Kinetics of micellization: its significance to technological processes[☆]

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Abstract

The association of many classes of surface active molecules into micellar aggregates is a well-known phenomenon. Micelles are often drawn as static structures of spherical aggregates of oriented molecules. However, micelles are in dynamic equilibrium with surfactant monomers in the bulk solution constantly being exchanged with the surfactant molecules in the micelles. Additionally, the micelles themselves are continuously disintegrating and reforming. The first process is a fast relaxation process typically referred to as τ_1. The latter is a slow relaxation process with relaxation time τ_2. Thus, τ_2 represents the entire process of the formation or disintegration of a micelle. The slow relaxation time is directly correlated with the average life-time of a micelle, and hence the molecular packing in the micelle, which in turn relates to the stability of a micelle. It was shown earlier by Shah and coworkers that the stability of sodium dodecyl sulfate (SDS) micelles plays an important role in various technological processes involving an increase in interfacial area, such as foaming, wetting, emulsification, solubilization and detergency. The slow relaxation time of SDS micelles, as measured by pressure-jump and temperature-jump techniques was in the range of 10^{-4}–10^1 s depending on the surfactant concentration. A maximum relaxation time and thus a maximum micellar stability was found at 200 mM SDS, corresponding to the least foaming, largest bubble size, longest wetting time of textile, largest emulsion droplet size and the most rapid solubilization of oil. These results are explained in terms of the flux of surfactant monomers from the bulk to the interface, which determines the dynamic surface tension. The more stable micelles lead to less monomer flux and hence to a higher dynamic surface tension. As the SDS concentration increases, the micelles become more rigid and stable as a result of the decrease in intermicellar distance. The smaller the intermicellar distance, the larger the Coulombic repulsive forces between the micelles leading to enhanced stability of micelles (presumably by increased counterion binding to the micelles). The Center for Surface Science & Engineering at the University of Florida has developed methods using stopped-flow and pressure-jump with optical detection to determine the slow relaxation time of micelles of nonionic surfactants. The results show relaxation times τ_2 in the range of seconds for Triton X-100 to minutes for polyoxyethylene alkyl ethers. The slow relaxation times are much longer for nonionic surfactants than for ionic surfactants, because of the absence of ionic repulsion between the head groups. The observed relaxation time τ_2 was related to dynamic surface tension and foaming

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experiments. A slow break-up of micelles, (i.e. a long relaxation time τ_2) corresponds to a high dynamic surface tension and low foamability, whereas a fast break-up of micelles, leads to a lower dynamic surface tension and higher foamability. In conclusion, micellar stability and thus the micellar break-up time is a key factor in controlling technological processes involving a rapid increase in interfacial area, such as foaming, wetting, emulsification and oil solubilization. First, the available monomers adsorb onto the freshly created interface. Then, additional monomers must be provided by the break-up of micelles. Especially when the free monomer concentration is low, as indicated by a low CMC, the micellar break-up time is a rate limiting step in the supply of monomers, which is the case for many nonionic surfactant solutions. Therefore, relaxation time data of surfactant solutions enables us to predict the performance of a given surfactant solution. Moreover, the results suggest that one can design appropriate micelles with specific stability or τ_2 by controlling the surfactant structure, concentration and physico-chemical conditions, as well as by mixing anionic/cationic or ionic/nonionic surfactants for a desired technological application. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Micelles; Molecules; Dynamic surface tension

1. Introduction

Almost from the very beginning of the study of surfactant solutions, it was recognized that the physical properties of surfactant solutions, such as surface tension, detergency, osmotic pressure, electrical conductivity, etc., show an abrupt change in the neighborhood of the critical micelle concentration (CMC) [1]. Surfactant molecules reside in three environments in a surfactant solution above the CMC. Surfactant molecules disperse as monomers in the aqueous phase, form aggregates (micelles), or adsorb as a film at the air/water interface. The surfactant is in dynamic equilibrium among all these compartments. Thus, at a given temperature, pressure and concentration, the number of monomers, micelles and monomers adsorbed at the air/water interface is fixed under equilibrium conditions.

Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecules that are constantly being exchanged between the bulk and the micelles. Additionally, the micelles themselves are continuously disintegrating and reforming. The kinetics of micellization have been studied by various techniques such as stopped-flow, temperature-jump, pressure-jump and ultrasonic absorption [2–6]. There are two relaxation processes involved in micellar solutions. The first one is the fast relaxation process with relaxation time τ_1 (generally of the order of microseconds), which is associated with the fast exchange of monomers between micelles and the surrounding bulk phase. This process is considered as the collision between surfactant monomers and micelles. The second relaxation time τ_2 (usually of the order of milliseconds to minutes) is attributed to the micelle formation and dissolution process. Fig. 1 shows the two characteristic relaxation times, τ_1 and τ_2, associated with micellar solutions. Micellar relaxation kinetics show dependence on temperature, pressure and concentration. The micelle formation and disintegration processes can be explained as follows. For a closed system containing water and water vapor in equilibrium, one can assume that the number of water molecules per unit area per second evaporating from the surface is the same as the number of water molecules condensing at the surface. Thus, the total number of molecules in the vapor phase or in the liquid does not change with time. So, the rate of condensation is equal to the rate of evaporation. The same principle holds for a micel-
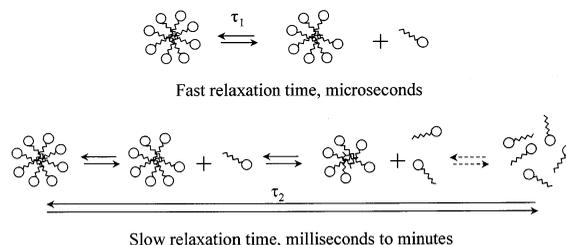

Fig. 1. Mechanisms for the two relaxation times, τ_1 and τ_2, for a surfactant solution above CMC.
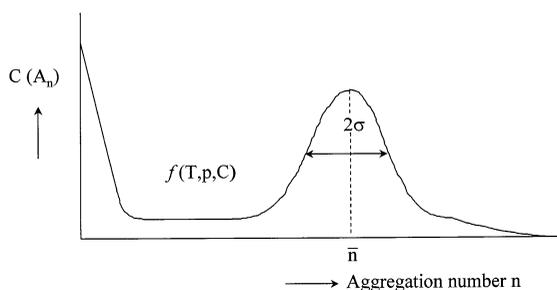
Fig. 2. Typical size distribution curve of aggregates in a micellar solution.

lar solution. At equilibrium the number of micelles formed in a given time is equal to the number of micelles disintegrated in the same time period. In this study more than one experimental technique was used to confirm that indeed both processes (i.e. micelle formation and disintegration) occur at the same rate.

