IMPACT OF AMPHIPHILIC NANOSTRUCTURES ON FORMATION AND RHEOLOGY OF INTERFACIAL LAYERS AND ON FOAM FILM DRAINAGE

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The aim of the present studies is to clarify how the surfactant adsorption layer properties are related to the course of the drainage parameters of microscopic foam films in the special case of aqueous solutions containing premicellar amphiphilic nanostructures. The scope of the research covers the adsorption dynamics, construction of equilibrium adsorption isotherms, surface rheology of interfacial layers, and foam film drainage kinetics. It is established that, in the premicellar domain, there are concentration intervals, where the considerable irregularities of adsorption layer properties are observed: several plateau regions in the surface tension isotherms, unusual changes of the surface rheological characteristics, *etc.* The systematic investigation of the drainage of foam films obtained from these solutions show that the dependences of basic kinetic parameters of the films on the amphiphile concentration run in synchrony with changes in the adsorption layer properties. Thus, the presence of smaller loose aggregates (premicelles) plays a significant role for the kinetic stability of films. The importance of this research is related to providing a better insight into the initial stages of self-assembling phenomena and into the factors determining the drainage and the stability of thin liquid films. The results have implications for the understanding and the correct prediction of properties of foam systems.

1. Introduction

The courses of surface tension isotherms (equilibrium surface tension data against the amphiphilic concentration) give valuable information about the state of adsorption layers. The construction of these isotherms is one of the basic methods for the experimental determination of the critical micellar concentration (CMC). Approaching the CMC domain, the smooth run of the equilibrium curve is abruptly changed. Above CMC, the surface tension value is preserved almost unchanged, because the major portion of added surfactant molecules goes to form micellar aggregates in the solution bulk. In certain cases, however, the surface tension isotherms do not run in a "regular manner". Instead of the expected more or less gradual change against the rise of the surfactant quantity, the kink and plateau regions are observed for intermediate surfactant concentrations. These effects depend on the structure of amphiphile. The earliest results of this type concern the measurements in aqueous solutions of sodium alkyl sulphates with different chain lengths [1]. They are obtained by the Du Nouy ring technique. More precise are the results from the application of the Scheludko spherotensiometric method which has a very high precision ($\pm 2 \times 10^{-3}$ mN/m) [2–4]. Special measures have been taken to ensure the purity of the substances (sodium dodecyl sulphate and sodium octyl sulfate) and of the aqueous solutions during the experimental procedures. The authors of these studies advanced the idea of that the surface tension peculiarities might be assigned to the possible onset of amphiphilic structures at concentrations lower than the CMC. They gave them the name 'premicelles'. In order to test this hypothesis, systematic experiments on the drainage kinetics of microscopic foam films obtained from solutions in the same concentration range as the surface tension measurements are performed [5–12]. The results show the onset of peculiarities in the drainage kinetics parameters as well. Thus, specific 'unstable' black patterns are observed in these films: black dots and black spots. In addition, several drainage characteristics change abruptly in concentration synchrony with the onset of the kink and plateau portions of surface tension isotherms [9, 12]. The coupling of these results presents an experimental evidence of the presence of amphiphilic self-assemblies in the premicellar concentration domain.

It is also well known that the presence of a surfactant is of crucial importance for the formation, time evolution, and stability of microscopic thin liquid films [2,13]. There are two important aspects of this interrelation:

(i) adsorption layer properties vs. surface forces and stability of foam films; (ii) adsorption layer properties vs. kinetic stability of foam films. Although these aspects are intermingled, depending on the specific conditions in a system, they have distinct peculiarities and one or the other may prevail and determine the properties of the films. Thus, if the first option is operative, the constitution of the interfacial layers, including possible conformation changes and/or phase transitions, is of primary importance, while the second option implies that the combination of the mass transfer of amphiphilic ingredients and the film hydrodynamics is mostly important. The present investigation is focused on the second option. The study deals with the coupling of dynamic and equilibrium surface tension data, the rheological properties of interfacial layers, and the kinetic stability of foam films. This coupling is significantly tuned and modified by the presence of amphiphilic nanostructures in the initial solutions.

The impact of amphiphilic nanostructures on the drainage behavior of foam films is related to two major cases. (i) At high surfactant quantities (above CMC), the presence of micelles imposes stepwise changes in the film thickness. In this case, the mechanism of foam film stabilization has much in common with the influence of nanoparticles and has been extensively studied in the last decade [14–17]. (ii) At intermediate concentrations (higher than the concentration where the Henry law is operative, but one-two orders of magnitude below the conventional CMC), the amphiphilic nanostructures are premicelles [2–12]. These are loose structures, which contain a lower number of amphiphilic molecules. In certain cases, the presence of premicelles becomes important, because they have an appreciable influence on the properties and the stability of the system.

The aim of the present study is to follow and to understand how the surfactant adsorption layer properties are related to a variation of the drainage parameters of microscopic foam films in the special case of aqueous solutions containing premicellar amphiphilic nanostructures. The scope of the research covers the adsorption dynamics, construction of equilibrium adsorption isotherms, study of surface rheology of interfacial layers, and foam film drainage kinetics. The leading initial idea is that the onset of premicellar nanostructures is a universal phenomenon. Due to the close interrelation of the time and length scales of the adsorption and film drainage parameters, the combined adsorption layer and microscopic film drainage experiments turned out to be very convenient for the investigation of the impact of amphiphilic nanostructures on the adsorption and foam-film-drainage properties of surfactant systems.

