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FEATURE ARTICLE

Importance of Micellar Kinetics in Relation to Technological Processes

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The association of many classes of surface-active molecules into micellar aggregates is a well-known phenomenon. Micelles are in dynamic equilibrium, constantly disintegrating and reforming. This relaxation process is characterized by the slow micellar relaxation time constant, τ_2, which is directly related to the micellar stability. Theories of the kinetics of micelle formation and disintegration have been discussed to identify the gaps in our complete understanding of this kinetic process. The micellar stability of sodium dodecyl sulfate micelles has been shown to significantly influence technological processes involving a rapid increase in interfacial area, such as foaming, wetting, emulsification, solubilization, and detergency. First, the available monomers adsorb onto the freshly created interface. Then, additional monomers must be provided by the breakup of micelles. Especially when the free monomer concentration is low, which is the case for many nonionic surfactant solutions, the micellar breakup time is a rate-limiting step in the supply of monomers. 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 showed that the ionic surfactants such as SDS exhibit slow relaxation times in the range from milliseconds to seconds, whereas nonionic surfactants exhibit slow relaxation times in the range from 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 times showed a direct correlation with dynamic surface tension and foaming experiments. In conclusion, relaxation time data of surfactant solutions correlate with the dynamic properties of the micellar solutions. Moreover, the results suggest that appropriate micelles with specific stability or τ_2 can be designed by controlling the surfactant structure, concentration, and physicochemical conditions (e.g., salt concentration, temperature, and pressure). One can also tailor micelles by mixing anionic/cationic or ionic/nonionic surfactants for a desired stability to control various technological processes. © 2002 Elsevier Science

Key Words: **surfactants; kinetics of micellization; slow relaxation time; pressure jump; stopped flow; lifetime of micelles; foams; emulsions; wetting; solubility; importance of micelle stability; technological applications.**

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1. INTRODUCTION

1.1. Micellization

Since the beginning of the study of surfactant solutions, it has been recognized that the physical properties of surfactant solutions, such as surface tension, osmotic pressure, electrical conductivity, and solubility (as a function of temperature), show an abrupt change in the neighborhood of a critical concentration when surfactant aggregation begins to occur. This unusual behavior of fatty acid salts in dilute aqueous solution was first investigated by McBain (1, 2) in the 1910s and 1920s and later by Hartley (3) in the 1930s. Other evidence for molecular aggregation was obtained from vapor pressure measurements and the solubility of organic material. The formation of colloidal-sized

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clusters of individual surfactant molecules in solution is now better known as micellization. Although first suggested by McBain (1), the earliest concrete model for spherical micelles is attributed to Hartley *et al.* (4). In a typical surfactant solution surfactant molecules disperse as monomers in the aqueous phase, form aggregates (micelles), or adsorb as a film at the air/liquid interface and at the solid/liquid interface of the container. The surfactant is in dynamic equilibrium between these states, implying that the rates of adsorption and desorption are equal. Thus, at a given temperature, pressure, and concentration, the number of monomers adsorbed at the air/water interface and the number of monomers and micelles present in solution is fixed under equilibrium conditions. The concentration of monomers and micelles changes with equilibrium conditions such as pressure, temperature, or surfactant and salt concentration.

The process of surfactant clustering or micellization is primarily an entropy-driven process (5, 6). When surfactants are dissolved in water, the hydrophobic group disrupts the hydrogen-bonded structure of water and therefore increases the free energy of the system. Surfactant molecules therefore concentrate at interfaces, so that their hydrophobic groups are removed or directed away from the water and the free energy of the solution is minimized. The distortion of the water structure can also be decreased (and the free energy of the solution reduced) by the aggregation of surface-active molecules into clusters (micelles) with their hydrophobic groups directed toward the interior of the cluster and their hydrophilic groups directed toward the water. However, the surfactant molecules transferred from the bulk solution to the micelle may experience some loss of freedom from being confined to the micelle. In addition, they may experience an electrostatic repulsion from other similarly charged surfactant molecules in the case of surfactants with ionic head groups. These forces increase the free energy of the system and oppose micellization. Hence, micelle formation depends on the force balance between the factors favoring micellization (van der Waals and hydrophobic forces) and those opposing it (kinetic energy of the molecules and electrostatic repulsion). The explanation for the entropy-dominated association of surfactant molecules is called the "hydrophobic effect" or "hydrophobic bonding" (7).

The concentration at which micelles first appear in solution is called the critical micelle concentration (CMC) and can be determined from the discontinuity or inflection point in the plot of a physical property of the solution as a function of the surfactant concentration (8, 9).

Representing the surfactant by S, the micellization process can be described by the reaction

$$nS \Leftrightarrow S_n, \qquad [1]$$

where S_n is a micellar aggregate composed of n surfactant molecules. The so-called aggregation number n (which represents the number of surfactant molecules in a micelle) has been found to increase with increasing length of the hydrophobic group and decrease with increasing size of the hydrophilic group (10). In general, the greater the hydrocarbon chain length of the surfactant molecules, the greater the aggregation number of micelles. Also, those factors that increase the aggregation number tend to decrease the CMC. For example, increasing the alkyl chain length of a surfactant decreases the CMC. The presence of electrolyte also decreases the CMC, due to the so-called "salting out" effect. The work required to accommodate a nonpolar solute in a given volume of water is increased in electrolyte solution because of strong water/ion interactions. When surfactant monomers are salted out by the presence of an electrolyte, micellization is favored and the CMC is decreased. Another factor favoring micellization in electrolyte solutions is the shielding of charges between ionic head groups (in the case of ionic surfactants) (10). It is important to emphasize that CMC represents the concentration of free surfactant monomers in a micellar solution under given conditions of temperature, pressure, and composition.

1.2. Structure of a Micelle

In the past couple of decades, the recognition that surfactant association structures can mimic biological structures has sparked considerable interest in self-assembled surfactant aggregates such as cylindrical, lamellar, and reverse micelles (11). Enzymes, for example, are protein molecules into which a substrate fits to form a reactive intermediate. The highly efficient and specific catalytic effect of enzymes makes their investigation an interesting area of biomedical and detergent research (as enzymes are often added to laundry detergents to improve performance) (12, 13). Likewise, cell membranes not only compartmentalize biological systems but also perform a variety of functions in cellular biochemical and physiological processes. Surfactant structures can be used as model systems to mimic both enzymes and membranes. Lipid aggregates known as liposomes are common in physiological systems, and specially designed liposomes are used, for example, as drug-delivery vehicles or in cosmetics (14). Self-assembled structures such as micelles or reversed micelles (surfactant aggregates with hydrophilic head groups shielded from, and lipophilic tails sticking out to an organic solvent) also play an increasingly important role in catalysis and separation processes in engineering and environmental science and technology (15–17).

A theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules, has been developed by Israelachvili *et al.* and Mitchell and Ninham (18, 19). In aqueous media, for example, surfactants with bulky or loosely packed hydrophilic groups and long, thin hydrophobic groups tend to form spherical micelles, while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form lamellar or cylindrical micelles. At concentrations slightly above the CMC, micelles are considered to be of spherical shape (20). Changes in temperature, surfactant concentration, or additives in the solution may change the size, shape, aggregation number, and stability of the micelles.

