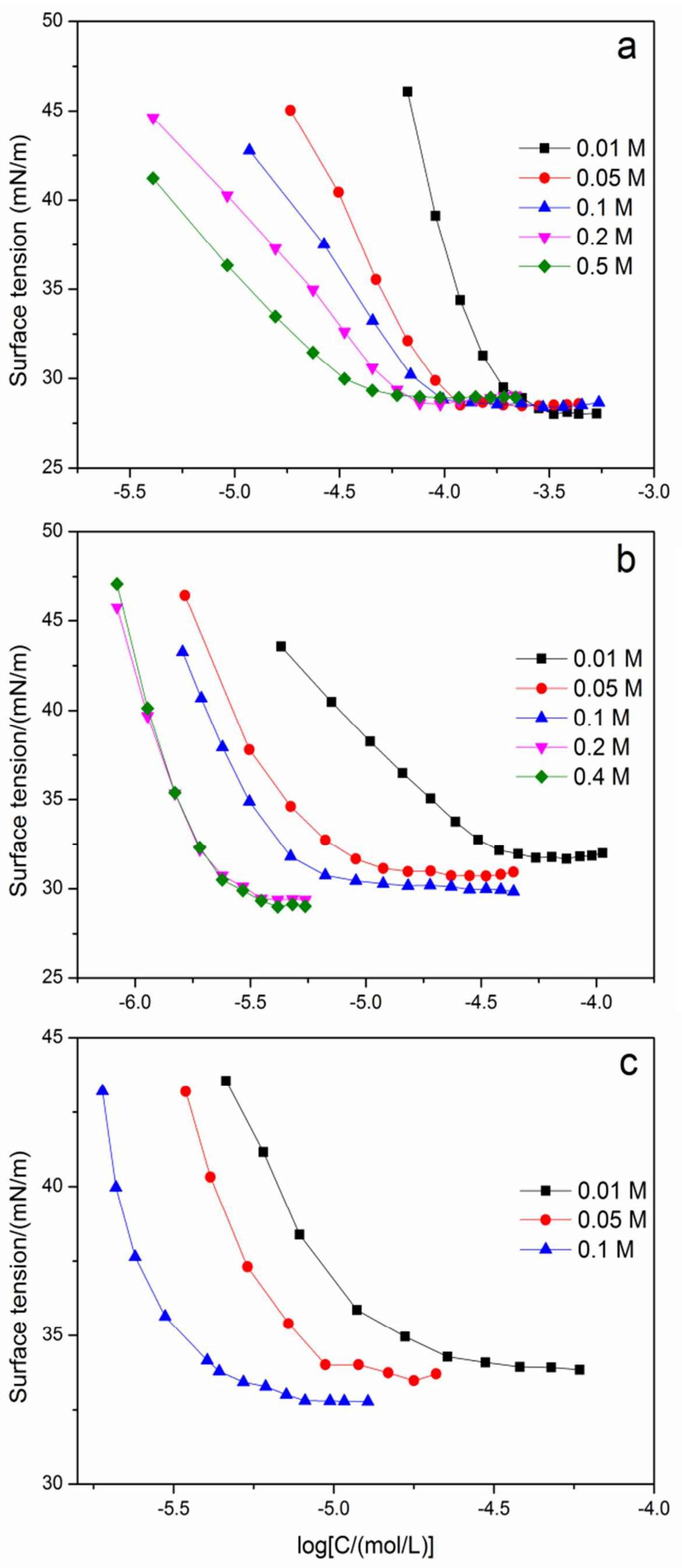


Fig. 2 Surface tension as a function of C_n-DADS concentration (C) with different NaCl concentrations at 25 °C: (a) C_8-DADS (b) C_{10}-DADS (c) C_{12}-DADS.

