

2 The nature and properties of foaming surfactants

Shampoo doesn't have to foam, but we add foaming chemicals because people expect it each time they wash their hair.

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2.1 The formation of self-assemblies from pre-micellar surfactant species

The adsorption of amphiphilic surfactant molecules at the bubble interface is not the only important phenomenon occurring during foam formation. Another extremely important process also occurs in bulk solution at high surfactant concentrations. This involves a spontaneous self-assembly process in which higher molecular structural aggregates or units of surfactant are formed from lower molecular weight pre-micellar species (monomer, dimer and trimer units). In the simplest case, this corresponds to the formation of a spherical micelle, and the transition concentration (of monomer) at which this occurs is called the “critical micelle concentration” (CMC). Marked changes in foaming behavior, as well as changes in electrical conductivity, surface tension, turbidity and uptake of organic dyes, occur in bulk solution above the CMC, but the molecular concentration of the surfactant in the water remains constant, with the surplus molecules forming additional micelles. Fig. 2.1 depicts the successive steps involved in the growth of the micelle from monomeric species, with monomers initially aggregating to form dimeric and trimeric species. As these complexes grow in size, an increasing proportion of the interface of the added monomer molecules achieves contact with the micellar hydrocarbon segments until the maximum degree of hydrocarbon/hydrocarbon interaction is reached.

For many simple long-chain linear amphiphilic surfactants, this results in the formation of a perfectly spherical complex which produces the maximum surfactant packing density. In this case, the micellar structure is complete, but difficulties may occur with some types of charged surfactants due to the repulsive charge on the head groups, and these interactions must be counterbalanced with the structure, which will result in different types of molecular arrangements within the micelle. A more detailed theoretical examination of the origins of the free energy changes which occur on eliminating the hydrocarbon/water interaction is described in considerable detail in an early classic text *The Hydrophobic Effect* by Tanford (1).

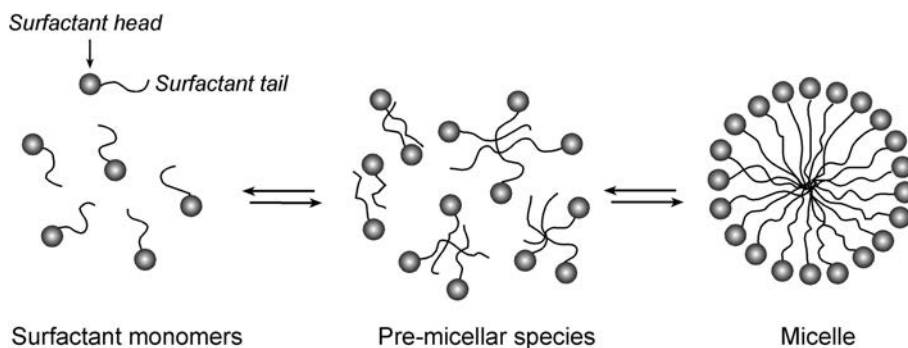


Fig. 2.1 Schematic representation of the steps leading to micelle formation.

Several different models have been used to describe the overall process of micellization, and these have been well documented in the literature (2). One model which describes the association in terms of a stepwise addition of monomer S to the aggregate S_{n-1} is represented as



where the S_n represents a micellar aggregate composed of n surfactant molecules. The aggregation number n represents the number of surfactant molecules in the micelle. If we neglect additional interactions between aggregates and monomers, the equilibrium can be expressed by the equation

$$K_n \rightleftharpoons \frac{S_n}{S(S_{n-1})} \quad (2.2)$$

This equation gives a simplified overview of the stepwise association process in dilute surfactant solutions. It has also been well established that the value of n increases with the increase in length of the hydrophobic group and decreases with increasing size of the hydrophilic group in the surfactant. It can also be shown that increasing the aggregation number and also the addition of electrolyte decreases the CMC – which can be further explained by the so-called salting-out effects. The formation of the micelle reduces the exposure of the hydrocarbon chains to water, and these small spherical micellar structures typically contain about 50–100 molecules, with the center of the micelles consisting of an essentially water-free, liquid hydrocarbon environment. Clearly, the size of the micelle is dependent on the number of hydrocarbon chains which can be inserted into the core and the density of the packing of the head groups, such that the repulsion between the charge head groups is optimized in terms of the free energy.

The conventional procedure for calculating the CMC of a strongly ionized surfactant is to measure the surface tension over a range of concentrations. In the low concentration range, the surface tension decreases linearly as a function of concentration, but beyond the CMC, the surface tension remains constant. The value of the

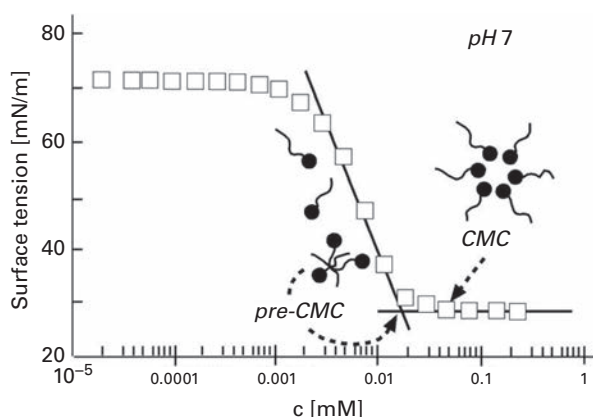


Fig. 2.2 Surface tension as a function of the concentration of soap solution. From ref (3).
The distinct break in the curve coinciding with the CMC which corresponds to the transformation of the monomer surfactant species.