The structure of a micelle could vary from spherical to rod- or disc-like to lamellar in shape. In concentrated solutions (much higher than the CMC), lamellar micelles form, such that water molecules occupy the region between parallel sheets of surfactants. Micelles may also form long cylinders packed together (known as lyotropic mesomorphs or liquid crystalline phases) at high surfactant concentrations (21, 22). The structure and stability of micelles significantly influence the dynamic properties of the system, as will be discussed in this paper.

2. DYNAMIC PROPERTIES OF SURFACTANT SOLUTIONS

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 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 reassembling. There are two relaxation processes involved in micellar solutions (23–47). The first is a fast relaxation process referred to as τ_1 (generally on the order of microseconds), which is associated with the quick exchange of monomers between micelles and the surrounding bulk phase. This process can be considered to be the collision between surfactant monomers and micelles. The second relaxation time, τ_2 (on the order of milliseconds), is attributed to the micelle formation and dissolution process (i.e., the lifetime of the micelle). It has been shown that in certain surfactants such as nonionic surfactants and mixed surfactant systems, τ_2 can be as long as minutes! For example, the τ_2 of a 0.80 mM solution of the nonionic surfactant Synperonic A7 is 150 s (24). Figure 1 shows the two characteristic relaxation times, τ_1 and τ_2, associated with micellar solutions. Micelle formation and disintegration is analagous to the equilibrium between water and water vapor at a given temperature and pressure. For a closed system containing liquid water and water vapor in equilibrium, the number of water molecules per unit area per second evaporating from the surface is equal to 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 micellar solution. Under equilibrium conditions, the rate of micelle formation is equal to the rate of disintegration into surfactant monomers.

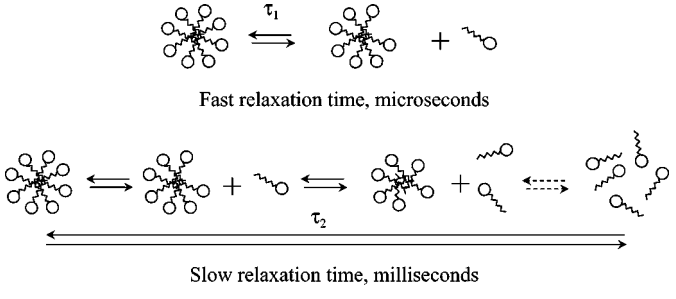

FIG. 1. Mechanisms for the two relaxation times, τ_1 and τ_2, for a surfactant solution above CMC.

Micellar relaxation kinetics show dependence on temperature, pressure, and concentration, as well as on the addition of other species such as short-chain alcohols. It was shown that the τ_2 of an SDS micelle decreases with increased concentration of C_1–C_5 alcohols (48). These kinetics have been studied by various techniques such as stopped-flow, temperature-jump, pressure-jump, and ultrasonic absorption (23–30). The two relaxation times can be used to calculate two important parameters of a micellar solution: (a) the residence time of a surfactant molecule in a micelle and (b) the average lifetime or stability of a micelle.

3. DEVELOPMENT OF THE THEORY FOR MICELLAR KINETICS

As was mentioned in Section 1, the study of surfactant aggregation began in the 1910's, and the concept of micelles and a "critical micelle concentration" was put forth in the 1930s (1–4). However, at that time micelles were thought of as static and stable surfactant aggregates. It was not until more than 30 years later in the 1960s and 1970s that researchers first discovered and observed the dynamic aspect of surfactant association and dissociation by various experimental methods such as pressure-jump, temperature-jump, concentration-jump (i.e., stopped-flow), and ultrasonic relaxation studies. In 1965, Mijnlieff and Ditmarsch (31) reported results on the rate of formation of sodium alkyl sulfate micelles in water studied by the pressure-jump technique. They did not at first distinguish between fast (τ_1) and slow (τ_2) relaxation times. This report was soon followed by temperature-jump (32–35), ultrasound (36–39), and stopped-flow (40–42) studies on micelle association/dissociation kinetics. These studies showed that there are well-defined τ_1 and τ_2 values for each surfactant system and that the time scale for τ_1 was on the order of microseconds while that of τ_2 was on the order of milliseconds.

3.1. Micelle Association by Stepwise Incorporation of Monomers

Experimental research on the kinetics of micellization reached its peak in the 1970s, when attention switched focus to analysis of the relaxation process in micellar solutions on the basis of stepwise formation and disintegration of micelles (43–46). The primary breakthrough in this area was the discovery of the existence of two (fast and slow) relaxation processes (47, 36, 46) and the development of a model for the kinetic process of micelle formation and disintegration by Aniansson and co-workers (49–51).

The first major assumption of this seminal work, which was derived for nonionic surfactants and later supplemented by Lessner *et al*. (52) and Hall (53) to include ionic surfactants, was that the free surfactant monomers are assumed to be completely dissociated and the size distribution of the aggregates in

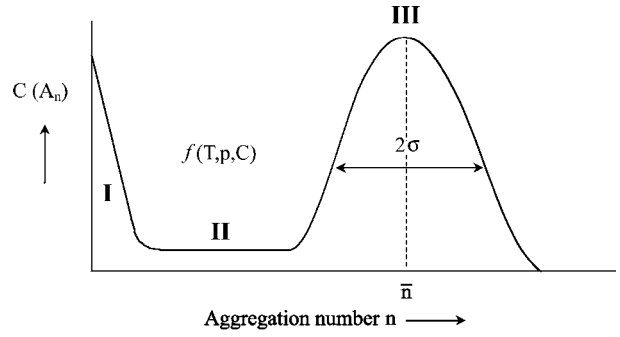

FIG. 2. Typical size distribution curve of aggregates in a micellar solution according to the Aniannson–Wall model of stepwise micellar association. Region (I) corresponds to monomers and oligomers; Region (III) to abundant micelles with a Gaussian distribution around the mean aggregation number, $\bar{n}$; and Region (II) to the connecting "wire" (heat transfer analogy) or "tube" (mass transfer analogy) between Regions (I) and (III).

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 and is a function of temperature (T), pressure (p), and total surfactant concentration (C). Notice the existence of three distinct regions where one can find monomers and oligomers (Region I), proper micelles (Region III), and a narrow passage connecting monomers and micelles (Region II). In other words, only monomers and proper micelles are assumed to be present in the solution in significant quantities.

The second major assumption Aniansson and co-workers make is that the association and dissociation of micelles is a stepwise process involving the entry and departure of one monomer at a time from the micelle. Thus, there is a series of equilibria,

$$A_1 + A_{n-1} \underset{k_n^-}{\overset{k_n^+}{\rightleftarrows}} A_n \quad n = 2, 3, 4, \ldots, \qquad [2]$$

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, respectively. Therefore, when the equilibrium of a surfactant solution is perturbed (e.g., by temperature or pressure jump), the excess population has to move through regions of different aggregation numbers (Region II of Fig. 2). According to Eq. [2], this occurs in steps that are very small compared to the distance in aggregate space traveled. Therefore, the process will have the characteristics of a flowing system, which is important because it allows the kinetics of the abstract process of micelle aggregation to be studied in terms of the more familiar phenomena of heat and material flow.

