Soft Matter

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Wetting films of aqueous solutions of Silwet L-77 on a hydrophobic surface

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Abstract

Formation of wetting films of aqueous solutions of Silwet L-77 on hydrophobic substrates takes place only at concentrations above critical aggregations concentrations (CAC). At concentrations above critical wetting concentration (CWC) a new phenomenon was found: formation of multilayered spots of thicker films in the wetting film of aqueous solutions of Silwet L-77 on hydrophobic surfaces. An expansion of the thicker spots within the film and formation of "channels" between the spots and the edge of film led to a continuous shrinkage of the wetting film and its disappearance in the end. We suggested that the multiple thicker films originate from multilayer structuring of trisiloxane bilayers within the wetting film.

Trisiloxane polyoxyethylene surfactants are of great importance in agricultural, textile and painting industries due to their ability to improve significantly wetting of low energy surfaces.[1,2] The phenomenon of spontaneous fast spreading of aqueous trisiloxane surfactant solutions is referred to as "superspreading".[1,2] The mechanism behind this phenomenon is a challenging problem and has been debated over two decades.[2] Most of researches on this phenomenon have been concentrated on studying spreading of trisiloxane solutions on hydrophobic surfaces,[1-3] adsorption of trisiloxanes on interfaces[2,4,5] or on phase behavior of molecules in the bulk solutions.[6] At the same time there are very limited published results on behavior of wetting films of trisiloxane surfactant solutions[7,8] that could give information on the role of surface forces responsible for superspreading mechanism. Churaev at al.[7] studied a spontaneous climbing of trisiloxane surfactant solution on an inclined hydrophobic substrate against gravity action and found that wetting film was up to 4 microns thick. It has been suggested that formation of such thick wetting film is due to mutual repulsion of vesicles and action of long-range structural forces.[7] Recently, Sett et al.[8] have shown that in the course of gravitational drainage of vertical free films of superspreader solutions the films stabilize at the thickness about 35 nm and have a longer lifetime before rupture compared to that of the non-superspreader trisiloxanes. The film stabilization of superspreader trisiloxanes was explained by formation of long bilayers hanging from the free surfaces.[8] The presence of vesicles and bilayers aggregates and their direct adsorption at the interfaces seems to be dominated hypothesis[1-5] proposed for explanation of superspreading mechanisms.

An important feature of the superspreading phenomenon is the existence of the critical wetting concentration (CWC), above which superspreading starts to occur.[3,9] The liquid/air surface tension of trisiloxane solutions reaches the minimum value at critical aggregation concentration (CAC) (concentration at which various aggregates in aqueous solutions appear and remain at equilibrium with monomers). However, superspreading or complete wetting is observed at critical wetting concentration (CWC), which is several times higher than CAC.[3,9] Using AFM Svitova et al.[3] have found a long-time multilayered adsorption of trisiloxanes on hydrophobic solid substrate (graphite) at/above CWC, whilst between CAC and CWC only monolayer or hemispherical micelles has been observed. Bezuglyi et al.[10] confirmed using FTIR that adsorption of trisiloxanes on moderately hydrophobic surfaces sharply increases at $C \geq$ CWC in comparison with CAC. Moreover, using Brewster angle microscopy Ritacco et al.[5] detected surface aggregates on the liquid/air interfaces at $C >$ CAC for the trisiloxanes which show superspreading on hydrophobic surfaces, while no aggregates were detected for the other trisiloxanes. It has been hypothesized[5] that those surface aggregates may act as reservoirs of surfactant molecules to maintain the required low surface tension in the course of spreading.

Below an influence of concentration of trisiloxane surfactants on disjoining pressure isotherms and the dynamics of wetting film of superspreader trisiloxane Silwet L-77 is investigated.

A commercial organosilicone surfactant Silwet L-77 (Momentive, Germany) was used without any further purification. Solutions of Silwet L-77 at concentrations ranging from C < CAC through C > CWC (where CAC is 0.007%[3,9] and CWC is 0.025%[3,9]) were prepared using 10^{-4} mol/l KCl aqueous solutions. According to manufacturer the surface tension of aqueous Silwet L-77 solution is 20.5 mN/m.

Glass slides were hydrophobized according to the following procedure. The slides were soaked in concentrated NH_4OH solution for one hour and then thoroughly rinsed in pure water (18.2 MΩ·cm, Millipore). After that the cleaned glass slides were dried for one hour at 140 °C and then the slides were silanized by placing them in a 5 mM solution of trimethoxy(octadecyl)silane (90 %, Sigma-Aldrich) in heptane (≥99%, Sigma-Aldrich) for 24 hours. The silanized glass slides were washed with heptane to remove unreacted materials, and then were heated for one hour at 70 °C. The slides were stored in methanol before use. The surface roughness of silanized glass slides measured by AFM was found 1.9 ± 0.2 nm. Advancing contact angles of pure water on the slides at the humidity 95% was $\theta_w = 98 \pm 1°$.