CMC is taken from the intersection of the two extrapolated plots of the reduced slope, and the virtually linear horizontal line corresponding to the post-CMC concentration, as indicated in Fig. 2.2. However, in the case of a weakly hydrolysable surfactant system such as long-chain fatty acids or soaps, the process of CMC formation is more complex, and changes in the pH of the solution cause different types of pre-micellar species to be formed (3).

2.1.1 Self-association in weakly hydrolysable soaps and fatty acids

Fatty acids and soaps (Na^+ and K^- derivatives of fatty acids) are other types of fatty acid derivatives that are extensively used in both domestic and industrial applications. They account for about 30% of the current surfactant market and are classified as natural (or green) surfactants. They are obtained from various oleochemical sources such as marine, animal and vegetable oils and have been well known since ancient times. They are manufactured by saponification (hydrolysis of the triglyceride components at high temperatures and pressures) followed by acidification to yield fatty acids. Carboxyl acids have the general formula RCOOH and as soaps $\text{RCOO}^- \text{M}^+$ (e.g. sodium stearate $\text{C}_{17}\text{H}_{35}\text{COO}^- \text{Na}^+$). Most natural fatty acids are mono-functional and possess even-numbered carbon chains. In the 19th century, oleate-type soaps were well-established washing and foaming agents. The foaming of fatty acid and fatty acid salts is dependent on their solubility in water, and differences between K^+ and Na^+ have also been attributed to this. Pure sodium stearate is too insoluble to foam during handwashing, but lower molecular weight fatty acid salts are more water soluble and produce acceptable foams. Oleates (Castile soaps) are non-irritating to the skin and are mild foamers. The molecular configuration of different types of saturated and unsaturated fatty acids is illustrated in Fig. 2.3. Stearic acid has only single carbon-carbon bonds, so its chain is flexible and can stretch into a zigzag or roll up into a compact ball. Oleic acid is an

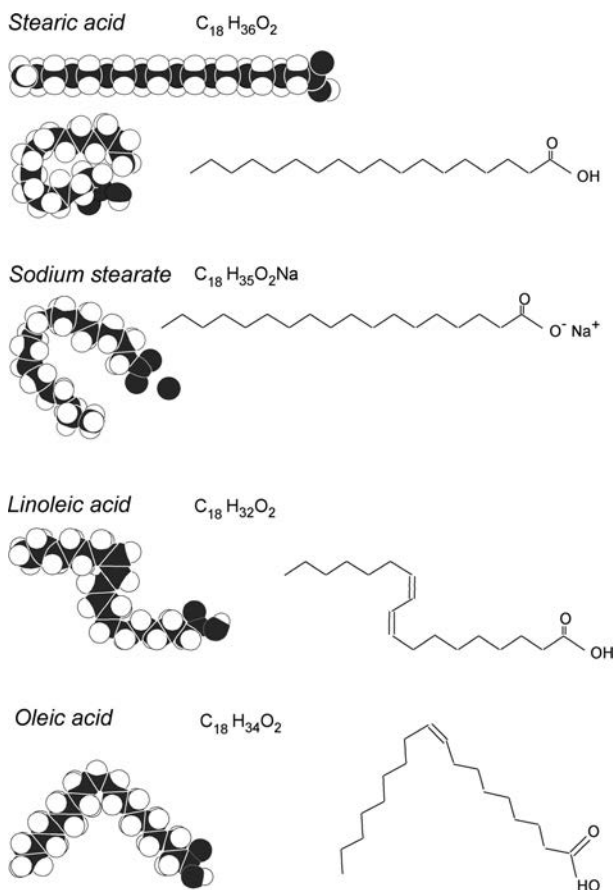


Fig. 2.3 Configuration and structure of fatty acid molecules which consist of a long chain of carbon atoms with a carboxylic end group.

unsaturated fatty acid with a double bond between neighboring carbon groups, and the double bond has an important influence on the shape of the molecule. Linolenic acid has three double bonds, and is a polyunsaturated fatty acid with a more rigid structure.