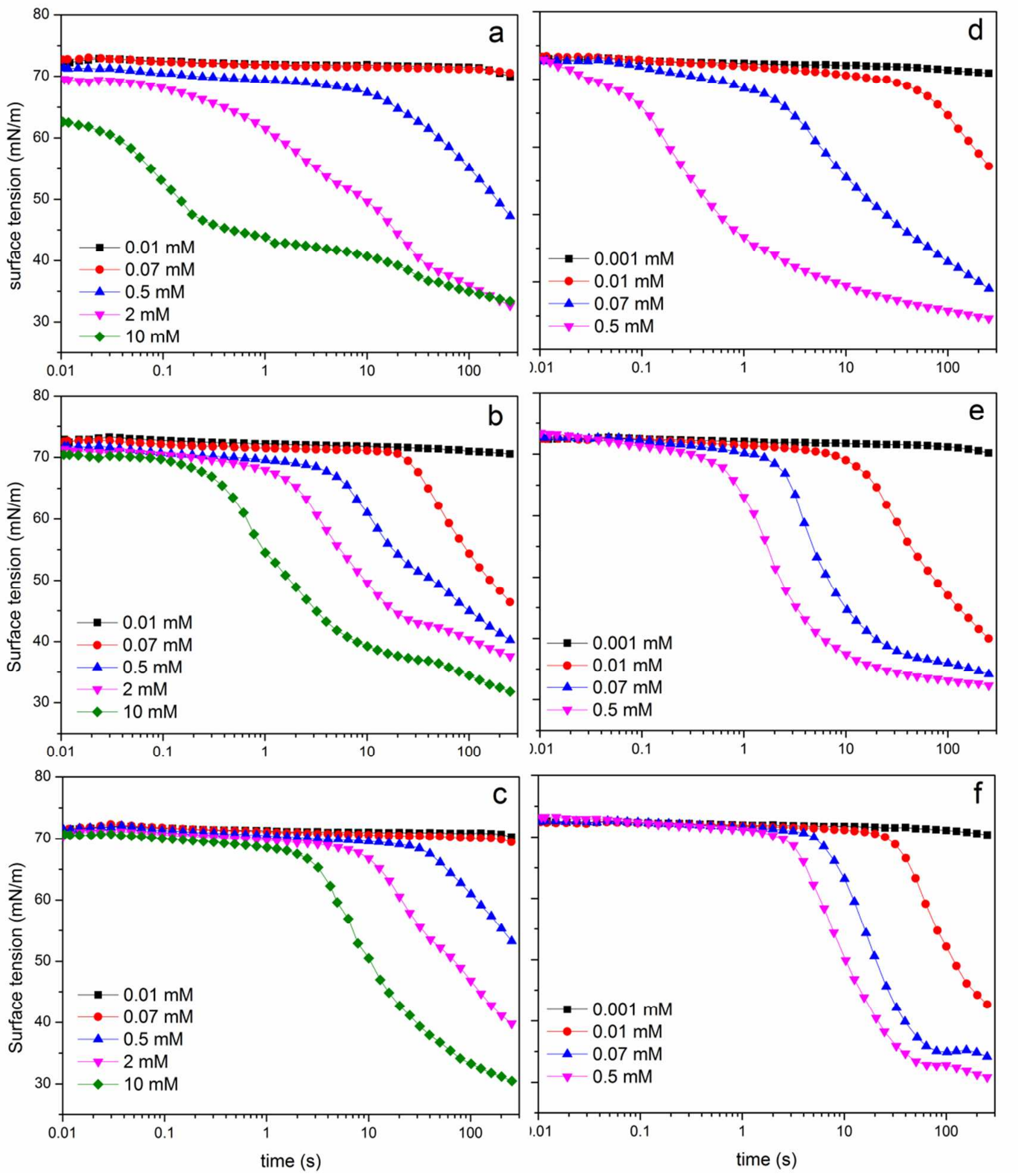


Fig. 3 Dynamic surface tension with surface age for C_n-DADS at 25 °C: (a) C_8-DADS (b) C_{10}-DADS (c) C_{12}-DADS (d) C_8-DADS + 0.1 M NaCl (e) C_{10}-DADS + 0.1 M NaCl (f) C_{12}-DADS + 0.1 M NaCl.