2. Experimental Conditions and Instrumentation

The investigated systems are aqueous solutions of ionic and non-ionic surfactants with added electrolyte (NaCl, Sigma, 99.5% purity, titration; heated at 600°C for several hours). The amphiphiles are: sodium dodecyl sulfate (SDS, Henkel), hexadecyltrimethyl-ammonium chloride (CTACl, Fluka, 99.9% purity), tetraethylene glycol monododecyl ether and pentaethylene glycol monododecyl ether ($C_{12}E_4$, $C_{12}E_5$, Fluka, $\geq 98\%$ purity, gas chromatography). The solutions were prepared using triply distilled water. In the case of SDS, the temperature was 22 °C $\pm$ 0.1 °C, while it was 20 °C $\pm$ 0.1 °C in all the other cases.

The adsorption properties are measured by a Profile Analysis Tensiometer PAT-1 (SINTERFACE, Berlin). The option of an emergent bubble is applied (see, e.g., [18, 19]). Aside from measuring the surface tension against the time through a special dosing system, the setup allows the possibility to invoke periodic changes of the bubble's volume and the surface area. The respective time changes in the surface tension on the bubble interfacial area are monitored. From these data, the surface dilational elasticities and viscosities are extracted. The measurements were performed within a low-frequency interval of 0.005÷0.2 Hz.

The foam film properties are investigated through the microinterferometric instrumentation supplied with a Scheludko–Exerowa measuring cell. The setup is constructed and developed at the Institute of Physical Chemistry, Sofia, Bulgaria. Its principle is described in details elsewhere (see, e.g., [2, 13]).

3. Adsorption Layer Properties on the Air/Solution Interface

The dynamics of the adsorption process is presented on Fig. 1,a,b. The results show that the adsorption dynamics with ionic surfactants is quicker than that in the case of non-ionic surfactants. This is related to the structure of the amphiphile. In the case of an ionic surfactant, there is a long hydrophobic "tail" and a comparatively small hydrophilic "head", thus resulting in a higher surface activity and a quicker dynamics of adsorption.

The most interesting results concern the surface tension isotherms. Kink and plateau regions have been detected in all the cases reported here (Figs. 2–4).
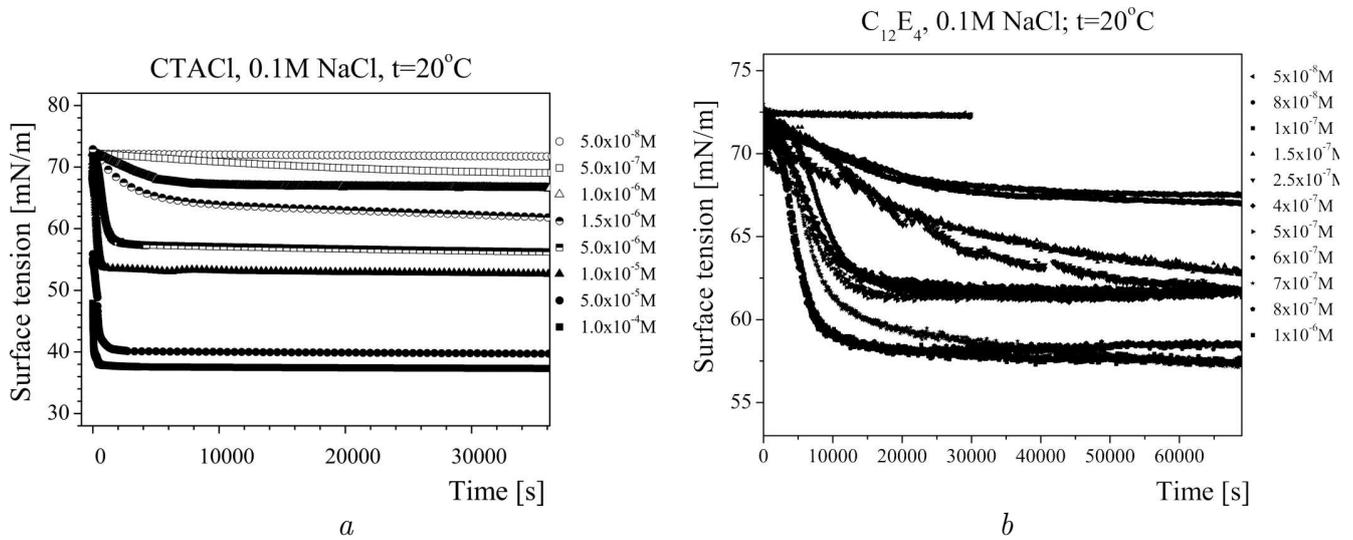
Fig. 1. Run of dynamic surface tension curves in the case of aqueous solutions from: (*a*) ionic surfactant – hexadecyltrimethyl-ammonium chloride, and (*b*) non-ionic surfactant – tetraethylene glycol monododecyl ether. The experiments are performed with PAT-1 at a temperature of 20 °C in the presence of 0.1 M NaCl
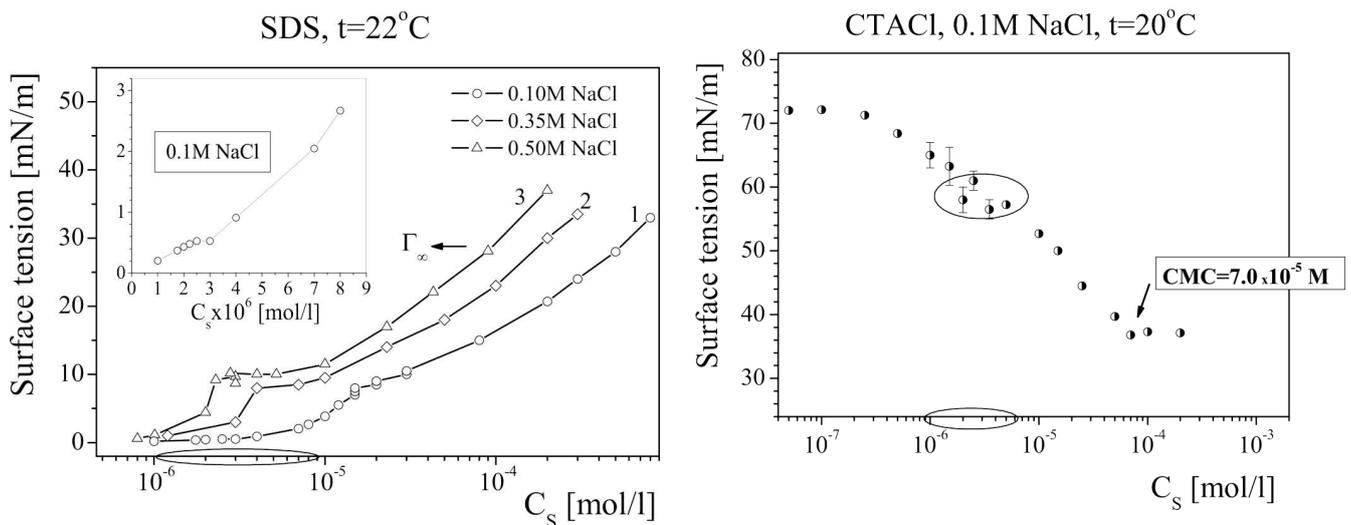