Fatty acids are weakly hydrolysable surfactants in water and are extremely sensitive to pH. Although they are usually fully ionized or dissociated at high pH, at lower pH values, the degree of dissociation and solubility is reduced. Essentially, the extent of dissociation of the fatty acids in water is defined by the dissociation constant pK_a which controls the number of surfactant molecules that can ionize to form carboxyl head groups, as indicated by



$$pK_a = (RCOO^- + H^+) / (RCOOH) \quad (2.4)$$

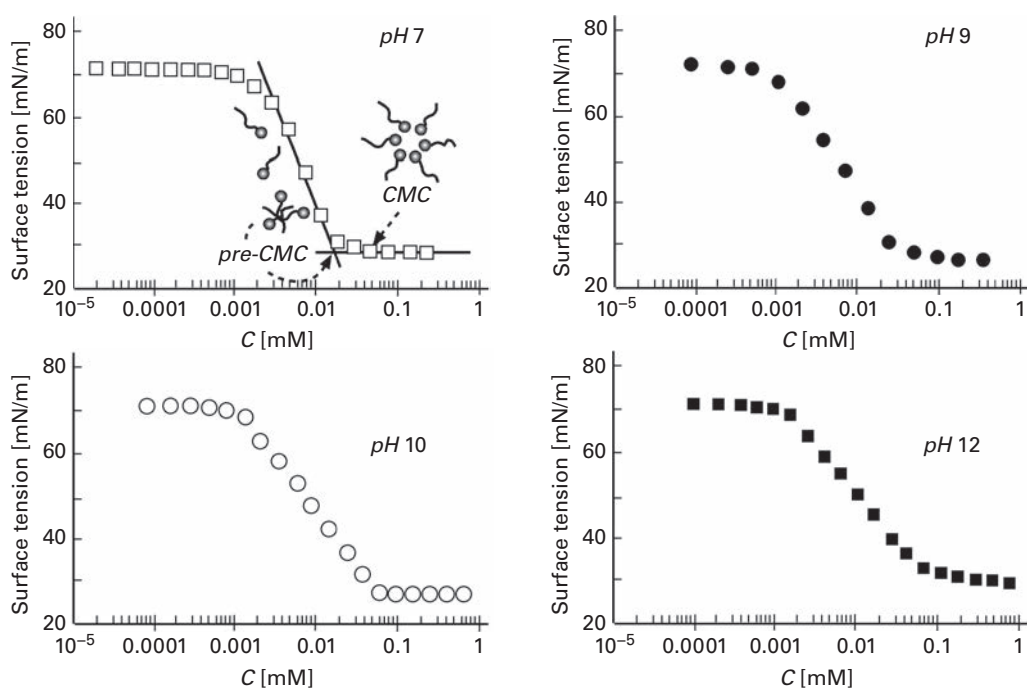


Fig. 2.4 The equilibrium surface tension of sodium oleate solution versus concentration, at four different pH values, measured with the du Noüy ring method at 25°C. From ref (3).

The pK_a value is defined as the critical pH of the solution where 50% of the molecules are ionized and 50% are in the un-ionized form. It has also been well established that the value of the pK_a of long-chain acids increases with the chain length of the molecule. For short-chain length, pK_a is about 4, but this value increases for longer chain fatty acids (e.g. stearic acid has a pK_a of ~8). Recent studies carried out with oleic acid/sodium oleate have shown that the equilibrium surface tension and foaming behavior are highly sensitive to pH over the range of 7–13, with the CMC fluctuating over different values (3). These effects have been explained by pronounced pre-micellar activity leading to the formation of complexes such as dimers and acid soaps in dilute solution (below the CMC at the intermediate pH region). Pre-micellar aggregates have also been well documented in the earlier literature for both anionic and cationic surfactants and play an important role in the flotation of mineral particles (4). For the oleic acid/sodium oleate system, the surface tension versus concentration plots at different pH values is shown in Fig. 2.4, where the influence of the CMC on pH can be noted.

At intermediate values of pH, the CMC can be easily identified by the conventional procedure (see Section 2.1), but at higher pH, a more gradual reduction in slope occurs and the CMC becomes less defined. This anomalous behavior has still not been fully explained, but it is believed to involve formations and interactions between pre-micellar fatty acid solution species. Pre-micellar aggregation has also been reported

for strongly ionizable anionic systems (such as sodium dodecyl sulfate), and the process has been shown to play a significant role in the drainage and stability of thin foam films (5) and has been detected at very low concentrations (two orders of magnitude lower than the CMC).

2.1.2 Solubility and the Krafft point

The Krafft point (also known as the Krafft temperature or the CMC temperature) is the minimum temperature at which ionic surfactants begin to solubilize and form micelles. Below the Krafft point, no micelles can form, and hence there is no CMC value, the surfactant exists in a crystalline form in aqueous solution and the solubility is restricted. Above the Krafft point, a phase change occurs, causing a pronounced increase in solubility. Since the micellization process is entropic, an increase in temperature causes stronger forces to break-up the crystalline state of the surfactant accompanied by self-solubilization of monomer species producing micelles. The value of the Krafft point can be obtained by the extrapolation of a plot of the surfactant concentration in solution versus temperature, which is usually represented in the form of a phase diagram. The intersection of the CMC concentration curve and the surfactant solubility curve corresponds to the Krafft point. This situation is illustrated in Fig. 2.5.