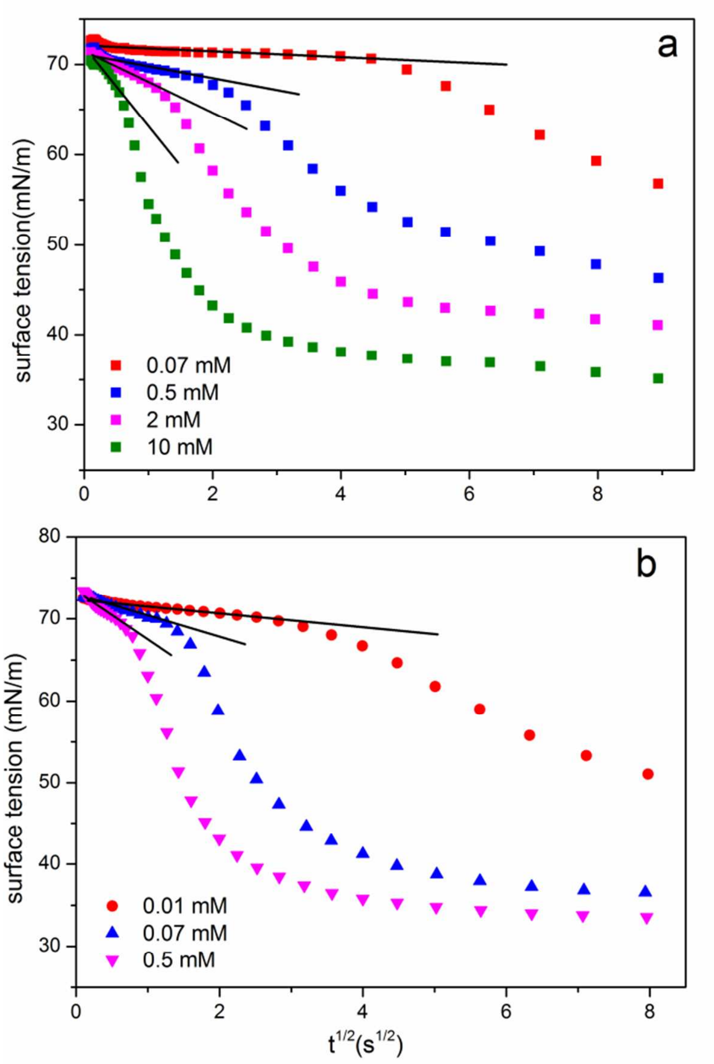


Fig. 4 Dynamic surface tension as a function of $t^{1/2}$ at different C_{10}-DADS concentrations: (a) salt free system (b) 0.1 M NaCl.