An experimental setup for studying the film formation and measurement of the disjoining pressure isotherms is shown in Fig. 1. The setup consists of an interference microscope and the cell with the hydrophobized glass slide on the top, connected by a plastic tube to a vessel. The wetting films were formed when a liquid meniscus in a cylindrical titanium capillary with the inner radius of $r_c = 0.575$ mm approached the hydrophobic surface of the slide. The distance between the capillary edge and the glass slide was around 0.2 mm. Changing the distance H (Fig. 1) between the level of solution in the vessel and the hydrophobic surface the position of the liquid meniscus can be varied that allows varying the capillary pressure inside the wetting film. The capillary pressure in this system was calculated according to the following equation.[11,12]

$$P_c = 2\gamma r_c/(r_c^2 - r_f^2), \tag{1}$$

where r_c is the radius of the capillary, r_f is the radius of the wetting film, γ is the surface tension of the trisiloxane solution. Let us rewrite the latter equation as $r_f = r_c\sqrt{1-2\gamma/r_cP_c}$. That is, the film radius, r_f, is equal to radius the capillary at $P_c = 2\gamma/r_c$ (at this pressure the meniscus touches the solid support) and then the radius of the film increases with P_c decrease in a non-linear way and tends to r_c as P_c decreases.

The equation for the disjoining pressure acting in the liquid film is $\Pi(h) = P_c + P_g$, or taking into account eqn (1):

$$\Pi(h) = 2\gamma r_c/(r_c^2 - r_f^2) + P_g, \tag{2}$$

where $P_g = \rho g H$ is the hydrostatic pressure, ρ is the density of liquid, g is the gravity acceleration. According to eqn (2) the disjoining pressure decreases if the film radius, r_f , decreases. According to Fig. 4 the latter means that the smaller the radius of the film, r_f, is the thicker the film becomes.

The film thickness and its dynamics were determined from an interference image formed by monochromatic light (λ = 715 nm) reflected from the wetting film. The film thickness was calculated from the intensities of reflected light using the following equation:[12]

$$h = \frac{\lambda}{2\pi n_f}\arcsin[(1-\Delta)/(1-b\Delta)]^{1/2}, \tag{3}$$

where $\Delta = (I_f - I_{min})/(I_{max} - I_{min})$, $b = (n_f^2 - 1)(n_s^2 - n_f^2)/n_f^2(n_s + 1)^2$, I_f is an intensity of the reflected light from the film, I_{max} and I_{min} are the intensities of the fist maximum and minimum of interference, n_f and n_s are the refractive indices of the liquid in film (assuming that it is equal to that of the bulk solution, n_f = 1.33) and the solid substrates (the glass n_s = 1.51), respectively. At these values of n_f and n_s the value of $b \sim 0.0353 << 1$. According to eqn (3) $I_f(h)$ reaches its maximum value I_{max} at $h = 0$.

Direct differentiation of dependency $I_f(h)$ according to eqn (3) results in

$$\frac{dI_f}{dh} = -\frac{2\pi n_f}{\lambda}(I_{max} - I_{min})(1 - b\Delta)^{\frac{3}{2}}\sqrt{\frac{\Delta}{1-b}} < 0 \quad (4)$$

The latter means: the thicker film is the darker image will be, or dark spots on the film show the presence of thicker spots.

It was allowed equilibrating for not less than 5 minutes before measurement of the film thickness.

Separately time evolutions of advancing contact angle of droplets of aqueous Silwet L-77 solutions on the hydrophobized glass slides at different concentrations were measured by goniometry technique at $T = 24 \pm 1°$ and the humidity of 95% to prevent evaporation of droplets.