The dramatic increase in the total solubility of the surfactant above the Krafft point is due to the interplay between the temperature-dependent solubility of the surfactant molecules and the dependence of the CMC on temperature. It has been shown that the Krafft point is dependent on the structure of the surfactant molecule and increases with an increase in length of the alkyl chain. Differential packing arrangements of surfactant molecules and their stability in the structural

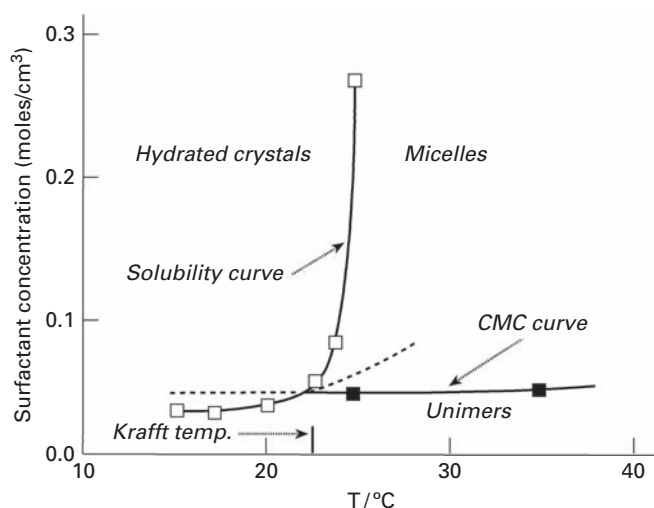


Fig. 2.5 The Krafft point (Krafft temperature) of sodium decyl sulfonate obtained from a phase diagram. From ref (6).

aggregates play an important role in defining the Krafft point. Generally, strong interactions between head groups increase the stability of the aggregates, leading to an increase in the Krafft temperature. An increase in electrolyte concentration (which causes a decrease in the head group repulsion) can also increase the packing density, which in turn increases the Krafft point. The degree of saturation of the hydrocarbon chain is also important and the addition of double bonds into the hydrophobic chain of the surfactant often reduces the stability of the aggregate, causing a reduction in the Krafft point. The presence of liquid crystal-type aggregates in the surfactant solution has an important influence on foaming and is discussed in detail in Chapter 6.

Many nonionic surfactants with polyethylene chains or glycol-type surfactants do not exhibit a Krafft point and as the temperature is increased the solubility decreases and a pronounced two-phase separation occurs, causing precipitation of liquid crystalline aggregates. This can act as a foam breaker. This reversible solubility occurs at a specific temperature known as the cloud point; it is due to the dehydration of the polyethylene chains and has an important influence on foaming.

2.2 Geometric packing of surfactant molecules in the interface and the critical packing parameter

In considering the interaction between surfactant molecules within a self-organized aggregate, either in bulk solution or within the gas–liquid interface, it is important to examine the packing of the molecules with respect to their most preferential structural arrangements (7). In fact, it is the simple geometry of a molecule (expressed in terms of the length, area and radius) that has been utilized to define its packing parameter, and this controls the aggregate shape. The dimensionless critical packing parameter (CPP), or molecular shape factor, is expressed as

$$\text{CPP} = \frac{V_h}{a_h l_c} \quad (2.5)$$

where V_h is the volume of hydrocarbon surfactant shape or chain, l_c is the length of the hydrocarbon chain and a_h is the effective head group area. In this simplified treatment, the molecule is assumed to be incompressible and fluid. The CPP concept provides valuable insight into how the molecular structure of the surfactant influences the architecture (size and shape) of the aggregate. In addition, the CPP defines the orientation and packing of the molecules at the air–water interface. It also plays an important role in defining the magnitude of the interfacial elasticity and rheology, and both these parameters influence the foamability. In Fig. 2.6(a), the packing arrangement of an amphiphile (sodium lauryl sulfonate) consisting of long, straight-chain aliphatic hydrocarbon tails within a spherical micelle is illustrated. The packing is controlled by the effective area of the head group, the hydrophobic chain length and the volume, according to Equation (2.5) and in Fig. 2.6(b), at the bubble interface,

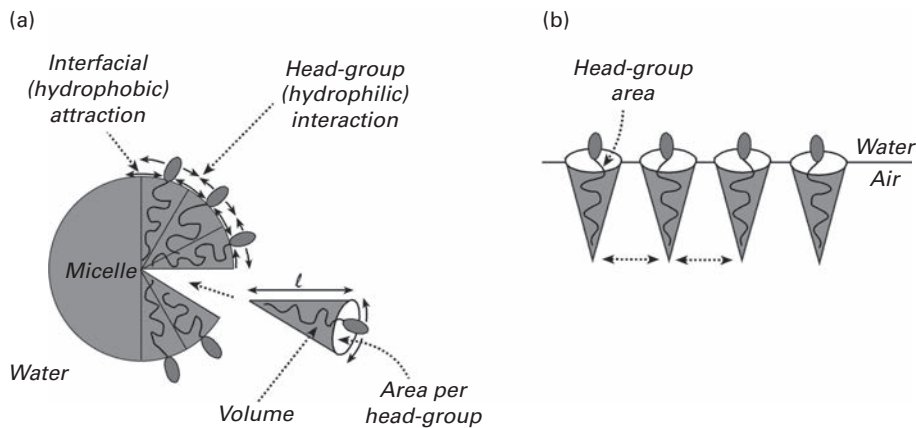


Fig. 2.6 The packing arrangement of long-chain aliphatic hydrocarbon molecules (e.g. sodium lauryl sulfonate) in (a) spherical micelles, (b) adsorbed at the bubble interface.