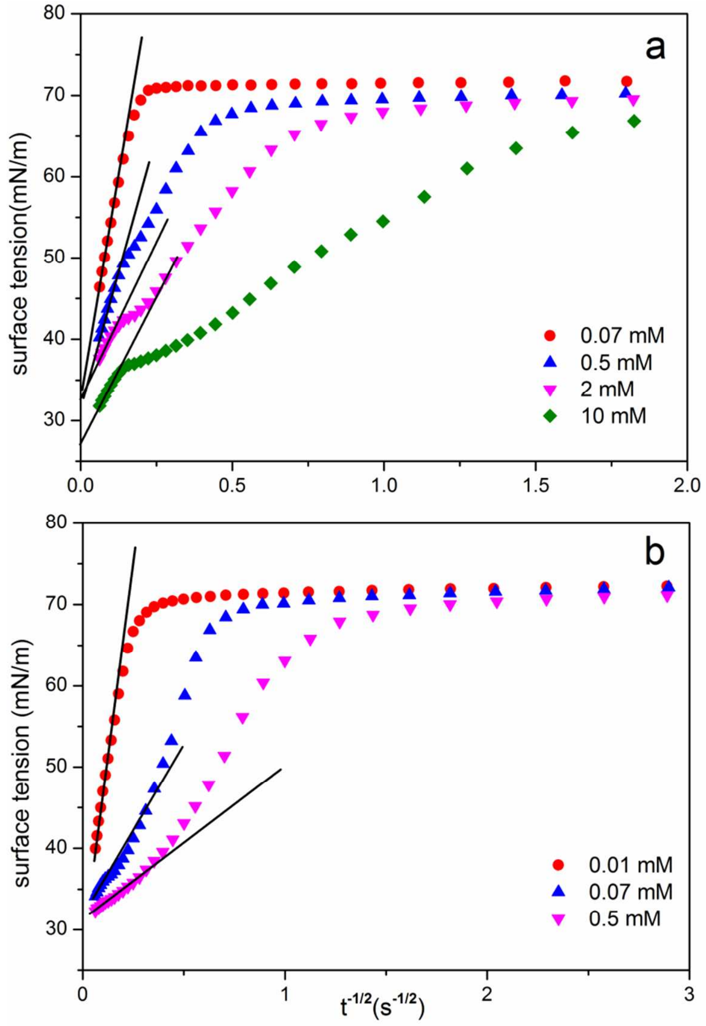


Fig. 5 Dynamic surface tension as a function of $t^{-1/2}$ at different C_{10}-DADS concentrations: (a) salt free system (b) 0.1 M NaCl.