The kinetic equation was first put into a form analogous to a heat conduction problem (49) and later (more appropriately) into a form analogous to a mass-transfer diffusion problem (51). Using this second analogy, the mechanism of micelle aggregation was likened to mass flow through a tube of variable width—two wide ends (Regions I and III in Fig. 2) connected by an extremely narrow section (Region II in Fig. 2). The diffusion of material through the narrow tube was considered to be the slow, rate-limiting step in the reaching of equilibrium between the two thick ends. Likewise, the extremely low concentration of transient intermediate submicellar aggregate states (Region II) that surfactant monomers must pass through (i.e., $A_2\ A_3\ A_4\ \ldots\ A_{n-1}$ in Eq. [2]) when a micelle is formed from, or disintegrated into, free monomers is the rate-limiting step in the formation or disintegration of a micelle. Assuming the aggregation number n to be a continuous variable and applying the above analogy to mass transfer, Aniansson and coworkers derived the expression for the fast relaxation process τ_1

$$\frac{1}{\tau_1} = \frac{k^-}{\sigma^2}\left(1 + \frac{\sigma^2}{n}a\right), \quad \text{with } a = \frac{C - CMC}{CMC}, \qquad [3]$$

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 is the total surfactant concentration, and CMC is the critical micelle concentration. Equation [3] predicts a linear relationship between $1/\tau_1$ and the total surfactant concentration, in agreement with pressure-jump and sound absorption experiments (51, 54). It is obvious that as the total surfactant concentration increases, so too does the number of micelles, 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 the relaxation time—since micelles composed of shorter-chain surfactants are more loosely packed structures due to smaller van der Waals attractive forces and less hydrophobic effect.

Using the same analogy of diffusion through a tube as described above, an expression for slow relaxation time τ_2 was derived and simplified to

$$\frac{1}{\tau_2} = \frac{n^2}{CMC * R}\left(1 + \frac{\sigma^2}{n}a\right)^{-1}, \qquad [4]$$

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

$$R = \sum_{n=n_1+1}^{n_2} \frac{1}{k_n^- A_n}, \qquad [5]$$

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 on R. Interestingly, the two relaxation times can be used to calculate two important parameters of a micellar solution: (a) the residence time of a surfactant molecule in a micelle and (b) the average lifetime or stability of micelles (29, 55–57). The residence time of a surfactant monomer in a micelle 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 (58):

$$T_m = \tau_2 \frac{na}{1 + \frac{\sigma^2}{n} a} \approx n\tau_2. \qquad [6]$$

When the concentration of surfactant is much greater than CMC, the micellar lifetime is approximately equal to $n\tau_2$.

3.2. *Micelle Association by Coagulation of Submicellar Aggregates Due to a Fusion–Fission Mechanism*

Although first derived for nonionic surfactants, the results of Aniansson and Wall's theory on micellar aggregation kinetics were compared primarily with experiments on ionic systems, simply because it was much easier to detect the relaxation times in ionic systems than in nonionic systems. Even so, the agreement between theory and experiment was, in general, satisfactory in the regime of low surfactant concentrations (49). At higher concentrations, however, the theory did not match experimental results (52). Equation [4] 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, passes through a maximum, and then decreases again (47, 52, 59). This behavior in the slow relaxation process of ionic micelles is not predicted in the Aniansson–Wall model. Kahlweit and coworkers, using their own T-jump and p-jump results (60–62), concluded that in ionic surfactant systems at high concentration, the reaction path for the formation of micelles must be different than that at low concentration. Therefore, the following model was proposed explaining the occurrence of a maximum in τ_2 (Fig. 3): Ionic micelles, including submicellar aggregates, can be considered charged particles. When ionic surfactant molecules such as SDS are added to water, the surfactant molecules dissociate into negatively charged dodecyl sulfate molecules and their positively charged counterions. These counterions are present in solution as a cloud surrounding the negatively charged micelle. At low surfactant counterion concentration, the micelles are stable with respect to coagulation due to repulsive electrostatic forces. Consequently they can grow only by stepwise incorporation of monomers according to Eq. [2] above.

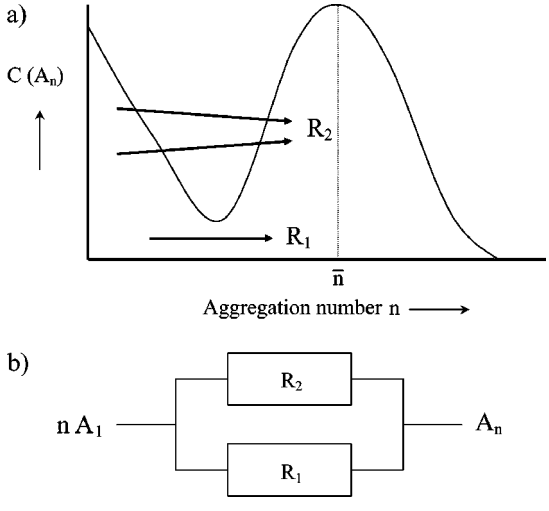

FIG. 3. Schematic representation of the two possible reaction paths for the formation of micelles (a) and the corresponding resistances (b): (1) formation by incorporation of monomers (Eq. [2]) and (2) formation by reverse coagulation of submicellar aggregates (Eq. [7]) (40).

As more and more surfactant is added into the system, the counterion concentration also increases, which compresses the electrical double layer and reduces charge repulsion, allowing the micelles to come closer to each other so that attractive dispersion forces (i.e., van der Waals forces) lead to a reversible fusion–fission coagulation according to

$$A_k + A_l \rightleftarrows A_i \quad k + l = i, \qquad [7]$$

where k and l are classes of submicellar aggregates.

Kahlweit (61) then represented the micelle formation reaction path by two parallel resistors, R_1 and R_2 (Fig. 3b), and compared the formation of micelles to the discharge of a capacitor through two parallel resistors (63), so that the change in the monomer concentration with time was given by

$$\frac{-d \ln A_1}{dt} = \frac{1}{\tau_{21}} + \frac{1}{\tau_{22}}, \qquad [8]$$

where τ_{21} refers to the reaction path in Eq. [2] and τ_{22} to the reaction path in Eq. [7].

At low surfactant concentration, and hence at correspondingly low counterion concentration, R_2 is very high due to electrostatic repulsion between submicellar aggregates, so stepwise aggregation dominates and R_1 (the same resistance term proposed by Aniansson and Wall in Eq. [5]) determines the rate of micelle formation. Equation 4 above can therefore be written as

$$\frac{1}{\tau_{21}} = \frac{n^2}{CMC * R_1} \left(1 + \frac{\sigma^2}{n} a\right)^{-1}, \qquad [9]$$

which is identical to Eq. [4] derived by Annianson and Wall.

As the surfactant concentration is increased, the counterion concentration also increases, and hence, R_1 increases as R_2 decreases. The concentration where R_1 equals R_2 is the point where $1/\tau_2$ passes through a minimum and τ_2 is highest (for the SDS micelle, this occurs at 200 mM) (64). If the counterion concentration is still further increased, R_1 becomes so high that R_2 determines the rate of micelle formation according to the reaction mechanism in Eq. [7],

$$\frac{1}{\tau_{22}} = \beta n a \left(1 + \frac{\sigma^2}{n} a\right)^{-1}, \quad \text{with } a = \frac{C - CMC}{CMC}, \qquad [10]$$

where β is a measure for the mean dissociation rate constant in Eq. [7] and is a function of counterion concentration. This result holds only at sufficiently high counterion concentration. A detailed explanation of β and its functionality with counterion

concentration has been provided in Ref. (64). This theoretical development by Kahlweit and co-workers has helped to explain the existence of a maximum in τ_2 of ionic surfactants.