The Center for Surface Science & Engineering at the University of Florida has performed extensive studies on micellar relaxation kinetics in relation to technological processes for the last 18 years [7]. In this paper the importance of the relaxation kinetics of ionic and very recently also nonionic surfactants will be discussed and related to technological processes, such as foaming, emulsification, wetting, solubilization and detergency. Furthermore, the importance of the foaming method on the foamability of surfactant solutions is discussed and related to micellar stability and dynamic surface tension measurements.

2. Historical perspective on micellar kinetics

The study of the kinetics of micellization reached its peak in the decade of the 1970's. However, as early as 1965, Mijnlieff and Ditmarsch [8] reported pressure-jump studies on sodium dodecyl sulfate and sodium tetradecyl sulfate. From that point on all attention was focused on the theoretical implementation of the step wise formation and disintegration of micelles. The primary breakthrough was the discovery of the existence of two (fast and slow) relaxation processes [9] and the development of a model for the kinetic

process of micelle formation and disintegration by Aniansson and coworkers [10–12]. This model was supplemented by Lessner et al. [13] and Hall [14]. The free surfactant monomers are assumed to be completely dissociated and the size distribution of the aggregates in a surfactant solution is assumed to have the shape schematically shown in Fig. 2, where $C(A_n)$ denotes the total concentration of aggregates containing n monomers. The size distribution curve is a function of temperature (T), pressure (p) and concentration (C). Aniansson considers the association and dissociation of micelles as a stepwise process involving the entry and departure of one monomer at a time from the micelle. Thus, there is a series of equilibria,

$$A_1 + A_{n-1} \underset{k_n^-}{\overset{k_n^+}{\rightleftarrows}} A_n \qquad n = 2, 3, 4, \dots , \qquad (1)$$
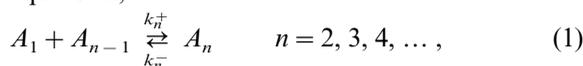
where A_n denotes an aggregate containing n monomers, and k_n^+ and k_n^- are the forward and reverse rate constants for a given step. Assuming the aggregation number n to be a continuous variable and applying a treatment analogous to heat conduction, Aniansson and coworkers found the following expression for the fast relaxation process τ_1,

$$\frac{1}{\tau_1} = \frac{k^-}{\sigma^2}\left(1 + \frac{\sigma^2}{n} a\right), \qquad \text{with} \quad a = \frac{C - \text{CMC}}{\text{CMC}} \qquad (2)$$

where σ is the half-width of the distribution curve of micellar sizes (assumed to be Gaussian, Fig. 2), k^- is the stepwise dissociation rate constant, which is assumed to be independent of n in the micellar region, C the total surfactant concentration and CMC the critical micelle concentration. Eq. (2) predicts a linear relationship between $1/\tau_1$ and the total surfactant concentration, in agreement with experiments [12]. It is obvious that as the total surfactant concentration increases, the number of micelles increases, resulting in a decrease in intermicellar distance. Hence, the time required for a monomer to collide with a micelle is shorter at higher surfactant concentration. The magnitude of τ_1 depends on the length of the hydrocarbon tail of the surfactant: the shorter the chain length, the faster is the relaxation time, since micelles are more loosely packed structures for shorter chain surfactants.

The expression for the slow relaxation time τ_2 can be simplified to,

$$\frac{1}{\tau^2} = \frac{n^2}{CMC*R}\left(1 + \frac{\sigma^2}{n}a\right)^{-1} \qquad (3)$$

where R is a term which may be visualized as the resistance to flow through the critical region (i.e. the narrow passage in Fig. 2 going from monomers to micelles) and is given by,

$$R = \sum_{n=n_1+1}^{n^2} \frac{1}{k_n^- A_n} \qquad (4)$$

where n is the aggregation number of some particle aggregate and A_n is the equilibrium concentration of aggregates of order n. The dependence of $1/\tau_2$ upon ionic strength, concentration and temperature has been interpreted in terms of their effect upon R. Interestingly, the two relaxation times can be used to calculate two important parameters of a micellar solution; (1) the residence time of a surfactant molecule in a micelle; and (2) the average lifetime or stability of micelles [15–18]. The residence time of a surfactant monomer in micelles is equal to n/k^-, where n is the mean aggregation number ($\bar{n}$ in Fig. 2) and k^- the dissociation rate constant of a monomer from a micelle. The average micellar lifetime T_m is given by,

$$T_m = \tau_2 \frac{na}{1 + \frac{\sigma^2}{n}a} \approx n\tau_2 \qquad (5)$$

When the concentration of surfactant is much greater than the CMC, the micellar lifetime is approximately equal to $n\tau_2$. Although derived for nonionic surfactants, the results by Aniansson and coworkers were used for ionic systems as well. The agreement between theory and experiment was, in general, satisfactory. Eq. (3) predicts that τ_2 should increase with concentration of a surfactant. However, it has been reported that for some ionic surfactant systems τ_2 first increases, then passes through a maximum and then decreases again [9,13,19]. Kahlweit concluded that in ionic systems at high concentration, the reaction path for the formation of micelles must be different than at low concentration. Therefore, the following model was proposed explaining the oc-

currence of a maximum in τ_2. Ionic micelles, including submicellar aggregates, can be considered as charged particles. At low counterion concentration, these particles are stable with respect to coagulation as a result of the repulsive electrostatic forces. Consequently they can grow by stepwise incorporation of monomers, according to

$$N_{i-1} + N_1 \rightleftarrows N_i \qquad (6)$$

where i is the aggregation number. With increasing counterion concentration, however, the electric double layer around each particle becomes increasingly compressed, so that the attractive dispersion forces (van der Waals forces) lead to a reversible coagulation, according to

$$N_k + N_l \rightleftarrows N_i \quad k + l = i \qquad (7)$$
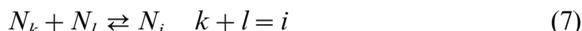
where k and l are classes of submicellar aggregates.