Fig. 2. Surface tension isotherm of aqueous solutions from sodium dodecyl sulphate. The data are taken from [2,3] and are obtained by the spherotensiometric method [20]

Fig. 3. Surface tension isotherm of aqueous solutions from hexadecyltrimethyl-ammonium chloride. The experiments are performed with PAT-1 at a temperature of 20 °C in the presence of 0.1 M NaCl

These peculiarities are characteristic of the intermediate concentration range. It also seems that their onset is strictly bound to the concentration range that spans over 1–2 orders of magnitude lower than the CMC-values. There are also some systematic differences related to the type and the structure of amphiphilic molecules. Thus, the plateau regions are more pronounced with non-ionic surfactants with a clear tendency of widening the low-

concentration plateau upon an increase of the number of ethylene glycol groups.

The surface dilational elasticities and surface dilational viscosities have also been extracted from experimental data via the surface tension changes when the equilibrium adsorption layer is disturbed with low frequency perturbations. The basic result refers to the surface dilational elasticities (Figs. 5 and 6). This quantity is a measure of the resistance against the creation of a
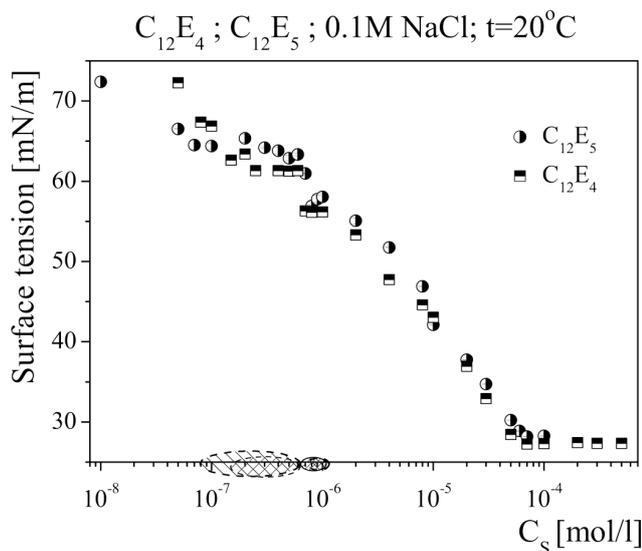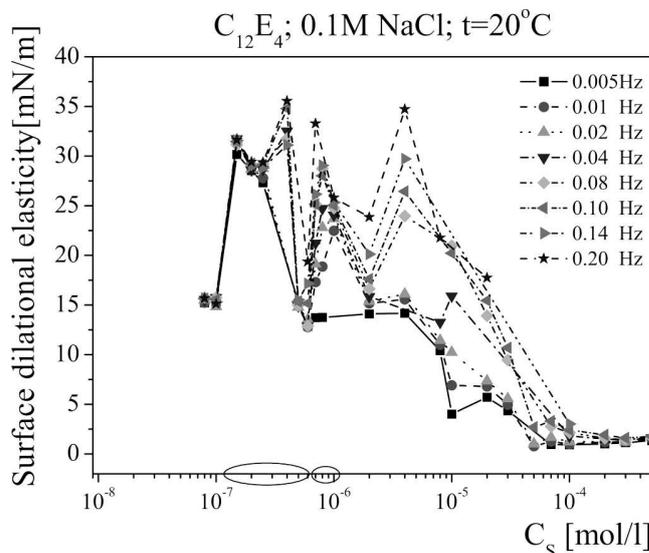
Fig. 4. Surface tension isotherm of aqueous solutions from tetraethylene glycol monododecyl ether and pentaethylene glycol monododecyl ether. The experiments are performed with PAT-1 at a temperature of 20 °C in the presence of 0.1 M NaCl

surface tension gradient on the interface and of the rate at which this gradient disappears, once the system is again left to itself and relaxes back to the equilibrium state. The experiments show that the surface dilational elasticities exhibit a sequence of maxima. These maxima span over the whole frequency range and are a characteristic feature of the premicellar concentration domain where the peculiarities in the adsorption isotherm are observed.