For ionic surfactant systems, the concept of one of two possible reaction pathways available depending on surfactant (and counterion) concentration does a good job of predicting and explaining the experimental maxima of slow relaxation times found in ionic surfactant micelles (Fig. 6). The model also accurately predicts a shift of the maximum τ_2 to lower surfactant concentrations by the addition of electrolyte and by the addition of nonionic amphiphiles such as alcohols (47, 52).

In the case of nonionic systems, electrostatic repulsion forces are absent, and both reaction paths compete right from the CMC on. Because of this, no pronounced maximum in τ_2 is ever encountered. Instead, the shape of the τ_2 versus concentration curve resembles that of an adsorption isotherm with an asymptotic increase to a maximum value and no decrease of τ_2 at higher concentrations.

A limitation present in both Aniansson's and Kahlweit's models is the absence of the consideration of intermicellar distance and conformational changes (e.g., changes from spherical to cylindrical or lamellar structures) in the micelle. The fusion–fission process of submicellar aggregation proposed by Kahlweit was studied for elongated micelles by Turner and Cates (65) and Waton and his co-workers (66, 67). In each case an increase in micellar lifetime was encountered.

3.3. Computer Simulations of the Kinetics of Micelle Formation and Disintegration

Computer molecular simulations have recently been used to complement experimental studies and further our understanding of surfactant structure and aggregation behavior at a molecular level. The basic idea of computer simulation is that one may explicitly follow and statistically analyze the trajectory of a system involving many degrees of freedom to simulate the behavior of a real assembly of particles (68). However, computer capacities, while growing, are finite. This implies that one may consider only a finite number of particles and a trajectory of finite length.

Two general classes of simulations exist: molecular dynamics and stochastic simulations. The most widely used molecular simulation technique presently in use is the molecular dynamics (MD) simulation, in which forces derived from an assumed potential are used to generate phase space trajectories from which observable properties are calculated by using statistical thermodynamics principles (69).

Most MD simulations performed on micellar aggregation to date have focused on the structure, shape, and size of micelles. More recently, however, there has been interest in using MD to study the kinetics of micellar self-assembly (70–77). Smit and co-workers (71, 72) have used simplified models of surfactants and a Lennard–Jones solvent to examine micelle formation. Because micelle formation takes a long time (milliseconds) compared to atomic time scales, it requires great computational power to use fully atomistic MD models to reproduce such self-assembly. However, DeBold and Kollman (73) were able to observe aggregation of alcohol molecules in an octanol/water system within a 2.0 ns MD simulation. Nowadays, due to the increase in computer power and due to algorithmic advances, it has become possible to simulate the self-aggregation of surfactants by using atomistic MD simulations. Maillet *et al.* (74) simulated the self-aggregation of both short- and long-chain ionic surfactants, while others (75–77) have shown self-aggregation of dodecylphosphocholine (DPC) surfactant molecules in water into a single micelle, either spherical or worm-like, depending on the surfactant concentration.

The main stochastic computer simulation technique is the Monte Carlo method. It is essentially a stochastic sampling experiment involving the generation of random numbers followed by a limited number of arithmetic and logical operations, which are often the same at each step. This method aims to generate a trajectory in phase space which samples from a chosen statistical ensemble. Several different variables, including chemical potential and number of molecules, can be fixed while the positions and momenta of molecules can be followed over a series of steps to an equilibrium state (78).

Extensive studies of the equilibrium properties of surfactant systems using Monte Carlo simulations have been performed in the past (79–83). However, work on the dynamics of micellization is very limited (84–88). Recently there have been studies on the dynamic properties of micelles at equilibrium and of the micellization process (84–87). There have also been studies on the exchange kinetics between the bulk solution and a spherical absorbent (88).

4. IMPORTANCE OF MICELLAR RELAXATION TIME IN VARIOUS TECHNOLOGICAL PROCESSES

The importance of micelle breakup in processes involving an increase in interfacial area was first reported by Mijnlieff and co-workers (31). For many years researchers 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 textiles, bubble volume, emulsion droplet size, and solubilization rate of benzene in micellar solutions was found by Shah and co-workers (24, 89). Figure 4 shows schematically the importance of micelle breakup in foaming processes. When air is blown through a surfactant solution, a substantial amount of new interfacial area is created in the form of bubbles. 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 (if above CMC) micelles. As monomers diffuse to the newly created surface, the equilibrium condition between monomers and micelles is disturbed, which forces existing micelles to break up to provide additional monomers to the surface. Very stable micelles are not able to augment the flux necessary to stabilize the newly created interface, and therefore,

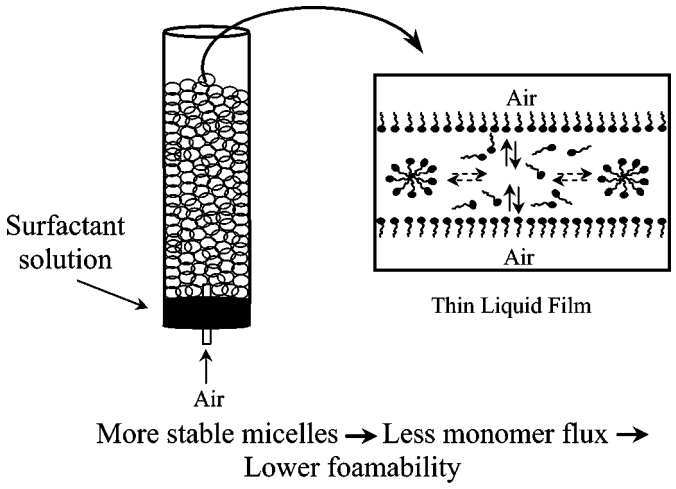

FIG. 4. Schematic representation of adsorption of surfactant onto the newly created air/water interface due to disintegration of micelles during foam generation.

foamability will be less. The micelle breakup process is also important in fabric wetting. When a piece of fabric is placed to float on top of a surfactant solution, the solution begins to penetrate the interfiber spaces of the fabric. The monomers deposit onto the hydrophobic sites of the surface and at the same time decrease the interfacial tension between the water and fabric. More stable micelles will cause less monomer flux to the fabric surface, which will slow down the wetting process and result in a longer wetting time. A picture similar to Fig. 4 can be drawn for micelle breakup during emulsification processes (Fig. 5). 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 relationship between surface tension or interfacial tension and the amount of interfacial area created in foams or emulsions can be given by (90)

$$W = \gamma \Delta A, \qquad [11]$$

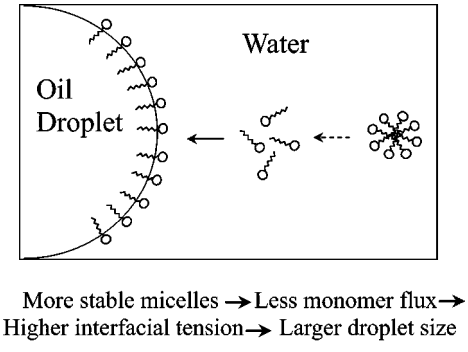

FIG. 5. Schematic diagram for the adsorption of surfactant monomers from the bulk to the oil/water interface during emulsification.