Kahlweit and coworkers [20] then represented the reaction path of the formation of micelles by two parallel resistors R_1 and R_2. At low counterion concentration, R_2 is very high as a result of electrostatic repulsion between submicellar aggregates. Therefore R_1 determines the rate of micelle formation, according to Eq. (6). By increasing the counterion concentration, R_1 becomes very high so that R_2 determines the rate of micelle formation and the reaction follows Eq. (7). The model also predicts a shift of the maximum τ_2 to lower surfactant concentrations, by the addition of electrolyte. For nonionic systems both reaction paths compete right from the CMC on. Kahlweit then compared the results with predictions of the DLVO theory, which were in good agreement with the experiments. Although many other kinetic treatments have been proposed, that of Aniansson and coworkers is possibly the most comprehensive.

3. The importance of micellar relaxation time on technological processes

The importance of micelle break-up on processes involving an increase in interfacial area was first reported by Mijnlieff et al. [8]. For several

years, researchers at the Center for Surface Science and Engineering tried to correlate the relaxation time, τ_2, with equilibrium properties, such as surface tension and surface viscosity, but no correlation was found. However, a strong correlation of τ_2 with various dynamic processes such as foamability, wetting time of textile, bubble volume, emulsion droplet size and solubilization rate of benzene in micellar solutions was found [7]. For example, Fig. 3 shows schematically the importance of micelle break-up in foaming processes. When air is blown through a surfactant solution, a substantial amount of new interfacial area is created. The increased interfacial area has to be stabilized by an adsorbed film of surfactant molecules. These molecules come from the bulk solution, which contains monomers and micelles. As monomers diffuse to the newly created surface, micelles have to break-up in order to provide additional monomers to the surface. Very stable micelles will not be able to augment the flux necessary to stabilize the newly created interface and therefore foamability will be less. The micelle break-up process is also important in fabric wetting. When the fabric is placed on a surfactant solution, the solution begins to penetrate the inter-fiber spaces of the fabric. The monomers deposit on the hydrophobic sites of the surface as well as decrease the interfacial tension between the water and fabric. More stable micelles will cause less monomer flux, which will slow down the wetting process and hence a longer wetting time is obtained. Micelle break-up in emulsification
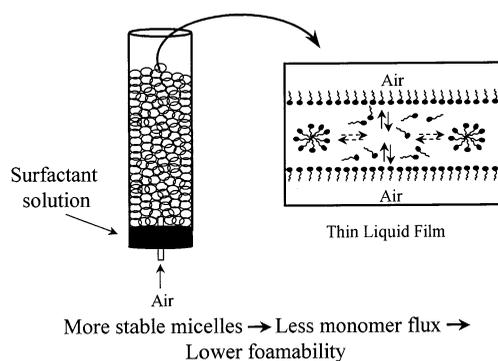

Fig. 3. Schematic representation of adsorption of surfactant on the newly created air/water interface as a result of disintegration of micelles during foam generation.

processes. When mechanical energy is applied to increase the interfacial area between oil and water to produce oil droplets, the newly created interface must be stabilized by the adsorption of monomers from the aqueous phase. More stable micelles cause less monomer flux, which leads to a higher interfacial tension at the oil/water interface. The relation between the surface tension or interfacial tension and the amount of interfacial area created in foams or emulsions can be given by [21],

$$W = \gamma \cdot \Delta A \qquad (8)$$

where W is the work performed, γ the surface or interfacial tension at the air/water or oil/water interface and ΔA the change in interfacial area. Obviously, when the same amount of work is performed, a lower surface tension results in more interfacial area (either by decreasing the bubble size or by increasing foam volume). Thus, one would expect a larger emulsion droplet size when micelles are very stable.

The micellar stability of sodium dodecyl sulfate (SDS) solutions was determined earlier by Lessner et al. [22] and later by Oh and Shah [23] using pressure-jump with electrical conductivity detection. This technique takes advantage of the fact that the CMC shifts to higher concentration when a surfactant solution is pressurized [15]. Hence, in case of ionic surfactants, the electrical conductivity increases with pressure. When the pressure is instantaneously released to atmospheric, monomers will reassociate to form new micelles, which can be followed as an exponential decay in the electrical conductivity with time [24]. The slow micellar relaxation constant, τ_2, can be calculated from the first order reaction constant, k ($\tau_2 = 1/k$). The pressure-jump technique with electrical conductivity detection is a very sensitive and powerful tool that also allows for the measurement of τ_2 of mixed micelles or micellar solutions in the presence of additives (see Section 7).

Fig. 4 shows the micellar relaxation time τ_2 as function of SDS concentration. A maximum micellar stability was found at 200 mM (5 s). Fig. 5 presents the various phenomena exhibiting minima and maxima at the liquid/gas interface. At 200 mM SDS, minimum foamability, maximum
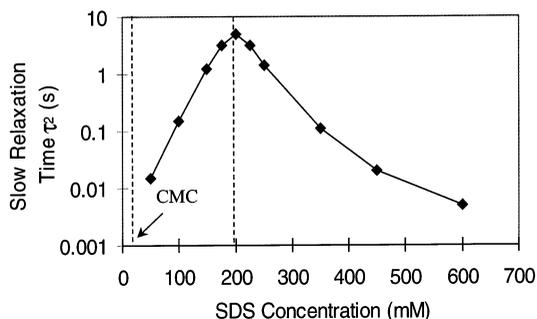
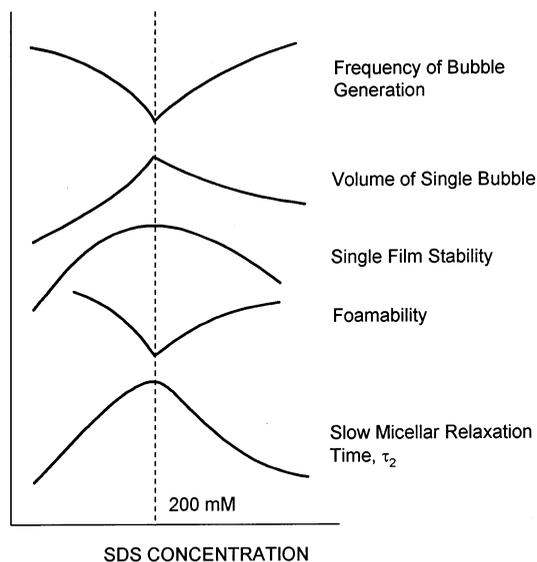Fig. 4. The slow relaxation time, τ_2, of SDS micelles at various surfactant.