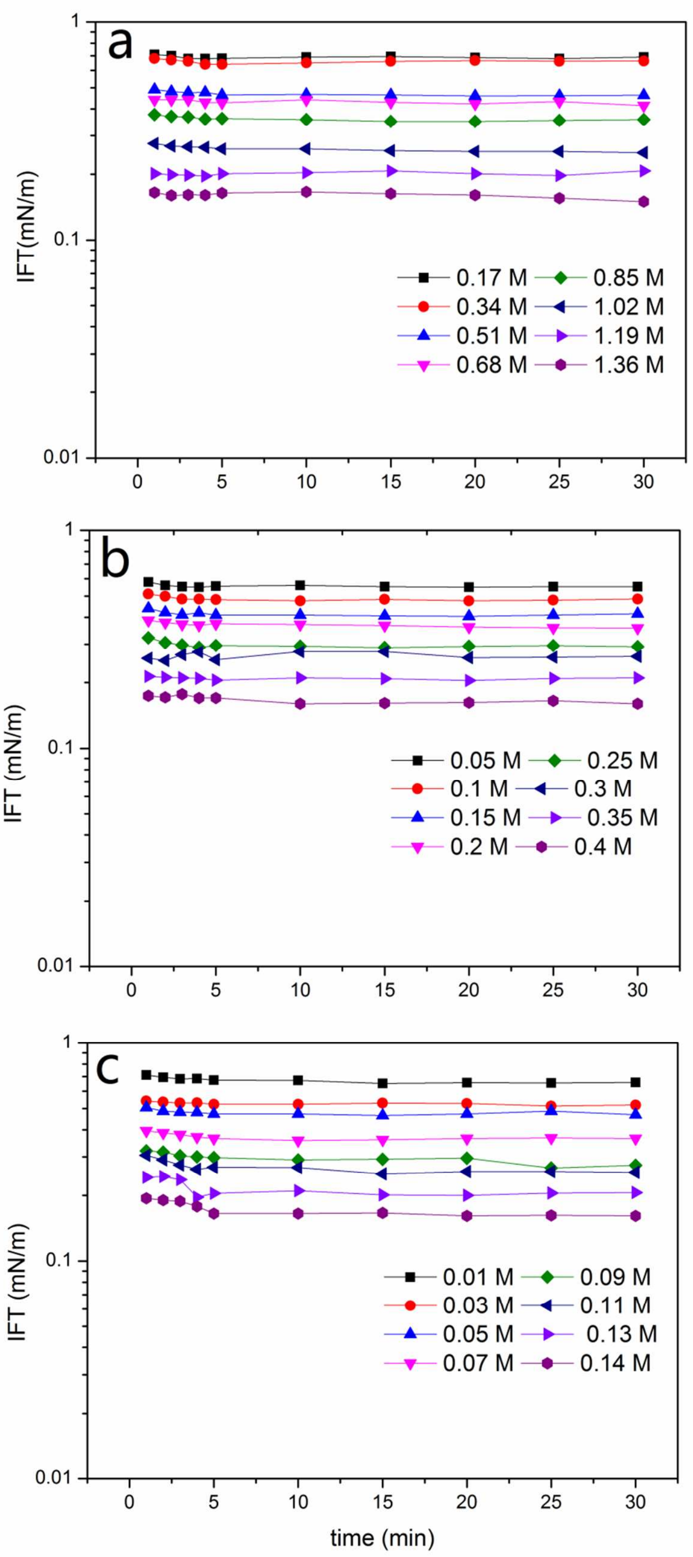


Fig. 6 Dynamic IFT response for 5 mM C_n-DADS aqueous solutions at different NaCl concentrations: (a) C_8-DADS (b) C_{10}-DADS (c) C_{12}-DADS. Measured at 25 °C, against dodecane.

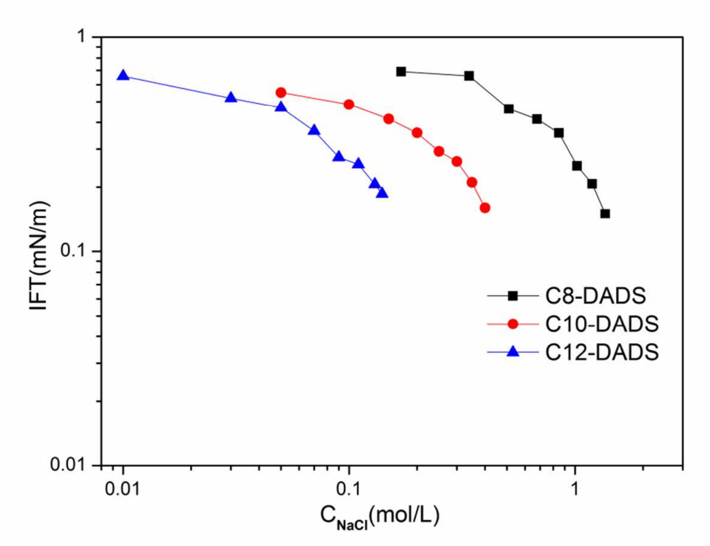


Fig. 7 Effects of NaCl concentration on IFT values for 5 mM C_n-DADS. Measured at 25 °C, against dodecane.

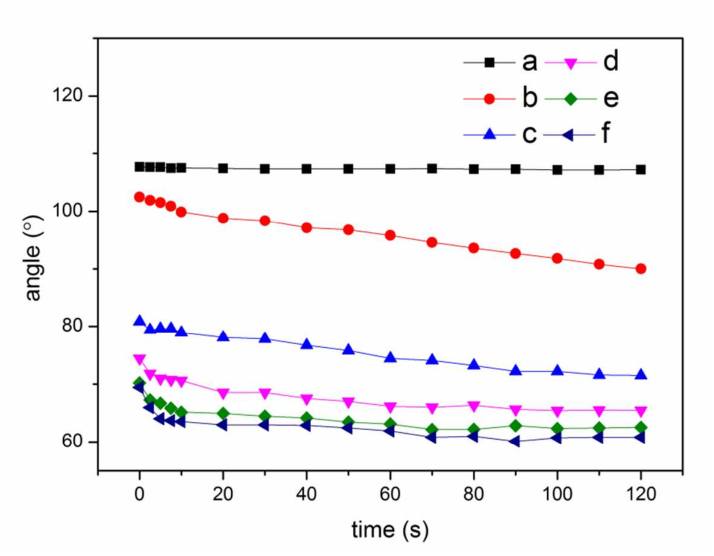


Fig. 8 Evolution of apparent dynamic contact angle of 0.5 mM C_8-DADS aqueous solutions at different salt concentrations on parafilm surface at 25 °C. (a) water (b) C_8-DADS (c) C_8-DADS + 0.01 M NaCl(d) C_8-DADS + 0.05 M NaCl (e) C_8-DADS + 0.1 M NaCl (f) C_8-DADS + 0.2 M NaCl