4. Foam Film Drainage Properties

The foam film drainage experiments produced two types of results: (i) qualitative observations – "unstable" black patterns are observed; (ii) quantitative results – specific drainage characteristics are extracted.

Generally, the observed black patterns in foam films can be classified into two types. The first type (black spots) is characteristic of a higher concentration ranges of amphiphile and are precursors of the classic black films (common black films (CBF) and Newton black films (NBF)) [2]. These patterns generally evolve into films that survive within longer time intervals (minutes, hours). They are well studied and have been related to the lifetimes and the stability of liquid films. The common feature of surfactant systems, where these precursors of black films are observed, is that the adsorption surfactant coverage on the liquid/air interface of the initial solutions is almost closely packed. These black pat-

a
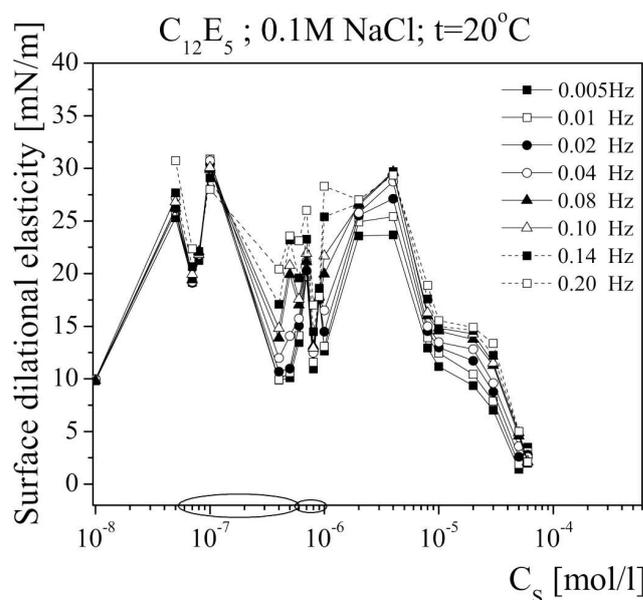
b

Fig. 5. Surface dilational elasticities of aqueous solutions from: (*a*) tetraethylene glycol monododecyl ether and (*b*) pentaethylene glycol monododecyl ether. The experiments are performed with PAT-1 at a temperature of 20 °C and in the presence of 0.1 M NaCl

terns, which expand and embrace the whole area of the background grey film, are observed at surfactant concentrations close to the CMC.