Fig. 5. Liquid/gas phenomena exhibiting minima and maxima at 200 mM SDS concentration.

single film stability, maximum single bubble volume and a minimum frequency of bubble generation were found. These phenomena were explained based upon the monomer flux to newly created interface. If the micelles in solution are very stable, they cannot provide monomer fast enough to the interface and thus the interfacial tension remains higher. Therefore, lower foamability, larger single bubble foam volumes and a minimum frequency of bubble generation were found [25,26]. Very unstable micelles, however, provide monomers fast enough to the surface resulting in lower interfacial tensions. A maxi-

mum single film stability was found at 200 mM, i.e. when the micelles are most stable [27]. An important point has to be made here. The single film stability measurements are not a dynamic condition, but a pseudo-equilibrium condition. Therefore, the slow relaxation time of micelles (τ_2) cannot explain the film stability data by itself. An important factor influencing single film stability is the in-layer micellar distribution in the thin film, which has been investigated by Wasan and coworkers [28,29]. The stratification of thin liquid films can be explained as a layer by layer thinning of ordered structures of micelles inside the film. This structured phenomenon is affected by micellar effective volume fraction, micellar stability, micellar interaction and polydispersity. Thus, the micellar stability affects the in-layer micellar packing, which in turn influences film stability. This hypothesis unifies the research carried out by Shah's [27] and Wasan's research groups [28,29].

Interfacial phenomena occurring at the liquid/liquid and solid/liquid interface in SDS solutions are shown in Fig. 6. The wetting time and droplet size in emulsions exhibit maxima at 200 mM. The wetting time is the time during which the fabric floats on a surfactant solution before it actually
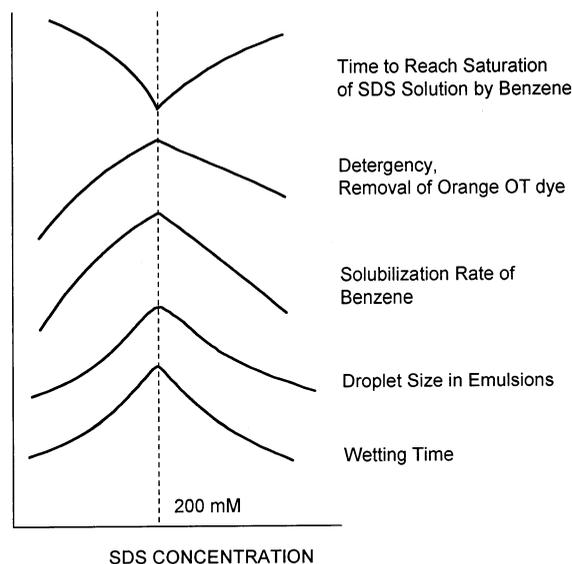

Fig. 6. Liquid/liquid and solid/liquid phenomena exhibiting minima and maxima at 200 mM SDS concentration.

sinks into the solution. During this time, water penetrates into the fabric structure to replace the air until the gravitational force exceeds the buoyancy of the entrapped air. When micelles are very stable, the flux of monomers decreases and hence the wetting process slows down. Different types of fabrics, such as polyesters, Dacron, Nylon, cotton and silk were investigated. The maximum wetting time of the investigated fabrics occurs at 200 mM SDS concentration. Although the absolute magnitude of the wetting time depends on the fabric, the maximum occurring at 200 mM is a property of the SDS solution and not of the fabric. The liquid/liquid and solid/liquid phenomena can also be explained based upon the monomer flux necessary to stabilize newly created interface. Very stable micelles result in high dynamic surface tensions and hence larger droplet sizes and longer wetting times are obtained [30,31]. The solubilization rate of benzene in SDS solutions as well as the detergency or removal of orange OT dye from fabric surface, show maxima at 200 mM concentration. The time required to reach saturation of the SDS solution upon the addition of benzene is minimum at 200 mM SDS concentration. This suggests that very stable micelles (i.e. tightly packed micelles) are more effective in the solubilization of oil [23]. This can be explained based upon the interior of the micelles. The interior of rigid (i.e. tightly packed) micelles is more hydrophobic as compared to that of loosely packed micelles and hence the stronger hydrophobic core causes more rapid partitioning or solubilization of benzene and Orange OT into the micelles at 200 mM SDS concentration.

In conclusion, the maximum stability of SDS micelles at 200 mM concentration manifests itself in various processes involving an increase in interfacial area such as foaming, bubble generation, rate of solubilization, detergency, wetting and emulsification.