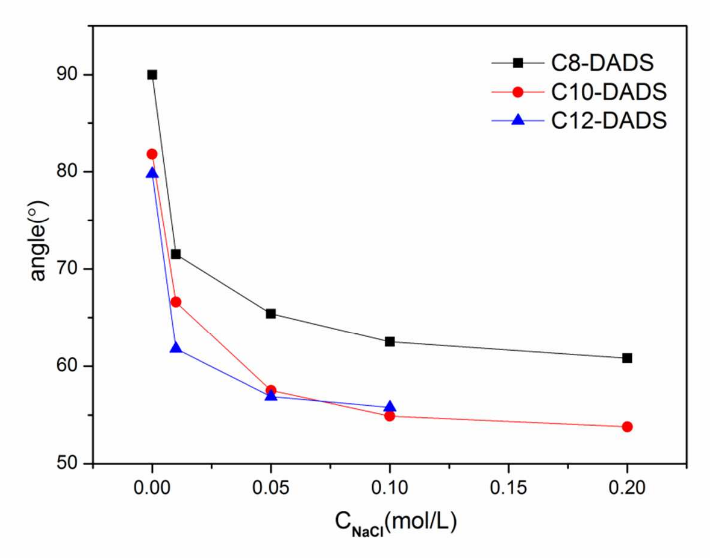


Fig. 9 Effects of NaCl concentration on apparent equilibrium contact angle values for 0.5 mM C_n-DADS on paraffin surface at 25 °C

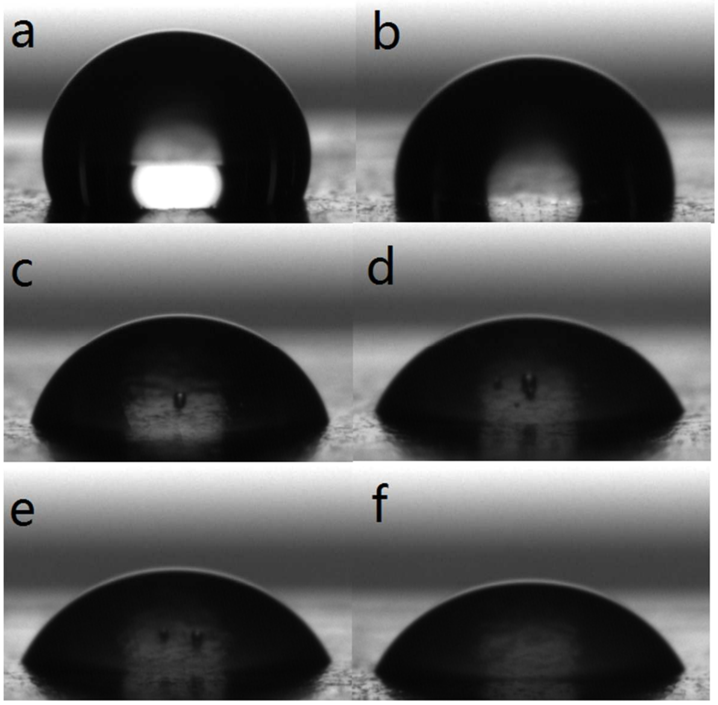


Fig. 10 Images of water and 0.5 mM C_8-DADS aqueous drops in equilibrium on paraffin surface with different NaCl concentration at 25 °C: (a) water (b) C_8-DADS (c) C_8-DADS + 0.01 M NaCl(d) C_8-DADS + 0.05 M NaCl (e) C_8-DADS + 0.1 M NaCl (f) C_8-DADS + 0.2 M NaCl