The "unstable" black formations (Fig. 7, *a,b*) belonging to the second type appear when there is some deficiency of the surfactant in the adsorption coverage on the interfaces for miscellaneous reasons [2, 9, 10, 12]. These
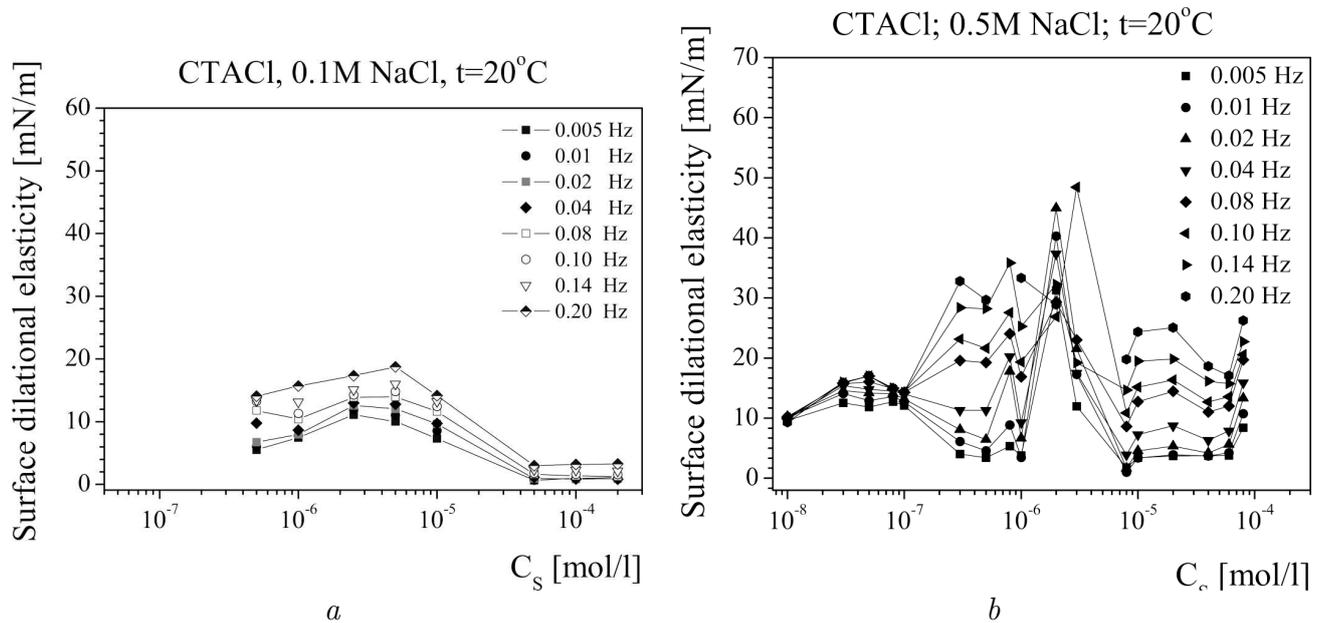
Fig. 6. Surface dilational elasticities of aqueous solutions from hexadecyltrimethyl-ammonium chloride. The experiments are performed with PAT-1 at a temperature of 20 °C and in the presence of electrolyte: (*a*) 0.1 M NaCl and (*b*) 0.5 M NaCl
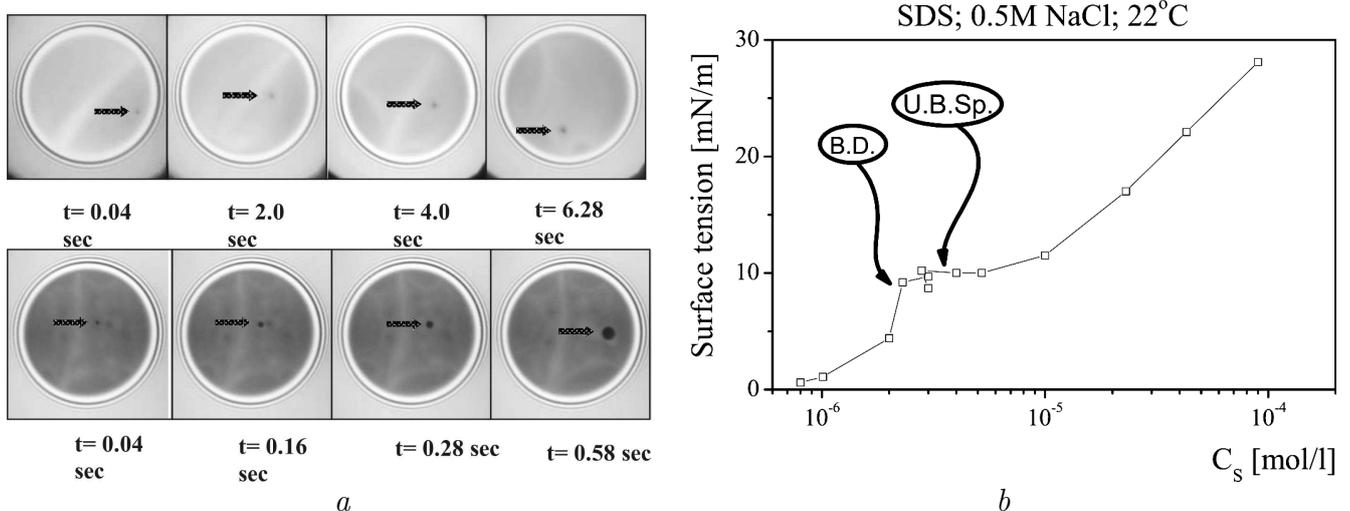

Fig. 7. "Unstable" black patterns: (*a*) sequential snapshots of black dots and black spots; (*b*) juxtaposition of their onset to the peculiarities of the surface tension isotherm. The experiments are performed with the foam film microinterferometric techniques of Scheludko–Exerowa

formations have lifetimes of several seconds. The respective foam films drain quickly and survive for a minute or two. The black dots appear at intermediate surfactant quantities and mark the concentration at which the first plateau portion in the adsorption isotherm begins. They live for $3 \div 10$ s and do not grow in size. These black patterns may be viewed as detectors of the presence of amphiphilic nanostructures in the initial aqueous surfactant solutions [11]. As for the "unstable" spots, they live for less than one second, quickly grow in size, but they never embrace the whole area of the background grey film. They are a characteristic feature of the concentration range, where the plateau portions of the surface tension isotherm are situated.

There is a clear concentration synchrony in the onset of unstable black patterns and the peculiarities of the
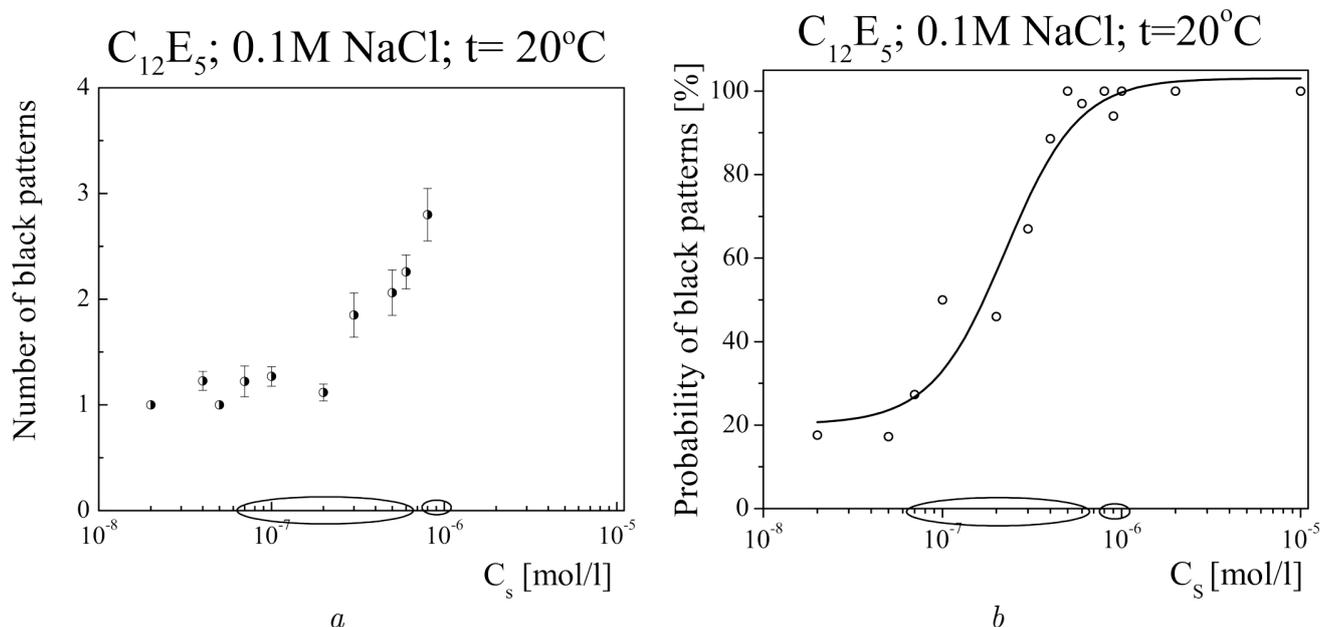
Fig. 8. Relationship between the surfactant concentration and (*a*) the number of unstable black patterns in microscopic foam films; (*b*) the probability of the onset of "unstable" black patterns in the case of aqueous solutions of pentaethylene glycol monododecyl ether. The experiments are performed with the foam film microinterferometric techniques of Scheludko–Exerowa