4. Intermicellar coulombic repulsion model (ICRM)

The maximum micellar stability resulting in the most rapid solubilization and detergency at 200 mM SDS, can be explained by the following proposed intermicellar coulombic repulsion model (ICRM). Knowing the aggregation number of the SDS micelles and the total SDS concentration, one can calculate the number of micelles at a specific SDS concentration in the solution. By dividing the solution into identical cubes, which are equal to the number of micelles, one can equate the distance between the centers of the adjacent cubes as the average intermicellar distance. By this approach, the intermicellar distance was found to be 130, 100, and 78.6 Å, respectively, at 50, 100 and 200 mM SDS concentration. This suggests that the adjacent micelles are one diameter apart at 200 mM concentration. The small gap of about 40 Å between the surfaces of adjacent micelles causes Coulombic repulsion and hence induces a rapid uptake of counterions to minimize the charge repulsion between adjacent micelles. This provides considerable stability to the micellar structure, resulting in a long relaxation time. Above 200 mM SDS concentration, a structural transition from spherical to cylindrical SDS micelles occurs to accommodate more surfactant molecules into the solution. Reis-Husson and Luzzatti [32] found this structural change of SDS micelles from spherical to cylindrical shape by X-ray scattering at 250 mM and 27°C. The present studies were carried out at 22°C, which probably shifts the concentration to 200 mM. Ekwall [33] showed this transition for sodium caprylate, which occurs over a wide concentration range. A similar phenomenon is proposed here, where the transition from spherical to cylindrical SDS micelles is gradual from 200 to 600 mM. Because the number of spherical micelles is less as compared to that at 200 mM concentration, as some of them have become cylindrical micelles, the intermicellar distance (between the spherical and cylindrical micelles or spherical and spherical micelles) increases, resulting in shorter relaxation times. In a binary mixture, it is the most labile structure (i.e. spherical micelles) which responds quickly to the pressure-change as compared to cylindrical micelles [24], because cylindrical micelles are believed to have a very long lifetime. The intermicellar distances obtained from the procedure at various SDS concentrations are shown
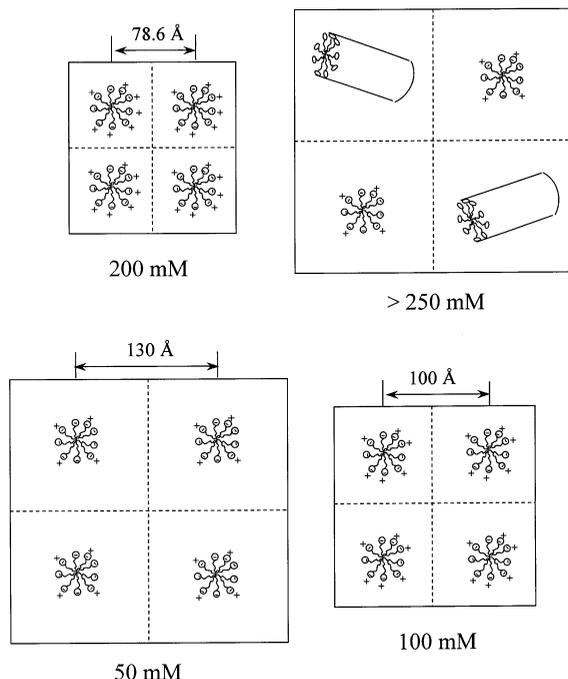
Fig. 7. Schematic diagrams showing micellar at 50, 100, 250 and 250 mM SDS concentrations.

in Fig. 7. This model also explains the shift of the maximum micellar stability to lower concentrations SDS, by the addition of salt or cosurfactants [22].

In summary, SDS solutions exhibit maxima and minima for various properties at 200 mM concentration as a result of maximum stability of SDS micelles at this concentration. Most ionic surfactants may exhibit such a characteristic concentration at which the micellar stability will be maximum as a result of an increase in Coulombic repulsion and reduction in intermicellar distance.

5. Relaxation kinetics of nonionic micelles

In the previous section, the micellar relaxation time measured for SDS solutions was determined by the pressure-jump technique with electrical conductivity detection. For nonionic surfactants, however, the electrical conductivity is not a sensitive parameter. Therefore, the use of a dye is necessary to obtain information about the micel-

lar kinetics of nonionic surfactants. A number of dyes or fluorescent compounds, such as Merocyanine, Eosin, Rhodamine and Sudan show an appreciable change of extinction coefficient depending on whether the dye resides in, or outside the micelle in aqueous phase. This effect is often used to determine the CMC [34,35], but it also provides a way of following the relaxation kinetics upon a fast temperature, pressure or concentration jump by employing spectrophotometric detection methods. Eosin Y in water shows a maximum absorbance (λ_{max}) at 518 nm. However, increasing the surfactant concentration causes the dye to partition between the water and the micelles, causing the maximum absorbance to shift to approximately 530 nm. The maximum shift in absorbance occurs at 542 nm. This shift is caused by a change in the microenvironment of the dye. Fig. 8 shows the shift in absorbance for a Triton X-100 surfactant solution.

The concept of change in absorbance as a result of the presence of micelles can be used in the determination of the slow relaxation constant, τ_2, for nonionic surfactants using the stopped-flow dilution technique. Stopped-flow is a method designed to measure the kinetics of fast reactions [36]. The apparatus employs two separate syringes which can be filled with reactants, which are pushed instantaneously into a transparent cell. The change in absorbance can be detected with a very sensitive photo multiplier detector as the reaction progresses. When one solution containing micelles and dye is instantaneously diluted with another solution containing water and dye of the same dye concentration, the absorbance of dye in micelles will decrease as micelles break-up, indicating the relaxation time of micelles. The exponential decay can be fitted to a first order reaction, resulting in the associated time constant τ_2. Table 1 shows the slow relaxation times τ_2 measured for a variety of nonionic surfactants using the stopped-flow dilution technique. It is clear that the relaxation time can vary from 2 to 150 s depending upon the molecular structure of the surfactant and the purity. The long relaxation time of 150 s for Synperonic A7, can be described as a frozen micelle as compared to those exhibiting a milliseconds time scale (usually ionic surfac-

tants). Nonionic surfactants show a much longer relaxation time (τ_2) than ionic surfactants, because of the absence of ionic repulsion between the head groups. The surfactants Synperonic A7, Brij 35 and Synperonic A50 have comparable alkyl chain lengths, but increasing degree of ethoxylation. It is clear that increasing the number of ethylene oxide units decreases the relaxation time, which was also observed for octylphenyl polyoxyethylenes by Lang and Eyring [37]. The relaxation times obtained for the ultra pure nonionic surfactants $C_{12}(EO)_5$ and $C_{12}(EO)_8$ are relatively small as
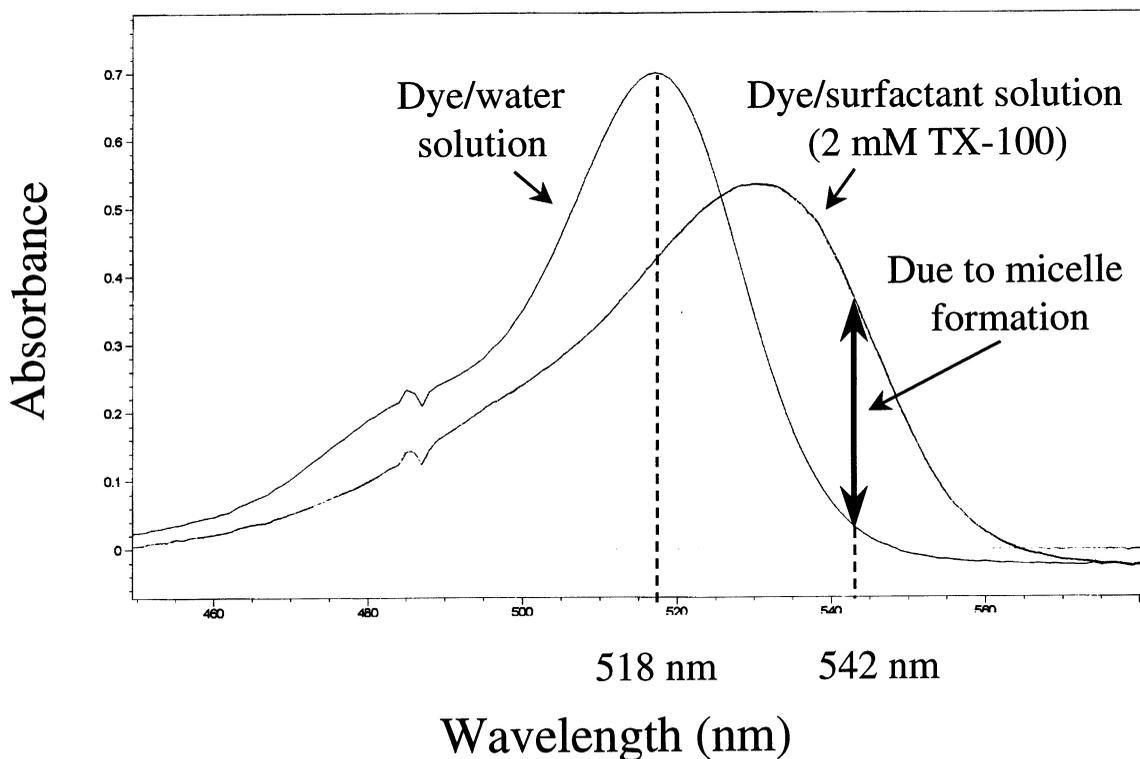
Fig. 8. Absorbance spectra of Eosin Y in water and 2 mM Triton X-100 solution (Eosin Y concentration: 0.019 mM).