Wetting and spreading kinetics results. Before film formation and measurements of the disjoining pressure the kinetics of spreading of trisiloxane solutions was investigated on the hydrophobized glass slides. Concentration range of Silwet L-77 was from 0.002 (below CAC) to 0.1 wt% (above CWC). In Fig. 2 time evolution of apparent advancing contact angles of Silwet L-77 solutions on the hydrophobized glass slides is shown. According to Fig. 2 solutions of Silwet L-77 in studied concentration range demonstrate either partial or complete wetting of the hydrophobized glass depending on concentration. The superspreading behavior on these substrates was observed only at C ≥ CWC. Note that in this case the droplets did not spread out to a very thin layer (e.g. a monolayer) in the course of superspreading but to a layer of a finite thickness around a few microns. At lowest concentration (0.002 wt%, which is below CAC) a time lag of spreading around 5 s was detected. This time lag is related to slow adsorption kinetics of surfactant molecules on both the liquid/air and the solid/liquid interfaces at C < CAC.[13] The trends observed (Fig. 2) are in agreement with our previous findings on spreading of trisiloxane solutions on hydrophobic polymer films.[9]

Disjoining pressure isotherms. It was found that at C = 0.002 wt% (below CAC) no wetting film was detected on the silanized glass either immediately after the cell was filled with surfactant solution or in almost half an hour after the solution was kept in the cell. Note that 30 minutes is enough for adsorption of molecules at interface to form a wetting film according to the data on dynamic surface tension at the liquid/air interface[13] and the data on spreading kinetics (Fig. 3). At C = 0.004 wt% (still below CAC) and C = 0.007 wt% (equal to CAC), appearance of the wetting films with dimples was observed. However, the films ruptured immediately after the dimples began to disappear (Fig. 3). This process (formation and rupture of films) occurred randomly, hence, there was no possibility to measure the film thickness and the pressures of the rupture. In the case of 0.004 wt % concentration the film rupture resulted in almost dry surface of silanized glass (see Fig. 3a). However, at C = 0.007 wt% (which is equal to CAC) small residual droplets remained on the surface, which meant the transition from a non-wetting to a partial wetting of the surface (Fig. 3b). At high concentrations in between CAC < C < CWC and at C ≥ CWC different types of aggregates (lamellas, vesicles and others) exist in solutions. In these cases thick films were formed in our experiments on the silanized glass slides. In Fig. 4 the disjoining pressure isotherms of films at different (0.01, 0.015, 0.025 and 0.1 wt %) concentrations obtained for Silwet L-77 in our experiments and data from Churaev et al[7] obtained for the thick wetting film of trisiloxane D-8 at C = 0.16wt% are presented. Note, that our experimental conditions allowed measurements of the thickness of wetting film only in a relatively narrow range of variation of the capillary pressure: increasing the pressure over the limit resulted in the condition $I_f < I_{min}$ at which eqn (3) is not valid any more. According to Fig. 4 the thickness of wetting film decreases significantly with an increase of the disjoining pressure, while an influence of concentration within the studied range of concentrations is almost undistinguishable. Note, that our data and data from Churaev et al[7] show a common trend.

Important to note that the wetting films did not rupture when the hydrostatic pressure was significantly increased. Taking into account the presence of aggregates in the studied solutions it is possible to assume that the wetting films were stabilized by the long-range structural forces between aggregates.[7] Fig. 4 also shows that the more multilayers are formed the lower the disjoining pressure becomes.

Multilayered films. Dark spots. At concentration C = 0.1 %, which is above CWC, within the stable wetting film in few minutes (~ 5 min) after the film was formed, an appearance of dark spot was observed, Fig. 5(a). The area of this dark spot expanded continuously and new spots appeared in the film in the multilayer manner: each new spot was darker than the previous one, Fig. 5(a). Increase of quantity of the dark spots and their expansion followed by formation of "channels" from the dark spots to the boarder of the film Fig. 5(a). After appearance of these "channels" the film began to shrink and disappeared in the end. This means that P_c according to eqn (1) began to decrease. The evolution of the diameter of wetting film is shown in Fig. 5(b), which shows that formation and growth of the dark spots did not changed substantially the film diameter, until appearance of the "channels". It proves that the channels served as a way to solution flow from the surrounding meniscus to the wetting film.

Note that appearance of dark spots in the free liquid films (similar to that in foam films) has been intensively studied for a long time.[11,14,15] Appearance of the dark spots is actually a demonstration of the stepwise thinning of the films.[14,15] It means that films exhibited a number of metastable equilibrium states until a final thinner equilibrium state was reached.