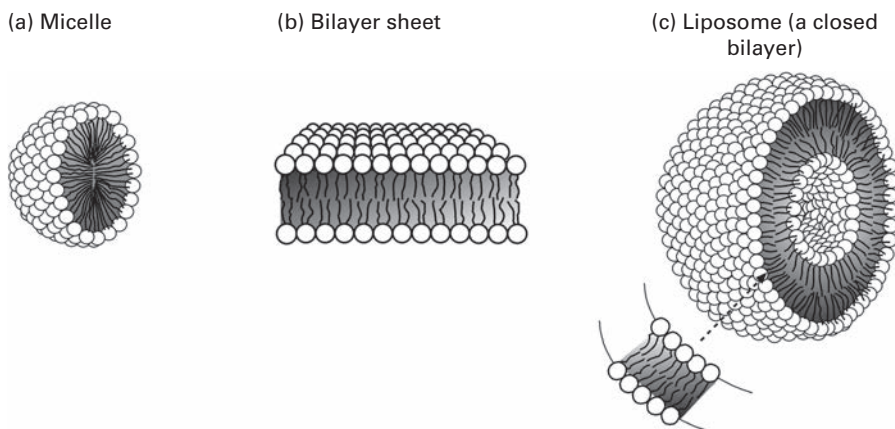


Fig. 2.7 Self-organized structures. Essentially, the aggregate shape depends on the packing parameters.

where the head groups and hydrocarbon tails are separated by well-defined intermolecular distances.

In addition to spherical micelles there are several other types of self-assembled structures that can be formed from surfactant molecules in solution. In fact, a wide variety of complex, associated structures can be formed. These include poly-dispersed cylindrical micelles, reverse micelles, vesicles, oblate micelles, bilayers; examples of these are shown in Fig. 2.7. Flexibility of chains, intermolecular forces and the physical restraints on the surfactant molecules – all contribute toward the nature of the aggregate structure, which must satisfy a minimum energy criterion. In all cases, a simple relationship exists between the molecular structure, the CPP value and the nature of the packing at the air/water interface; this is illustrated in Fig. 2.8. Small values of CPP infer a closely packed curved aggregate, but when CPP is close

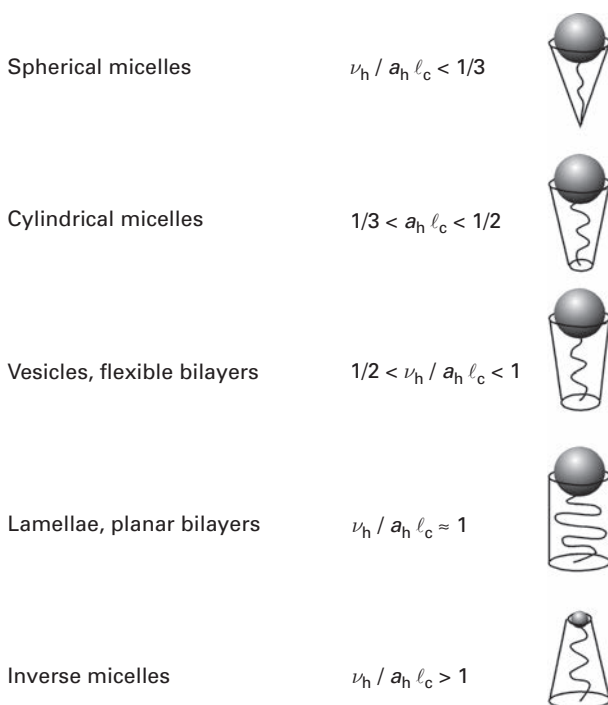


Fig. 2.8 Surfactant packing parameters for different surfactants corresponding to cones, truncated cones and cylinders in bulk solution and the packing at the air/water interface. From ref (7).

to unity, planar bilayers usually form in bulk solution. Due to shielding of the head group, which enables the molecules to pack closer, the presence of salt in the solution can increase the packing density of ionic surfactants. This also has the effect of reducing the CMC and lowering the surface tension in the region of the CMC.

Spontaneous self-organization processes are an important part of nature and an essential part of natural evolution. Interestingly, many of these more complex structures have some resemblance to that of biological cells, and these aggregates closely resemble the kind of structures observed in living membranes. Many biological complex structures evolve through such packing arrangements. The Nobel Prize in Physiology or Medicine in 2013 was awarded for research in vesicles. Understanding the functionality of these self-assembles is important in cell division and the regulation of bodily systems which are related, for example, to diabetes and botulism.