Table 1
Micellar relaxation constants, τ_2, measured by the stopped-flow dilution technique

Surfactant	Structure	Conc. [mM]	CMC_{Dye} [mM]	τ_2 [s]
Tween 20	Sorbitan laurate ester (EO_{20})	0.47	0.042	6
Tween 22	Sorbitan laurate ester (EO_{80})	0.37	0.084	2
Tween 80	Sorbitan oleate ester (EO_{20})	0.49	0.028	8–10
Triton X-100	Octyl phenol ether (EO_{10})	0.40	0.20	3.5
Synperonic A7	C_{12}–C_{15} alkanol ether (EO_7)	0.80	0.050	150
Brij 35	Lauryl alcohol ether (EO_{23})	0.50	0.068	80
Synperonic A50	C_{12}–C_{15} alkanol ether (EO_{50})	0.40	0.084	40
$C_{12}(EO)_5$[a]	Lauryl alcohol ether (EO_5)	0.80	0.060	10
$C_{12}(EO)_8$[a]	Lauryl alcohol ether (EO_8)	0.40	0.072	4

[a] Pure (monodisperse) nonionic surfactant. Merocyanine 540 dye was used for the CMC and τ_2 determination. Both dyes resulted in the same CMC and τ_2 data.
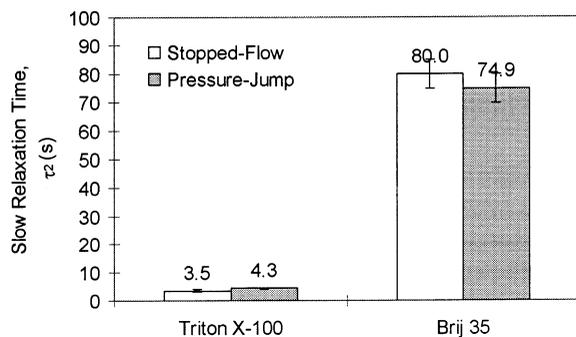
Fig. 9. Validation of relaxation constants, τ_2, by pressure-jump and stopped-flow technique, both with optical detection (Dye: Eosin Y, 0.019 mM).

compared to the Synperonics (respectively, 10 and 4 s as compared to 150 s). The difference might be attributed to the broad molecular weight distribution and the presence of impurities. It is known [38] that Synperonic A7 contains a significant amount of long chain alcohols that apparently contributes to the stability of the micelles.

In the stopped-flow dilution technique the number of micelles decreases and thus the kinetics of micelle break-up is measured. However, in the pressure-jump technique, the kinetics of micelle formation is measured after the pressure is released to ambient pressure. For a surfactant solution in equilibrium, the rate of micellar dissociation equals the rate of association. Therefore, if the perturbation caused by pressure-jump or stopped-flow is small enough, both techniques should yield the same relaxation constant τ_2 [39] In order to show that both micelle break-up and micelle formation exhibit the same relaxation kinetics, pressure-jump studies with optical detection were performed [40] on Triton X-100 and Brij 35 solutions. Fig. 9 shows the relaxation time τ_2 of Triton X-100 and Brij 35 measured by stopped-flow and pressure-jump with optical detection. It is evident that the relaxation time measured for both surfactants is the same by both techniques within the experimental error. This suggests that the relaxation time, τ_2, reflects the formation or disintegration kinetics of micelles at equilibrium.

6. Relation between dynamic surface tension and micellar stability of nonionic surfactants

Dynamic surface tension is a physical quantity associated with the deformation of fluid interfaces when a surface active specie is present in the liquid. The understanding of dynamic surface tension is important in any technological application where a new gas/liquid or liquid/liquid interface is rapidly being created in a surfactant solution. In most cases the equilibrium surface tension is never reached and the actual surface tension experienced at the interface is much higher. The dynamic surface tension can be measured by the maximum bubble pressure method [41,42] and depends on several factors: monomer concentration (CMC), micellar stability, diffusion rate of the surfactant molecule to the interface and surfactant concentration. The measurement of dynamic properties is relevant to technological processes where new interface is being formed, such as foaming or film formation, as well as situations where surfactants diffuse to a new liquid/liquid interface, such as emulsification, or to a solid/liquid interface, such as fabric wetting. During the formation of bubbles, surfactant monomers adsorb onto the freshly created interface from the bulk solution. If the monomer is depleted by the adsorption process, micelles must break-up to provide additional monomers. If the micelles in solution are very stable, they cannot provide monomer fast enough and the dynamic surface tension remains higher. However, if the micelles are relatively unstable, their disintegration resupplies the depleted monomer and lower dynamic surface tensions are obtained. In conclusion, for long bubble lifetimes, the equilibrium surface tension determines the interfacial tension at the air/water interface. However, when the bubble lifetime decreases, more and more monomer is depleted from the bulk solution and thus micelles have to break-up in order to provide additional monomers. In that case, the break-up of micelles and thus the micellar stability determines the surface tension lowering. This is schematically illustrated in Fig. 10. In order to show the importance of micellar break-up in the dynamic surface tension measurement, a dimensionless parameter θ was introduced,