However, in our case back spots meant not thinner but thicker parts. After a number of metastable equilibria the wetting film became very thick and eventually converted in a part of the surrounding meniscus. We assume that this behavior is related to some long range structural transformation processes occurring within the film at C ≥ CWC: trisiloxane molecules in a stepwise manner form of multilayer structures (for instance, bilayers) above the monolayer adsorbed at interfaces. Svitova et al.[3] observed a long-time multilayer adsorption of trisiloxanes at C ≥ CWC on graphite surface under spreading droplets. Later a considerable rise of adsorption at the hydrophobic solid/liquid interface at C ≥ CWC was found by Bezuglyi et al.[10]

An increase of the film thickness leads to the shrinkage of the film radius and it disappearance. Measurement of I_f for two subsequent dark spots within the wetting film and using eqn (2) allowed estimating the difference in thickness between two subsequent dark spots, which turns out to be within the range of 7 - 9 nm. According to Kunieda et al.[6] for trisiloxane surfactants in the L_α phase (where the bilayers and/or lamellar aggregate are present) the interlayer spacing is ranged from 6 to 10 nm that in a good agreement with our estimations of the interlayer spacing.

Conclusions

It was shown that wetting films do not form at concentrations below critical wetting concentration (CAC) but form such films at higher concentrations. At concentrations at/above CWC in equilibrium wetting films of aqueous solutions of Silwet L-77 on silanazed glass a spontaneous multilayered spots of thicker formation occurred. Multilayer adsorption of trisiloxane bilayers aggregates within the wetting film at C ≥ CWC is a possible reason for the observed behavior. Indeed, the interlayer thickness estimated at each black film corresponds to the interlayer spacing for bilayers formed by trisiloxane molecules. The multilayer adsorption of trisiloxane aggregates increases the thickness of the wetting film that leads to the film shrinkage and final disappearance.

Acknowledgement

This research was supported by the Royal Society UK-Russia collaboration grant, European Space Agency EVAPORATION MAP project, CoWet EU project and COST MP1106 EU project; Engineering and Physical Research Council, UK (EP/J010596/1). N Ivanova was supported by the RFBR (Grant no. 14-01-92602 KO_a) and the Ministry of Education and Science of the Russian Federation, the program of The Organization of Scientific Research.

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List of figure captions

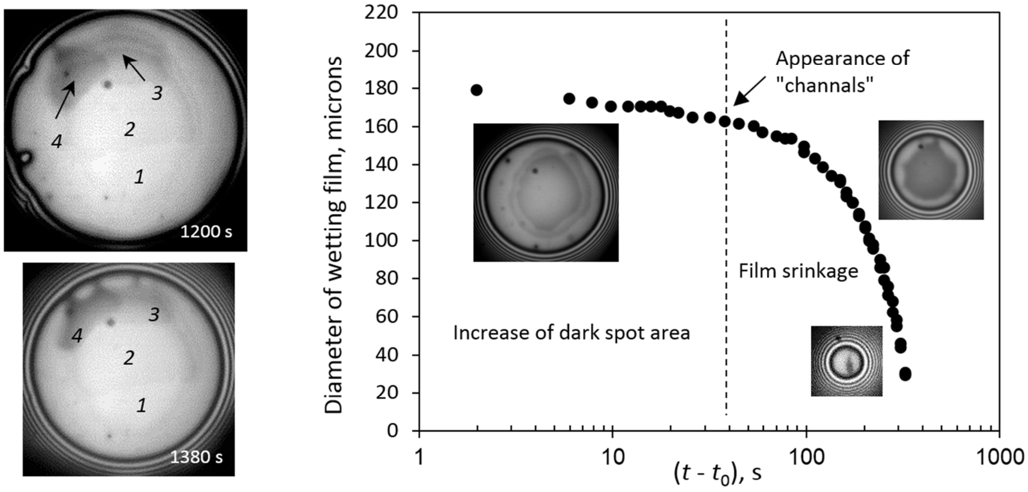
Fig. 1 Diagram of experimental cell for the wetting film formation/measurements.

Fig. 2 Time evolution of advancing contact angle of aqueous solutions of Silwet L-77 on silanized glass slides at different surfactant concentrations.

Fig. 3 Images of the film ruptures in solutions of Silwet L-77 at concentrations: (a) 0.004 wt% and (b) 0.007wt%.

Fig. 4 Disjoining pressure isotherms of films at different concentrations of Silwet L-77 and data adopted from Churaev et al [7] for trisiloxane with a similar number of ethylene oxide units at concentration 0.16%.

Fig. 5 (a) Long time multilayer films structuring within the wetting film at concentration 0.1%wt. 1,2,3,4 – the dark spots appeared in the film. Spots 3 and 4 are darker in comparison with spots 1 and 2. (b) Diameter of the wetting film as a function of time. Initial thickness of the film is 60 nm ($t_0 \cong 600$s). Concentration of solution is 0.1% wt.



(a)

(b)

Long time multilayer films structuring within the wetting film at concentration 0.1%wt. 1,2,3,4 – the dark spots appeared on the film.