surface tension isotherms and the surface dilational elasticities of the adsorption layers. As the overall surfactant concentration increases, both the number and the probability of the onset of black patterns are increased (Fig. 8).

Insofar as the films originate from aqueous solutions at intermediate (premicellar) concentrations, the films drain and rupture without reaching the equilibrium thickness. The time evolution of the film thickness runs in a rather interesting manner. The curves for different concentrations are grouped together in such a way that a "broom" is formed. At large thicknesses, when the disjoining pressure in the films is still not operative, the curves run in a bunch together. At lower thicknesses, when a notable effect of the disjoining pressure is expected, the "broom" separates into distinct bunches which stretch out. These bunches indicate the onset of concentrations where the peculiarities of the adsorption properties are observed (Fig. 9,*a*–*d*).

In all cases, the drainage time of films rises sharply within the concentration domain where the irregularities of the adsorption properties are observed (Fig. 10,*a*,*b*).

5. Discussion

The general outcome of the experiments is the observed concentration coincidence of the course of the film drainage characteristics and the irregularities of the adsorption layer properties.

These results are conceivable if one takes into account the following:

1. The initial surfactant solutions from the intermediate concentration range have amphiphilic nanostructures – premicelles. These are symmetric loose aggregates which contain less surfactant molecules than the regular micelles above CMC and can be visualized by the so-called Plateau bodies. Depending on the structure of amphiphilic molecules, one or more of these symmetric configurations can prevail at a given concentration value.

The onset of premicellar nanostructures is related to the appearance of kink and plateau portions in the surface tension isotherms. During the rheological experiments with PAT-1, the surface area of an emerging bubble is periodically increased and compressed. This results in the onset of surface tension gradients that depend on the surfactant concentration in the system. The dilational surface elasticity is a measure of the scale of these surface tension changes. Generally, the curve of dilational elasticity against the amphiphile concentration at a fixed frequency passes through a maximum and falls down toward CMC. The existing micelles can also disintegrate and participate in the mass transfer of the surfactant molecules.
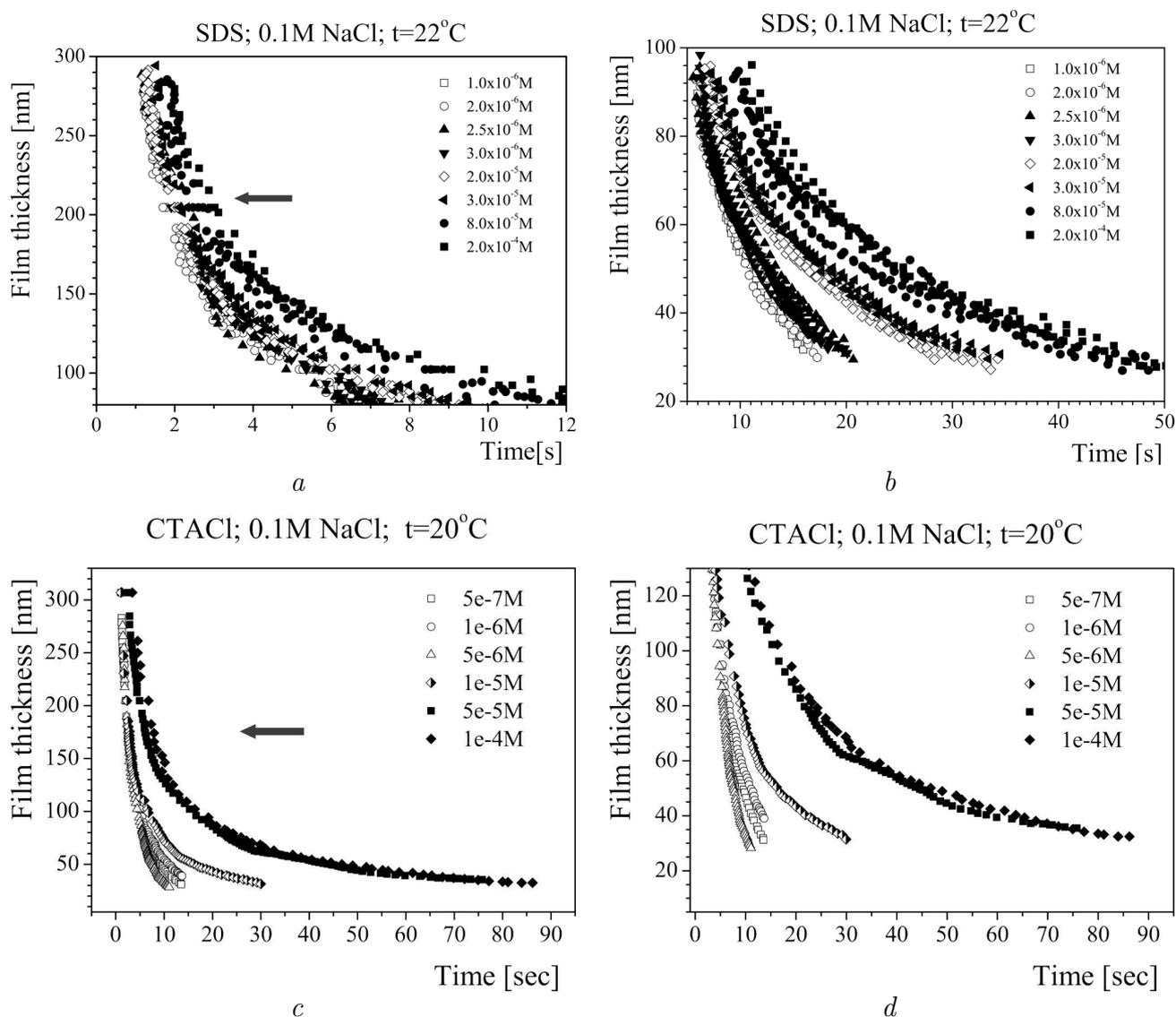
Fig. 9. Mean thickness evolution of the microscopic foam film thickness with time – formation of a characteristic "broom". (*a*) aqueous solution of sodium dodecyl sulphate, the temperature is 22 °C. (*b*) aqueous solution of hexadecyltrimethyl-ammonium chloride, the temperature is 22 °C. The experiments are performed in the presence of 0.1 M NaCl