$$\theta = \frac{\gamma_D - \gamma_{eq}}{\gamma_w - \gamma_{eq}} \qquad (9)$$

where γ_D is the dynamic surface tension, γ_{eq} the equilibrium surface tension as measured by the Wilhelmy plate method, and γ_w the surface tension of pure water. This equation normalizes the surface tension with respect to the surface activity of the solution. The denominator $(\gamma_w - \gamma_{eq})$ can be considered as the effectiveness of the surfactant [1]. When $\gamma_D = \gamma_{eq}$, $\theta = 0$, which indicates that the surfactant concentration at the surface of the bubble is the same as that under equilibrium conditions. However, when $\gamma_D = \gamma_w$, $\theta = 1$, indicating that no surfactant is present at the interface of the bubble. Values between 0 and 1 are a measure for the surfactant concentration at the surface and hence, the stability of micelles, assuming the diffusion time of monomers to be negligible [25,39]. This assumption is known to hold for ionic surfactants, but is currently under investiga-
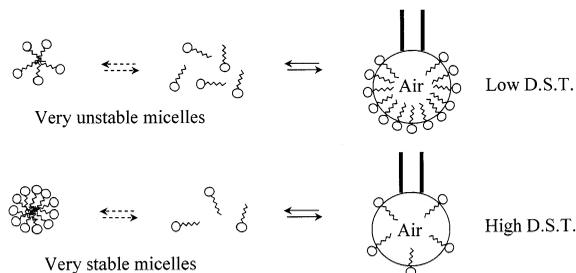
tion for the nonionic surfactants in this study. The more stable the micelles, the less monomer flux and hence θ values closer to 1 are obtained. In this study, the dynamic surface tension behavior of three nonionic surfactants was studies, Synperonic A7, Brij 35 and Synperonic A50. These three surfactants have comparable structures and very similar CMC's (Table 1). Fig. 11 shows the dimensionless parameter θ versus the bubble lifetime for 2 mM solutions of Synperonic A7, Brij 35 and Synperonic A50 (with relaxation times, 150, 80 and 40 s, respectively). It is clear that Synperonic A7 shows the slowest rate of adsorption of surfactant molecules as a result of the stability of micelles, resulting in θ values close to 1. On the other hand, Synperonic A50 shows a faster adsorption of surfactant molecules, indicated by the lower θ values. In conclusion, dynamic surface tension is a useful tool to confirm the relaxation data or micellar stability obtained by either stopped-flow dilution or the pressure-jump technique with optical detection.

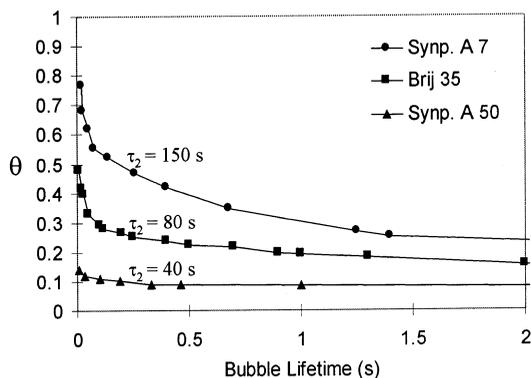Fig. 10. Effect of micellar stability on dynamic surface tension.

Fig. 11. Dimensionless dynamic surface tension (θ) versus bubble lifetime for 2 mM solutions of Synperonic A7, Brijn 35 and Synperonic A50.

7. Tailoring micellar stability to control surface properties of surfactants solutions

The ability to determine the micellar stability of ionic as well as nonionic surfactants allows us to tailor micelles with specific stability. It was shown recently [43] that the stability of SDS micelles can be greatly enhanced by the addition of 1-dodecanol ($C_{12}OH$). In fact, any long chain alcohol will increase τ_2, and hence the SDS micellar stability below 150 mM, as a result of the strong ion-dipole interaction between the SDS and the alkyl alcohol (Fig. 12). However, above approximately 150 mM SDS, all alcohols except $C_{12}OH$ decrease the micellar stability as a result of mismatching of the alkyl chains [43,44]. When the chain length of the alcohol and SDS are not equal, the excess hydrocarbon chain exhibits thermal motion, thereby increasing the area per molecule in micelles as well as at the air/water interface. Even more significant is the effect of alkylammonium bromides on SDS micellar stability [45]. In this case ion-ion interactions are introduced, causing the micelles to become even more
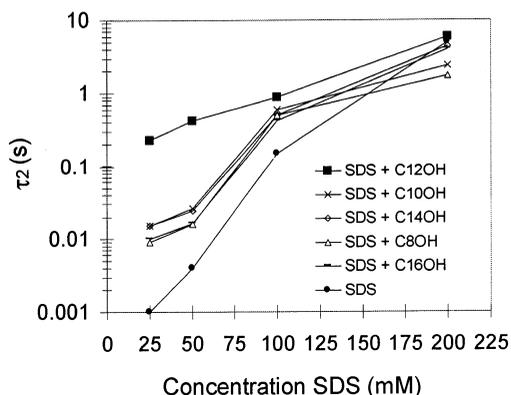
Fig. 12. Effect of long chain alcohols (5 mol.% C_nOH for $n = 8, 10, 12, 14$ and 16) on the SDS micellar stability.
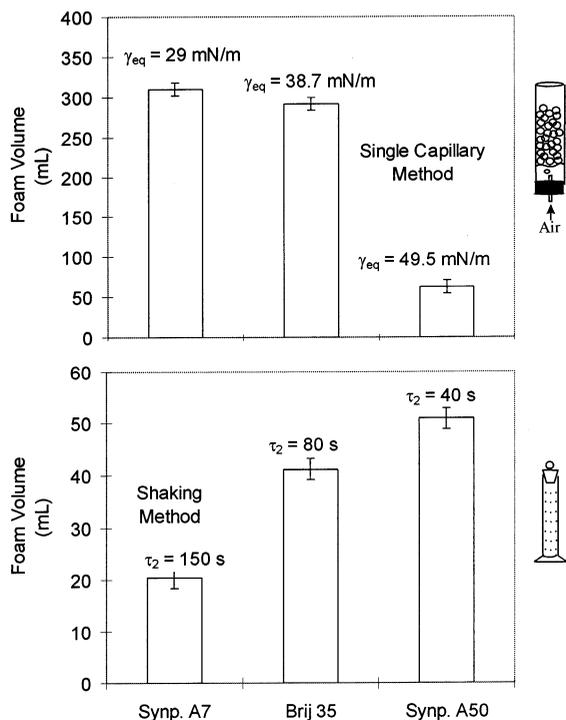