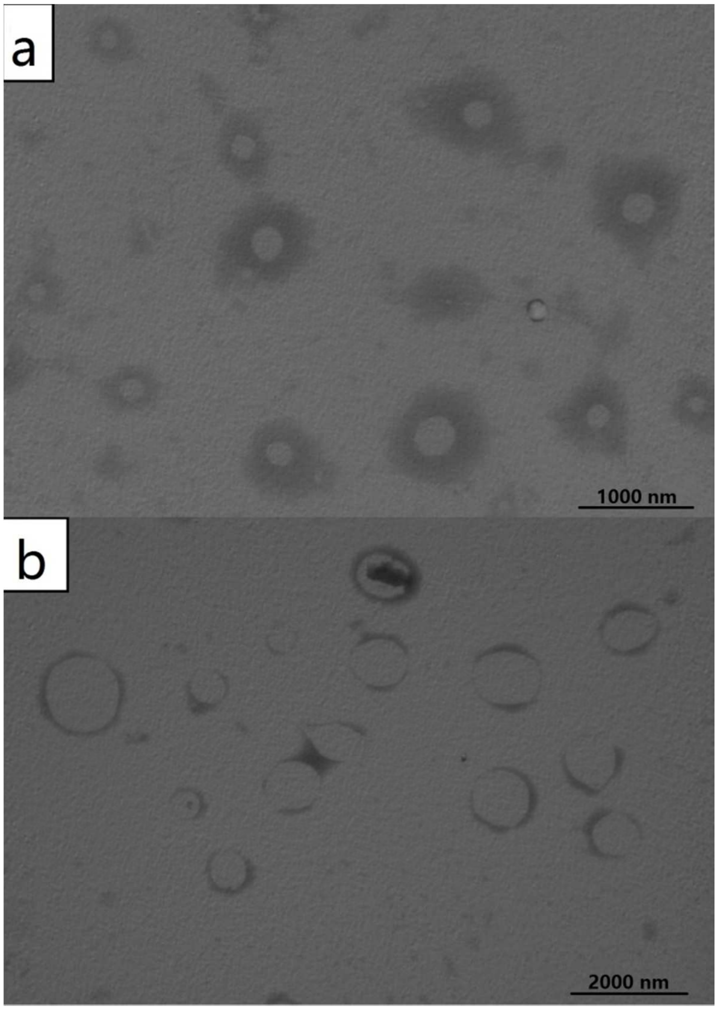
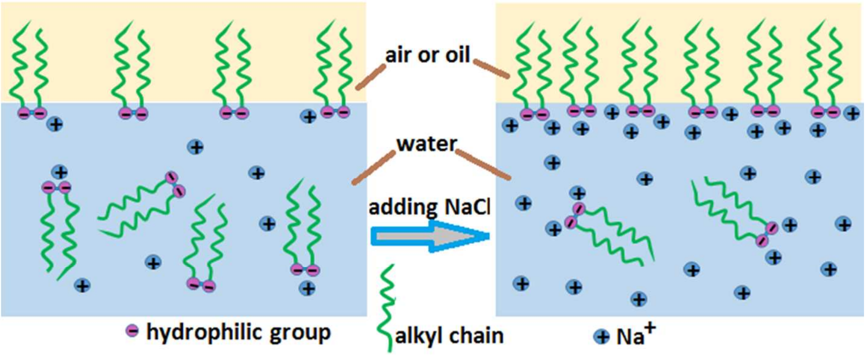


Fig. 11 Negative-strained TEM images of vesicles formed in C_8-DADS aqueous: (a) 2 mM C_8-DADS solution; (b) 0.5 mM C_8-DADS solution with 0.1 M NaCl.



Schematic illustration of NaCl effects on the adsorption of C_n-DADS molecules at different interfaces (Cl^- is not shown).