2.3 Phase behavior of more concentrated surfactant formulations

A knowledge of the phase behavior of surfactants in *concentrated solutions* is important since this plays a dominant role in defining the bulk viscosity and hence the drainage rate in foams. It is well known that high viscosity solution can drastically reduce drainage and enhance foaming. This effect is very important in (a) mixed surfactant

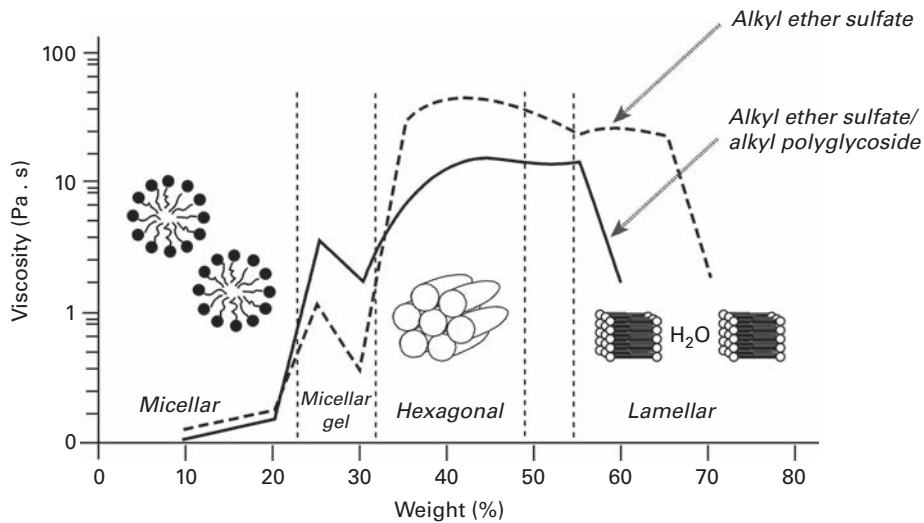


Fig. 2.9 The relationship between the viscosity and concentration of alkyl ether sulfate surfactant and a mixture of alkyl ether sulfate and alkyl polyglycoside. From ref (11).

systems, (b) surfactant/polymer and (c) surfactant/particle mixtures. In Fig. 2.9, the relationship between viscosity and the concentration is shown for an anionic surfactant (alkyl ether sulfate) and for a mixture of alkyl ether sulfate and a nonionic surfactant (alkyl polyglycoside). In the region between 20 and 30 w% surfactant, a micellar gel is formed, and at a higher concentration, transformation into the hexagonal crystalline phase occurs, producing high viscosities but it is considerably reduced on reaching the lamellar phase

2.4 The influence of the Critical Packing Parameter on foaming

The CPP is very sensitive to foaming and it has been generally accepted that increasing the CCP leads to an increase in the adhesive interactions between the well-packed, long-chain molecules adsorbed at the air/water interface, resulting in an increase in resilience of the interfacial film and a positive effect for foaming. However, other factors need to be taken into consideration, such as the charge on the surfactant head group which can lead to a decrease in packing density and poor film resilience. In addition, disturbances can occur from external thermal fluctuations, and these may be of sufficient magnitude to cause holes that can lead to rupture of the thin film foam lamellar. In fact, surfactants with high CCP values are more vulnerable to film rupture caused by the formation of cavities. This film destructive process tends to counter the positive cohesive force effect (which is positive for foaming) such that there may be a critical CCP which corresponds to maximum foaming performance.

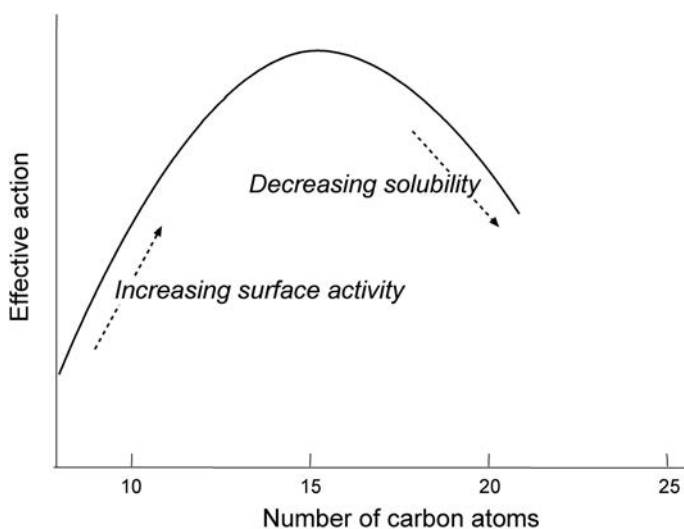


Fig. 2.10 Variation in effectiveness of surface activity (e.g. foaming) versus the carbon chain length of the surfactant. From ref (9).