Fig. 13. Effect of foaming method on foamability of 2 mM solutions Synperonic A7, Brij 35 and Synperonic A50.

stable. For example, the slow micellar relaxation time τ_2 increases from 1 to 230 ms after the addition of 1.25 mM $C_{12}OH$. The addition of 10 mM $C_{12}TAB$ to 100 mM SDS solution results in a relaxation time of 5000 ms, a significant increase! Thus, the ability to induce ion-dipole or

ion-ion interactions as well as varying the concentration allows us to control the dynamic surface tension and in turn dynamic interfacial processes, such as foaming, emulsification, wetting and solubilization.

8. Effect of the foaming method on foaming ability

It was shown in Section 3 that the micellar stability of SDS solutions significantly influences foaming properties (Fig. 5). More stable micelles result in less monomer flux and hence lower foaming ability. The same relation is expected to hold for the three nonionic surfactants Synperonic A7 ($\tau_2 = 150$ s), Brij 35 ($\tau_2 = 80$ s) and Synperonic A50 ($\tau_2 = 40$ s). Fig. 13 shows the foam volumes generated by two different foaming methods: (1) air blowing through a single capillary submerged in the surfactant solution; and (2) vigorously hand shaking. Interestingly, the amount of foam generated shows opposite results. Synperonic A7 produces the most foam when using the single bubble capillary foam column. However, it produces the least amount of foam when used in the shaking test. The results can be explained using the dynamic surface tension data shown in Fig. 14. When enough time is allowed for the interface to form (in case of single bubble foam generation), the dynamic surface tension approaches the equilibrium surface tension (long bubble lifetimes).
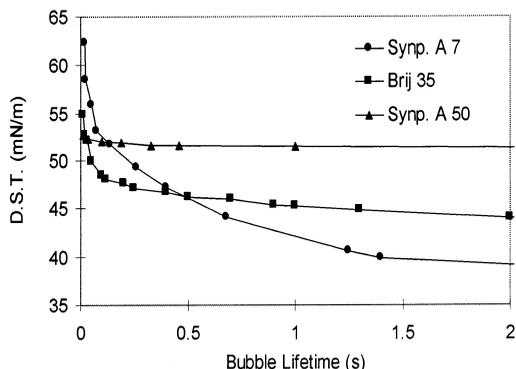

Fig. 14. Dynamic surface tension versus bubble lifetime for 2 mM solutions of Synperonic A7, Brij 35 and Synperonic A50.

Because the equilibrium surface tension of Synperonic A7 (29 mN/m) is significantly lower than that for Brij 35 (38.7 mN/m) and Synperonic 50 (49.5 mN/m), the foam volumes produced will be in the following order: Synperonic A7 > Brij 35 > Synperonic A50, according to equation 8. However, in very high shear rate processes (e.g. vigorously hand shaking), the break-up time of micelles determines the flux of surfactant molecules to the interface and hence the foamability. Because the micelles of Synperonic A7 are more stable (longer relaxation time, τ_2) than Brij 35 and Synperonic A50, higher dynamic surface tensions are attained and thus less foam is generated with Synperonic A7. Thus, at large bubble lifetimes, the equilibrium surface tension determines the amount of foam generated, whereas at short bubble lifetimes (high bubble frequencies), the micellar break-up (i.e. micellar stability) determines surface tension lowering and hence the foamability. In conclusion, we have shown that the foamability can exhibit opposite behavior depending upon the rate of foam generation (i.e. specific method used for foaming).

9. Conclusions

1. The slow micellar relaxation time τ_2, which is directly related to micellar stability, plays an important role in processes involving a rapid increase in interfacial area, such as foaming, wetting, emulsification, solubilization and detergency.
2. The stability of sodium dodecyl sulfate (SDS) micelles is a strong function of concentration. The increase in number of micelles, causes a strong intermicellar repulsion, resulting in more stable micelles, showing a maximum at 200 mM.
3. The stability of SDS micelles can be greatly enhanced by the addition of long chain alcohols or cationic surfactants.
4. A slow break-up of micelles, (i.e. a long relaxation time τ_2) corresponds to a higher dynamic surface tension, lower foamability and higher solubilization rate of benzene, whereas a fast break-up of micelles, leads to a lower dynamic surface tension, higher foamability and a lower rate of solubilization.
5. Two spectroscopic techniques (stopped-flow and pressure-jump) were used to develop a method to measure the relaxation time of nonionic surfactants. Nonionic surfactants show a much longer relaxation process than ionic surfactants, because of the absence of ionic repulsion between the head groups.
6. Increasing degree of ethoxylation leads to shorter relaxation times for nonionic surfactants.
7. For micellar solutions under equilibrium conditions, the rate of formation of micelles is equal to the rate of disintegration of micelles.
8. A dimensionless dynamic surface tension parameter, θ, was introduced, indicating the importance of micellar stability in processes involving an increase in interfacial area. θ values close to 0 indicate a very fast break-up of micelles, resulting in low surface tensions. θ values close to 1 indicate a very slow break-up of micelles, resulting in very high surface tensions.
9. For the first time it has been shown that the foam volume generated by a surfactant solution depends on the method of producing foam. If enough time is allowed for the interface to form, the dynamic surface tension approaches the equilibrium surface tension and thus more foam is generated. However, in very high speed foam generation processes, the micellar stability and thus the time it takes for micelles to break-up determines the rate of adsorption of surfactant molecules to the interface, resulting in higher surface tensions. In the latter case, less foam is generated, even though the equilibrium surface tension of the system is lower. Thus, different methods of foaming can produce opposite results, depending on the dynamic surface tension and micellar stability as demonstrated by the foamability measurements in this study.

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