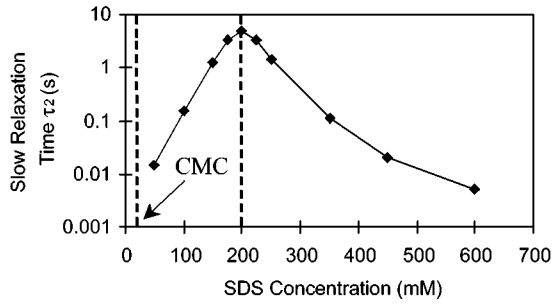

FIG. 6. The slow relaxation time, τ_2, of SDS micelles at various surfactant concentrations. A maximun in τ_2 is found at 200 mM (cmc ~8.3 mM at 25°C).

where W is the work done, γ is the surface or interfacial tension at the air/water or oil/water interface, and ΔA is the change in interfacial area. If the work on a system is kept constant, 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 by Oh and Shah (91) by using pressure-jump with electrical conductivity detection (92). Figure 6 shows the micellar relaxation time τ_2 a as function of SDS concentration. Maximum micellar stability was found at 200 mM ($\tau_2 = 5$ sec), in agreement with previous observations (64). Figure 7 presents the various phenomena exhibiting minima and maxima at the liquid/gas interface. At 200 mM SDS, minimum foamability, maximum single film stability, maximum single bubble volume, and a minimum frequency of bubble

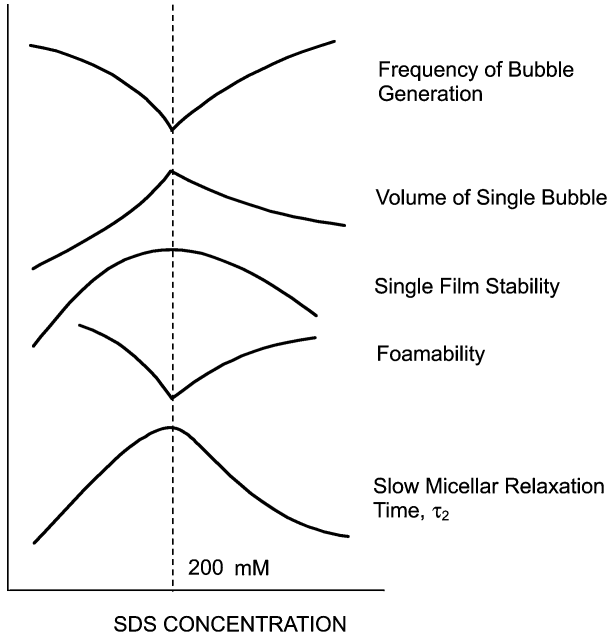

FIG. 7. Liquid/gas phenomena exhibiting minima and maxima at 200 mM SDS concentration.

generation were found. These phenomena were explained based upon the monomer flux to newly created interfaces. If the micelles in solution are very stable, they cannot provide monomers to the interface quickly enough and thus the interfacial tension remains higher. Therefore, lower foamability, larger single bubble foam volumes, and a minimum frequency of bubble generation were found (93, 94). Very unstable micelles, however, provide monomers to the surface fast enough, resulting in lower interfacial tension. A maximum single film stability was found at 200 mM, i.e., when the micelles were most stable (95). An important factor influencing single film stability is the micellar structure inside the thin liquid film, which has been investigated by Wasan and co-workers (96, 97). 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, stability, interaction, and polydispersity. Therefore, the results from this study indicate that very stable micelles contribute to the stability of thin liquid films.

Interfacial phenomena occurring at the liquid/liquid and solid/liquid interfaces in SDS solutions are shown in Fig. 8. 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 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 a newly created interface. Very stable micelles result in high dynamic surface tensions, and hence, larger droplet sizes and longer wetting times are obtained (98, 99). The solubilization rate of benzene in SDS solutions, as well as the detergency or removal of orange OT dye from the surface of a fabric, shows a maximum at 200 mM concentration. The time required to reach saturation of the SDS solution upon the addition of benzene is a 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 (91). This can be explained by examining the interior of the micelles. The interior of rigid (i.e., tightly packed) micelles is more hydrophobic than 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.

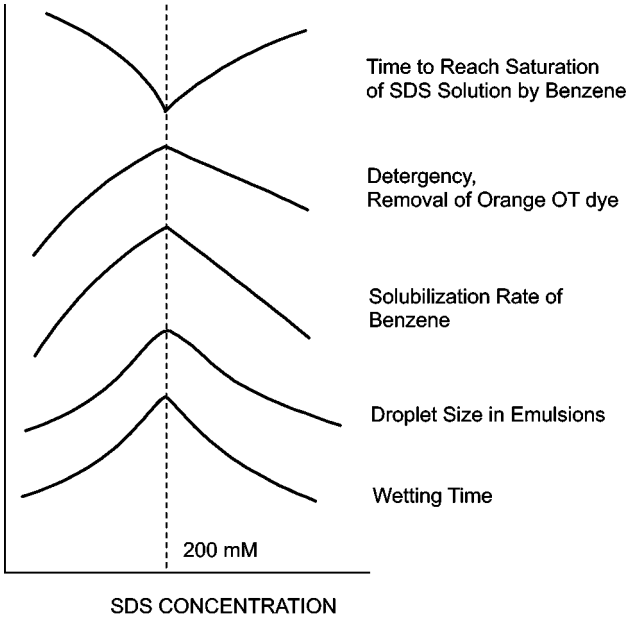

FIG. 8. Liquid/liquid and solid/liquid phenomena exhibiting minima and maxima at 200 mM SDS concentration.

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 (24, 89).

5. 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 equal to the number of micelles, one can equate the distance between the centers of the adjacent cubes to 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 250 mM SDS concentration, a structural transition from spherical to cylindrical SDS micelles occurs. However, this structural transition is gradual and hence in this concentration range (250–400 mM) the solution consists of a mixture of spherical and cylindrical micelles (22, 100). Since the number of spherical micelles is less than at 200 mM concentration, as some of them have become cylindrical micelles, the distance between spherical micelles increases, which leads to