2.5 The influence of surfactant solubility on foaming

In many surfactant systems, particularly for a homogeneous series of straight chain aliphatic surfactants, solubility plays an important role. In the short alkyl chain length regimes, the surface activity increases with chain length, but beyond a critical value, the solubility begins to decrease with increasing chain lengths so that a maximum or optimum value in surface activity occurs, resulting from a balance between the two opposing effects. This is known as the Ferguson effect and has been used to explain why an increase in the molecular weight of the linear alkyl chain of a homogeneous series of surfactants causes an increase in surface activity (foaming) until a decrease occurs at a critical chain length. This situation is illustrated in Fig. 2.10 and is particularly important, not only for foaming, but also in processes such as detergency and emulsification.

2.6 Anionic surfactants

The concept of CCP and both the Krafft temperature and the Ferguson effect can be used to explain the foaming behavior of a homogeneous series of linear alkyl chain anionic surfactants; for example, the alkyl sulfate series as shown in Fig. 2.11, where the foaming properties vary over a wide range of chain lengths (at 60°C), with the maximum foam volume corresponding to an alkyl chain with 16 carbon atoms.

From the point of view of the CCP concept, this result can be explained by the balance between the two opposing interactions: the strong cohesive interactions which dominate

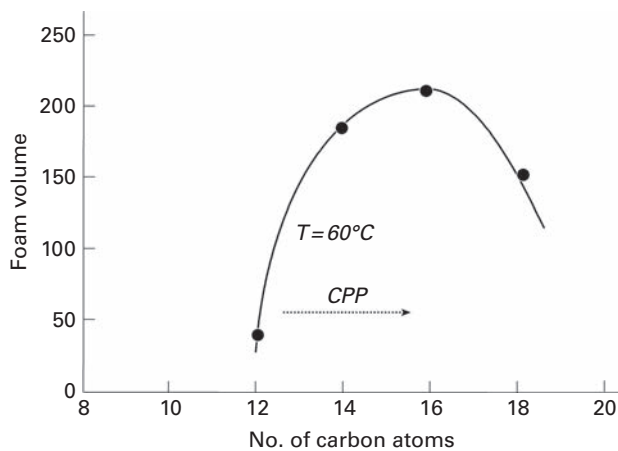


Fig. 2.11 Foam volume (at 60°C) for a homogeneous series of straight chain alkyl sulfates showing a maximum for the surfactant alkyl chain with 16 atoms. From ref (10).

in the shorter chain length regimes and increase with chain length and the longer chain length cavity formation that dominates and also increases at higher chain length. However, temperature is critical, and at lower temperatures, the Krafft point may play a role, since at 40°C it has been reported that the C₁₄ alkyl chain length gives the highest foaming while at 20°C the C₁₂ is the highest. It has also been reported that for sodium dodecylbenzene sulfonate and sodium dodecyl sulfate (SDS) as the temperature is raised the foam volume (in shaking tests) is increased but the stability is reduced. However, in some of these studies, it is possible that hydrolysis of sodium dodecyl sulfate occurred producing alcohol impurities (10).

2.7 Nonionic surfactants

In the case of nonionic polyoxyethylene (POE) surfactants, the foaming performance (foaming volume and stability) was reported to reach a maximum at a particular oxyethylene chain length before decreasing (11). This was explained by the balance between the intermolecular cohesive forces and van der Waals interactions between molecules in the adsorbed film. The POE chains in the nonionic surfactants are coiled in the aqueous phase and the cohesive forces (due to intra- and intermolecular hydrogen bonding) pass through a maximum with increasing oxyethylene content. For the nonyl phenolics, the maximum foam height of the series has been determined by changing the length of the polyethylene chain, and maximum foaming was found to occur in the region of 70–80 wt% of the polyoxyethylene chain content. This maximum corresponds to 20 ethoxy groups per molecule (NP-E20), as shown in Fig. 2.12. This behavior has also been explained by the cavity formation effects dominating at low chain lengths (low CPP region) but with cohesive chain interactions increasing at high chain lengths.

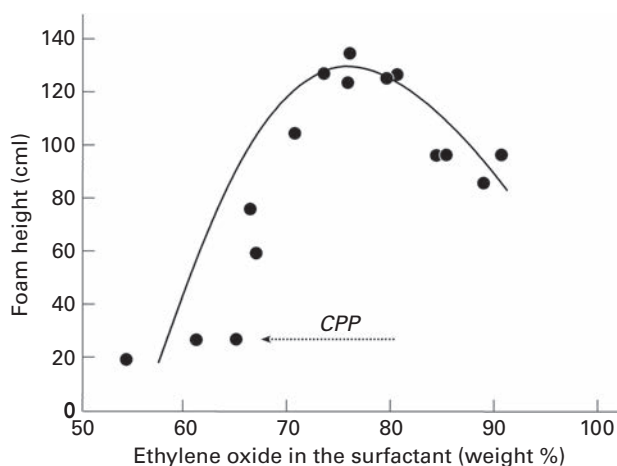


Fig. 2.12 Ethoxylated nonyl phenols show a maximum foamability (as determined by the Ross–Miles test) when the polyethylene chain constitutes about 75% of the surfactant. From ref (10).