However, the amphiphilic concentration in the reported experiments is lower than CMC. So, several sequential minima and maxima are registered in the curves presenting the relationship of the surface dilational elasticity and the surfactant concentration (see Fig. 6). This observation is a clear sign that amphiphilic premicellar aggregates exist in the solutions in the intermediate concentration domain. If there is a perturbation of the equilibrium conditions, as is the case in rheological measurements, these nanostructures act as an additional source of amphiphilic molecules. If only one premicellar

configuration is predominant at a given solution concentration, there will be one minimum in the surface dilational elasticities against the concentration. It appears because, during the expansion of the surface area of the bubble, the underlying premicelles are destroyed and release an additional amount of surfactant molecules that quickly compensate the emerging surface tension gradients on the interface. The result is a decrease of surface dilational elasticities. This effect is analogous to a decrease of the dilational elasticities of the interface of solutions above CMC. However, within the intermedi-
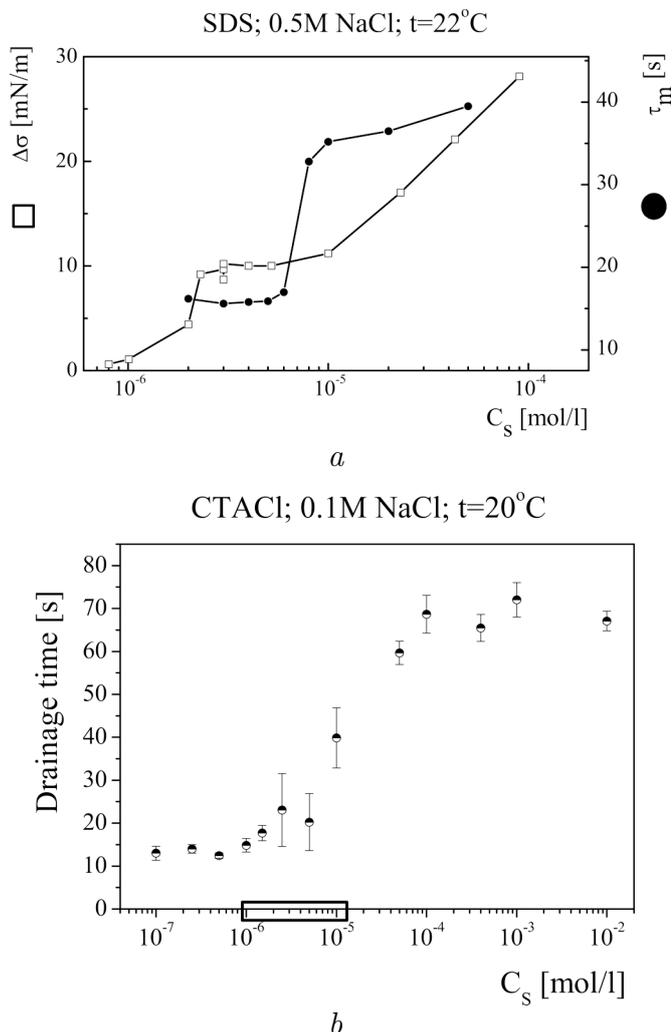
Fig. 10. Mean drainage time of foam films versus the surfactant concentration. (*a*) aqueous solution of sodium dodecyl sulphate, the temperature is 22 °C with 0.5 M NaCl. (*b*) aqueous solution of hexadecyltrimethyl-ammonium chloride, the temperature is 22 °C, in the presence of 0.1 M NaCl

ate concentration domain, there is still not enough surfactant molecules for the formation of a closely packed adsorption layer. Upon the further raise of the concentration, these minima are again followed by an increase of the dilational elasticities.