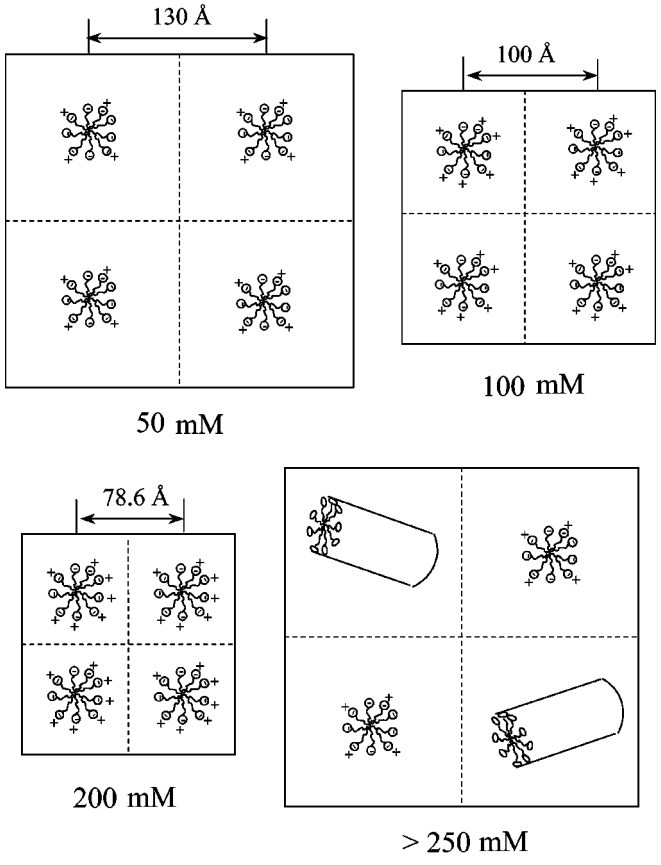

FIG. 9. Schematic diagrams showing micellar packing at 50, 100, 200, and 250 mM SDS concentration.

shorter relaxation times. In a binary mixture, it is the most labile structure (i.e., spherical micelles) which responds quickly to the change in pressure in the pressure-jump studies, as compared to cylindrical micelles (92). The intermicellar distances obtained from the procedure at various SDS concentrations are shown in Fig. 9. This model also explains the shift of the maximum micellar stability to lower concentrations of SDS by the addition of salt or cosurfactants (64).

In summary, SDS solutions exhibit maxima and minima for various properties at 200 mM concentration due to 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 due to an increase in Coulombic repulsion and reduction in intermicellar distance.

6. RELAXATION KINETICS OF NONIONIC MICELLES AS COMPARED TO IONIC MICELLES

In the previous section, a micellar relaxation time in the range of milliseconds to seconds was measured for SDS solutions by the pressure-jump technique with electrical conductivity detection. This technique takes advantage of the fact that the CMC shifts to higher concentration when a surfactant solution is pressurized. Hence, in the case of ionic surfactants, the electrical conductivity increases with pressure. When the pressure is instantaneously released to atmospheric pressure, monomers will associate to form new micelles, which can be followed as an exponential decay in electrical conductivity with time. For nonionic surfactants, however, the electrical conductivity is not a sensitive parameter. Because of this, conductometric techniques are not an effective way of measuring the kinetics of micelle formation and breakup for nonionic micelles. Therefore, spectroscopy with the use of a dye is necessary to obtain information about the micellar 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 inside or outside the micelle in the aqueous phase (49, 101). This effect is often used to determine the CMC (8, 9), 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. This shift is caused by a change in the microenvironment of the dye. Figure 10 shows the shift in absorbance for a Triton X-100 surfactant solution.

It is possible that the absorbance shift can be influenced by the aggregation state of the dye itself. For example, a dye monomer may exhibit different absorbance characteristics than an aggregate of dye molecules. For this reason, it is important to use the lowest concentration of dye possible. Also, testing light absorbance at various dye concentrations is advisable to ensure that the dye itself does not play a significant role in the relaxation measurements. Careful measurements were carried out to ensure that the shift in absorbance was caused by the breakup of micelles and not by a change in the aggregation state of the dye itself. Several experiments were performed by diluting the

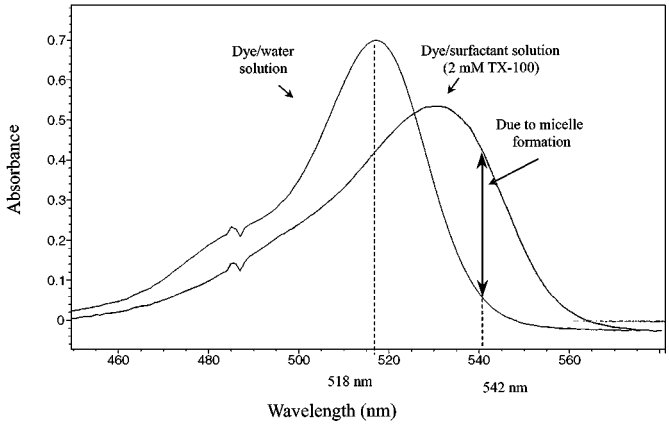

FIG. 10. Absorbance spectra of Eosin Y dye in water and 2 mM Triton X-100 solution (Eosin Y concentration: 0.019 mM).

dye only, mixing two dye solutions, mixing two surfactant solutions with and without dye, etc. These experiments clearly showed that the shift in absorbance is truly due to the breakup of micelles, indicating the slow micellar relaxation time. In case the dye did show any form of aggregation, the time scale would have been too short to measure with the stopped-flow apparatus.

The shift in wavelength observed due to 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 (23). 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 photomultiplier 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 peak associated with dye in micelles will decrease as micelles break up, indicating the relaxation time of micelles. This exponential decay can be fitted to a first-order reaction, resulting in the associated time constant τ_2.

Micelles of nonionic surfactants show a much longer relaxation time (τ_2) than those of ionic surfactants, presumably because of the absence of ionic repulsion between the head groups. Table 1 shows the slow relaxation times τ_2 measured for a variety of nonionic surfactant micelles using the stopped-flow dilution technique. As indicated in Table 1, the relaxation time can vary from 2 to 150 s depending upon the molecular structure of the nonionic surfactant. Because of its long relaxation time of 150 s, Synperonic A7 can be described as a frozen micelle as compared to those exhibiting a millisecond time scale (usually ionic surfactants). The relaxation times obtained for the ultrapure nonionic surfactants $C_{12}(EO)_5$ and $C_{12}(EO)_8$ are relatively small as compared to those for 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 that Synperonic A7 contains a significant amount of long-chain alcohols that apparently contributes to the stability of the micelles.

TABLE 1
Micellar Relaxation Constants, τ_2, Measured by the Stopped-Flow Dilution Technique (Dye: Eosin Y, 0.019 mM)

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 Eosin Y and Merocyanin resulted in the same CMC and τ_2 data.

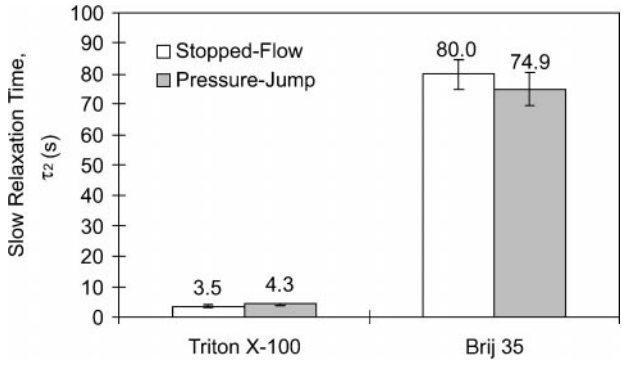

FIG. 11. Validation of relaxation constants, τ_2, by pressure-jump and stopped-flow technique, both with optical detection (Dye: Eosin Y, 0.019 mM).

The surfactants Synperonic A7, Brij 35, and Synperonic A50 have comparable alkyl chain lengths but increasing degrees 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 (102).

In the stopped-flow dilution technique the number of micelles decreases and thus the kinetics of micelle breakup 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, both techniques should yield the same relaxation constant τ_2. To show that both micelle breakup and micelle formation exhibit the same relaxation kinetics, pressure-jump studies with optical detection were performed (103) on Triton X-100 and Brij 35 solutions.

Figure 11 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 each surfactant is the same as that measured by both techniques within the experimental error. This suggests that the relaxation time, τ_2, reflects the formation or disintegration kinetics of micelles under equilibrium conditions.

7. RELATIONSHIP BETWEEN DYNAMIC SURFACE TENSION AND STABILITY OF MICELLES

Dynamic surface tension is a physical quantity associated with the deformation of fluid interfaces when a surface-active species is present in the liquid. The understanding of dynamic

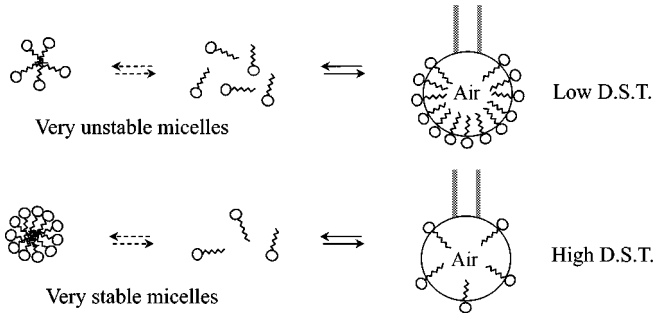

FIG. 12. Effect of micellar stability on dynamic surface tension.

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 (104, 105) 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 interfaces are being formed, such as foaming or film formation, as well as to 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 monomers fast enough and the dynamic surface tension remains higher. However, if the micelles are relatively unstable, their disintegration supplies the depleted monomers and lower dynamic surface tensions are obtained.

In summary, for long bubble lifetimes (or small bubble frequency), the equilibrium surface tension determines the interfacial tension at the air/water interface. However, when the bubble lifetime decreases (i.e., high bubble frequency), more and more monomer is depleted from the bulk solution and thus micelles have to break up to provide additional monomers. In that case, the breakup of micelles and thus the micellar stability determines the surface tension lowering. This is schematically illustrated in Fig. 12.

To show the importance of micellar breakup in the dynamic surface tension measurement, a dimensionless parameter θ was introduced,

$$\theta = \frac{\gamma_D - \gamma_{eq}}{\gamma_w - \gamma_{eq}}, \qquad [12]$$

where γ_D is the dynamic surface tension, γ_{eq} is the equilibrium surface tension as measured by the Wilhelmy plate method, and γ_w is the surface tension of pure water at 25°C (72.96 mN/m). This equation normalizes the surface tension with respect to the surface activity of the solution. The denominator $(\gamma_w - \gamma_{eq})$ can be considered to be the effectiveness of the surfactant (10). 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. Assuming that micelles do not adsorb at the air/water interface (106), this implies that diffusion and adsorption of surfactant monomer to the interface is quick, presumably due to very unstable micelles (i.e., small τ_2). However, when $\gamma_D = \gamma_w$, $\theta = 1$, indicating that no surfactant is present at the interface of the bubble (i.e., at high bubble frequency and very stable micelles). Values between 0 and 1 are a measure of the surfactant concentration at the surface and, hence, the stability of micelles, assuming the diffusion time of monomers to be negligible (94, 107). The more stable the micelles, the less monomer flux and hence θ values closer to 1 are obtained. The less stable the micelles, the more monomer flux and hence θ values closer to zero are obtained. In this study, the dynamic surface tension behavior of three nonionic surfactants—Synperonic A7, Brij 35, and Synperonic A50—was studied. These three surfactants have comparable structures and very similar CMCs (Table 1). Figure 13 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

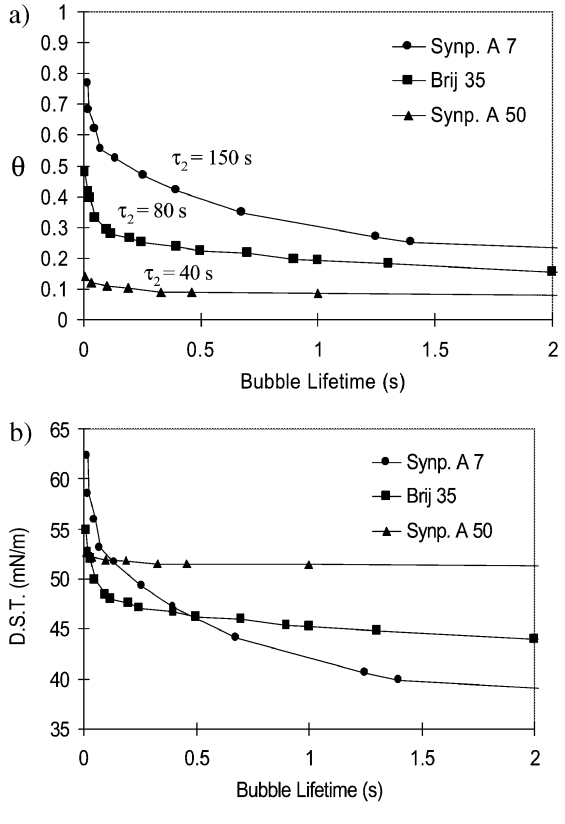

FIG. 13. (a) Dimensionless dynamic surface tension and (b) dynamic surface tension vs bubble lifetime for 2 mM solutions of Synperonic A7, Brij 35, and Synperonic A50.

rate of surfactant adsorption due to 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 or micellar stability data obtained either by stopped-flow dilution or by the pressure-jump technique with optical detection.

8. TAILORING MICELLAR STRUCTURE AND STABILITY TO CONTROL SURFACE PROPERTIES OF MICELLAR SOLUTIONS

The ability to determine the micellar stability of ionic as well as nonionic surfactants allows us to tailor micelles to specified stabilities. It was shown recently (108) 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 micellar stability below 150 mM SDS due to the strong ion/dipole interactions between the SDS and the alkyl alcohol (Fig. 14). However, above approximately 150 mM SDS, all alcohols except $C_{12}OH$ decrease micellar stability due to mismatching of the alkyl chains (108). 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 cationic alkylammonium bromides on SDS micellar stability (109). In this case, ion/ion interactions and charge neutralization between the SDS molecules and a small amount of cationic surfactants are introduced, causing the micelles to become even more stable. The effect of 5 mol% $C_{12}OH$ and $C_{12}TAB$ on 25 mM SDS solutions is shown in Fig. 15. The slow micellar relaxation time τ_2 increases from 1 to 230 ms after the addition of 5 mol% $C_{12}OH$. In the case of 5 mol% $C_{12}TAB$ a relaxation time of 2000 ms was found, a 2000 times increase! Thus, the ability to induce ion/dipole or ion/ion (Coulombic) interactions allows us to control the dynamic surface tension and in turn dynamic interfacial processes, such as foaming, emulsification, wetting, and solubilization. Similar effects are expected for ionic/nonionic surfactant mixtures, which are currently under investigation.