This hypothesis is also substantiated by the run of the respective curves for the ionic amphiphile (CTACl in Fig. 6,*a,b*). If the concentration of the electrolyte is increased, the elasticity curve changes from the usual one-maximum case to the onset of sequential maxima and minima. The reason is the effective shift of the HLB of a molecule due to 'reducing' the hydrophilic "head"

of the surfactant because of the shrinkage of the Debye atmosphere.

2. The foam films drain in a regime of high interfacial mobility. So, the specific film hydrodynamics is coupled with the mass transfer of a stabilizing surfactant via the Marangoni effect [21, 22]. The observed "unstable" black patterns are a clear sign of the thickness inhomogeneities. The latter create an extra option for the onset of local differences in the general coupling mechanism of the film hydrodynamics and the surfactant mass transfer [9, 12].

In the thinner portions of the film, the black pattern regions, the local flow is retarded. The mechanism of this retardation is related to the specific manifestation of the Marangoni effect in the confined domain of the film. The flow sweeps surfactant molecules outside the black pattern region toward the thicker portions of the film. Due to the uneven distribution of these molecules at the interfaces, a local surface tension gradient emerges. This causes the onset of additional tangential forces which act in a direction opposite to the fluid outflow. Diffusion fluxes are directed toward the places of deficiency of amphiphilic molecules. The normal flux from the black pattern bulk results in a constant depletion of amphiphilic molecules. In addition, all existing amphiphilic nanostructures in the thinner places are already destroyed. So, a concentration difference emerges between the pattern bulk and neighbouring thicker portions of the film. A bulk diffusion flux is directed toward the black pattern region. This flux covers, however, a longer path until reaching the interfacial portions depleted of surfactant molecules. If there would not be the enough number of them, the pattern interfaces should very quickly become bare of amphiphiles, and the film would most probably rupture in these thinner places. But, in the neighboring thicker regions, there are still premicelles. These regions drain further on, and these premicelles are destroyed. Thus, they provide an additional amount of monomers, which can participate in the feed up of the black pattern interfaces. This gives a certain additional time to the emerged tangential force, opposite to the outflow, to be maintained for a while and to the interfacial outflow to be retarded. This results in a retardation of the drainage process within the black pattern region. An increase of the overall surfactant concentration results in the onset of more and more of these unstable black patterns. The larger their number, the sharper is the rise-up of the overall drainage time of the films.

This slow-down mechanism couples the presence of amphiphilic self-assemblies with the specific film hydro-

dynamics and the mass transfer of amphiphilic molecules in the drainage of microscopic foam films. Thus, this allows a unified explanation of the results from both tensiometric measurements and foam film drainage experiments.

6. Concluding Remarks

The results presented might be summarized as follows:
– surface tension isotherms have kink and plateau portions in the intermediate (premicellar) concentration domain;
– surface dilational elasticities go through a sequence of maxima and minima in the premicellar concentration domain, the same where the peculiarities of the surface tension isotherms are observed;
– the same premicellar domain is also marked by the onset of "unstable" black patterns – dots and spots – in the draining films;
– the film thickness evolution curves and the drainage times run in a concentration synchrony with the irregularities of the interfacial layer properties;
– the presence of premicelles stabilized the draining films.

We may conclude that
– the concerted results present the experimental evidence for the amphiphilic self-assembly in the premicellar concentration domain;
– this trend of research gives clues for the better comprehension of the interrelation between the amphiphilic self-assembly, interfacial rheology, and stability of foam films.

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ВПЛИВ АМФІФІЛЬНИХ НАНОСТРУКТУР
НА УТВОРЕННЯ ТА РЕОЛОГІЮ ШАРІВ
ПОВЕРХНІ ПОДІЛУ І СТІК ПЛІВКИ ПІНИ

Д. Арабаджиєва, П. Чуков, Е. Мілєва, Р. Міллер, Б. Соклєв

Р е з ю м е

Досліджено вплив властивостей поглинаючого шару ПАВ на зміну параметрів стоку плівок мікроскопічної піни у спеціальному випадку водних розчинів, що мають преміцелярні амфіфільні наноструктури. Вивчено динаміку поглинання, вигляд ізотерм рівноважного поглинання, поверхневу реологію

шарів поверхні поділу і кінетику стоку плівки піни. Встановлено, що у преміцелярній області є інтервали концентрації, де спостерігається значна нерегулярність властивостей поглинаючого шару: декілька плато на ізотермах поверхневого натягу, незвичні зміни поверхневих реологічних характеристик і т. ін. Дослідження стоку плівок піни показало, що залежність основних кінетичних параметрів плівок синхрон-

на змінам властивостей поглинаючого шару. Присутність невеликих рихлих агрегатів (преміцел) відіграє суттєву роль в кінетичній стабільності плівок. Дана робота покращує розуміння початкових стадій явищ самоорганізації і факторів, що визначають стік і стабільність тонких рідких плівок. Отримані результати дозволяють коректно передбачити властивості систем піни.