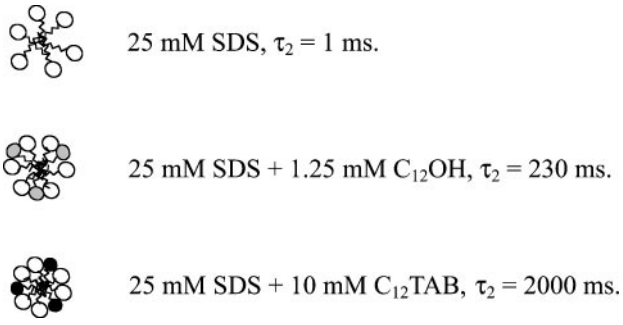

FIG. 15. Tailoring SDS micellar stability by the addition of 1-dodecanol ($C_{12}OH$) or alkyltrimethylammonium bromide ($C_{12}TAB$).

9. EFFECT OF THE FOAMING METHOD ON FOAMING ABILITY AND FOAM STABILITY IN RELATION TO MICELLAR STABILITY, DYNAMIC SURFACE TENSION, AND MICELLAR STRATIFICATION IN THIN FILMS

It was shown in Section 4 that the micellar stability of SDS solutions significantly influences foaming properties. More stable micelles result in less monomer flux and hence lower foaming ability. The same relationship 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). Figure 16 shows

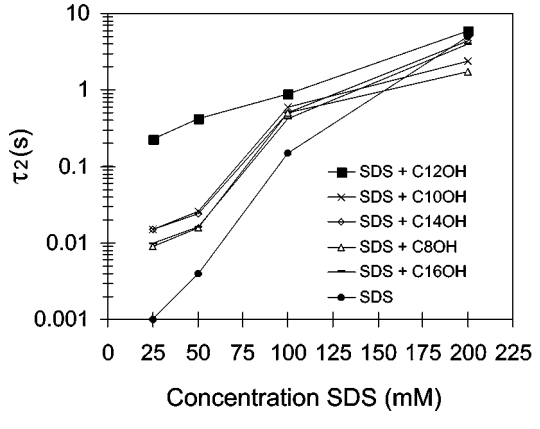

FIG. 14. Effect of long-chain alcohols (5 mol% C_nOH for $n = 8$, 10, 12, 14, and 16) on the SDS micellar stability.

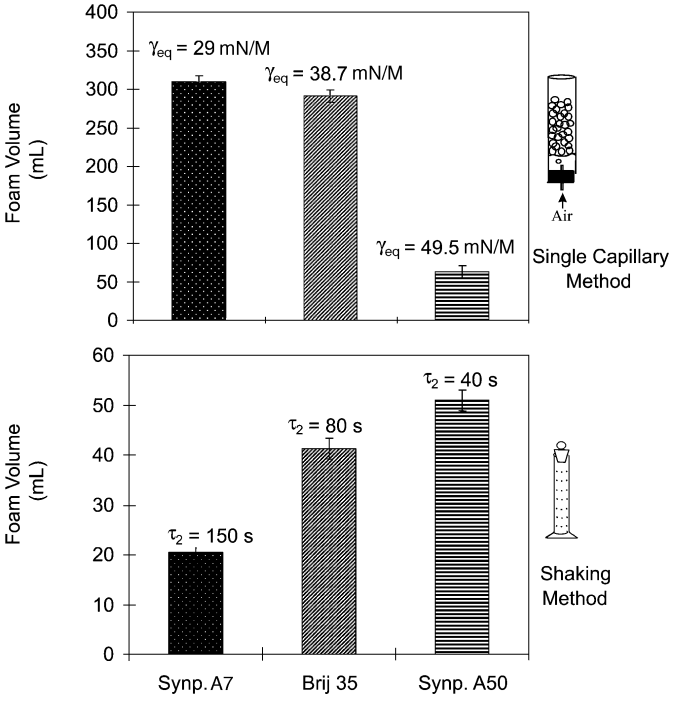

FIG. 16. Effect of foaming method on foamability of 2 mM solutions of Synperonic A7, Brij 35, and Synperonic A50.

the foam volumes generated by two different foaming methods: (a) air blowing through a single capillary submerged in the surfactant solution and (b) vigorous hand shaking. Interestingly, the amounts of foam generated using each method show opposite results. Synperonic A7 produces the most foam when the single bubble capillary foam column is used. 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. 13 and their micellar stability.

When sufficient time is allowed for the interface to form (in case of single bubble foam generation), the dynamic surface tension approaches the equilibrium surface tension values (long bubble lifetimes). Since 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 order Synperonic A7 > Brij 35 > Synperonic A50, according to Eq. [12].

However, in very-high-shear-rate processes (e.g., vigorous hand shaking) where a large interfacial area is created very quickly, the breakup time of micelles determines the flux of surfactant molecules to the interface and hence the foamability. Since the micelles of Synperonic A7 are more stable (longer relaxation time, τ_2) than the micelles of Brij 35 and Synperonic A50, higher dynamic surface tensions are attained and thus less foam is generated with Synperonic A7. Therefore, at large bubble lifetimes, the equilibrium surface tension determines the amount of foam generated, whereas at short bubble lifetimes (high bubble frequencies), the micellar breakup (i.e., micellar stability) determines surface tension lowering and hence the foamability.

Interestingly, it has also been found that the stability (or persistence) of a foam also depends on the method used to generate it. Foam that is formed slowly tends to have a greater stability. For example, foam created from a 200 mM SDS solution had half-lives ranging from 250 min for low (12 L/h) air flowrates to 60 min for fast (48 L/h) air flowrates (110).

Micellar stability is also a factor when foam stability is considered. The stability of a foam depends on how quickly the liquid present in the thin liquid film of the foam lamellae drains (95). The micellar structure inside the thin liquid film of foam lamellae was studied by Wasan and co-workers (111, 112). They showed that the stratification of thin liquid films can be explained by a layer-by-layer thinning of ordered structures of micelles inside the film. This structured phenomenon is affected by micellar effective volume fraction, stability, interaction, and polydispersity.

10. FUTURE DIRECTIONS OF RESEARCH ON KINETICS OF MICELLIZATION

The previous theoretical models discussed in Section 3 have done a good job of predicting the association–dissociation kinetics of micelle self-assembly. Anniansonʼs model very nicely predicts micelle kinetics at low surfactant concentrations based on stepwise association of surfactant monomers. Hence the major parameters in this model are the CMC and the total concentration of the surfactant in solution.

At higher surfactant (and hence counterion) concentrations, experimental results begin to deviate from Aniansson's model. Kahlweit's fusion–fission model takes into account the concentrations and ionic strengths of the counterions in these solutions and proposes that, as the counterion concentration increases, the charge-induced repulsion between micelles and submicellar aggregates decreases, leading to coagulation of these submicellar aggregates.

In both of these previous studies, the effect of intermicellar distance as well as the distance between submicellar aggregates has not been taken into account. As the surfactant concentration is increased, the average distance between aggregates decreases (see ICRM model in Section 5 above), thereby increasing the probability of collision between aggregates. To date, this aspect of micellar association kinetics has not been thoroughly investigated. The effect of change of micelle shape (i.e., from spherical to cylindrical and lamellar micelles) and the corresponding change in τ_2 must be carefully studied. Most importantly, the dissociation kinetics of these complex nonspherical micellar systems must be systematically investigated, as many products are supplied in concentrated form in household and industrial applications to subsequently be diluted by water for their applications.

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