In addition, the influence of the cloud point on the performance of nonionic surfactants is well noted in the literature, and it has been established that for POE, the foam performance decreases at or above the cloud point (11). This was originally attributed to the aggregation of the dehydrated micelles and a reduction in the rate of diffusion of monomer from these aggregates to the newly created interface. However, an alternative explanation is based on the idea that, above the cloud point, liquid crystal-structured aggregates attach to the lamellar interface, reducing drainage. In the case of the polyethylene oxide series ($C_{16}E_4$), according to the CCP theory, the shorter chain length molecules pack at the interface with a higher density and the CPP increases with increase in chain length. Lower CPP values usually promote higher cohesion between hydrocarbon chains, giving improved interfacial elasticity and higher foaming.

2.8 Weak hydrolysable fatty acids

Several studies have shown that it is important to understand the orientation and packing of the associated solution complexes at the bubble interface (12, 13, 14). These parameters play an important role in defining both the dynamic and equilibrium surface tension and also dictate the strength, elasticity and stability of a surface film. With an increase in the degree of ionization of the head groups, the magnitude of the net charge on the surface polar groups is increased, causing an increase in the intermolecular repulsion.

It has been reported that the association between ionized and nonionized molecules occurs at the pK_a value of the fatty acid and causes strong attractive ion–dipole interactions which result in high packing densities (minimum area per molecule) in critical pH regions. At pH values lower than pK_a , the film is largely un-ionized (in the molecular

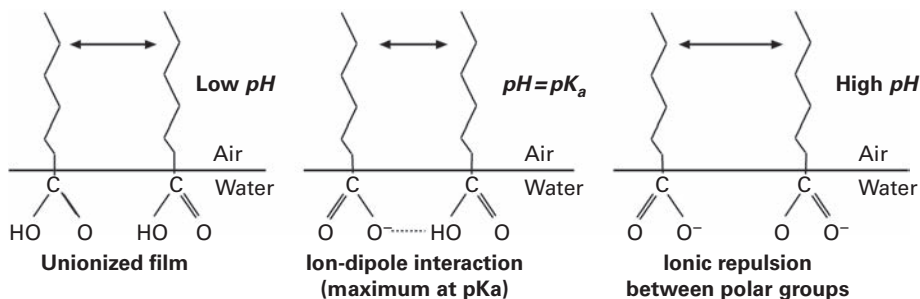


Fig. 2.13 The interaction between ionized and nonionized fatty acid species at different pH values. From ref (12).

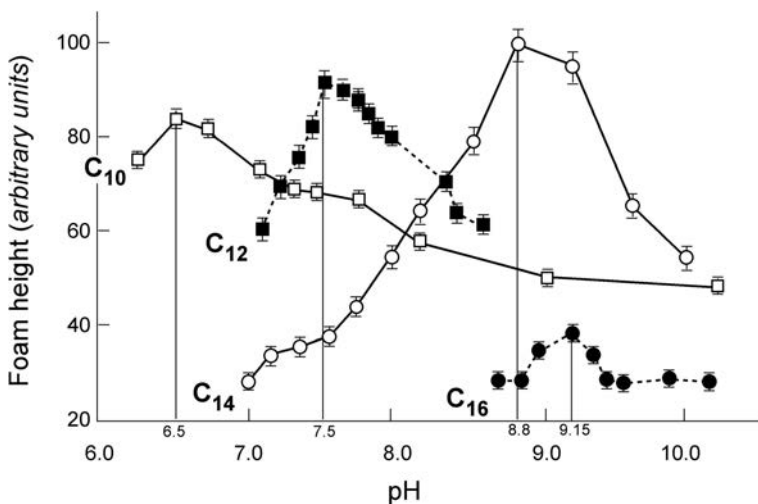


Fig. 2.14 Relationship between chain length pK_a and foamability (initial foam height) of a series of fatty acids. For C_{10} , pK_a 6.5., for C_{12} pK_a 7.8, for C_{14} , pK_a 8.8 and for C_{16} pK_a 9.15. Results obtained by shaking tests. From ref (27).

form), but at pH values higher than the pK_a , the film is almost completely ionized, causing repulsive head group interactions and low compactness. In Fig. 2.13, the ion–dipole interaction between ionized and un-ionized molecules of a fatty acid is shown at different pH values (at the pK_a and at high pH above and at low pH below pK_a).

Kanicky and coworkers (12, 13) showed that by changing the pH of solutions of a series of long alkyl chain fatty acids, the maximum foaming correlated with the pK_a , as illustrated in Fig. 2.14, and it was also found that the highest interfacial packing and surface rheology also corresponded to this value.

Moreover, these studies also revealed that in addition to foaming performance (foam height, foam stability and single bubble stability), the magnitude of several other physicochemical parameters (evaporation rate, surface viscosity and wetting) correlated with the pK_a of the fatty acid. The results obtained from the study on the

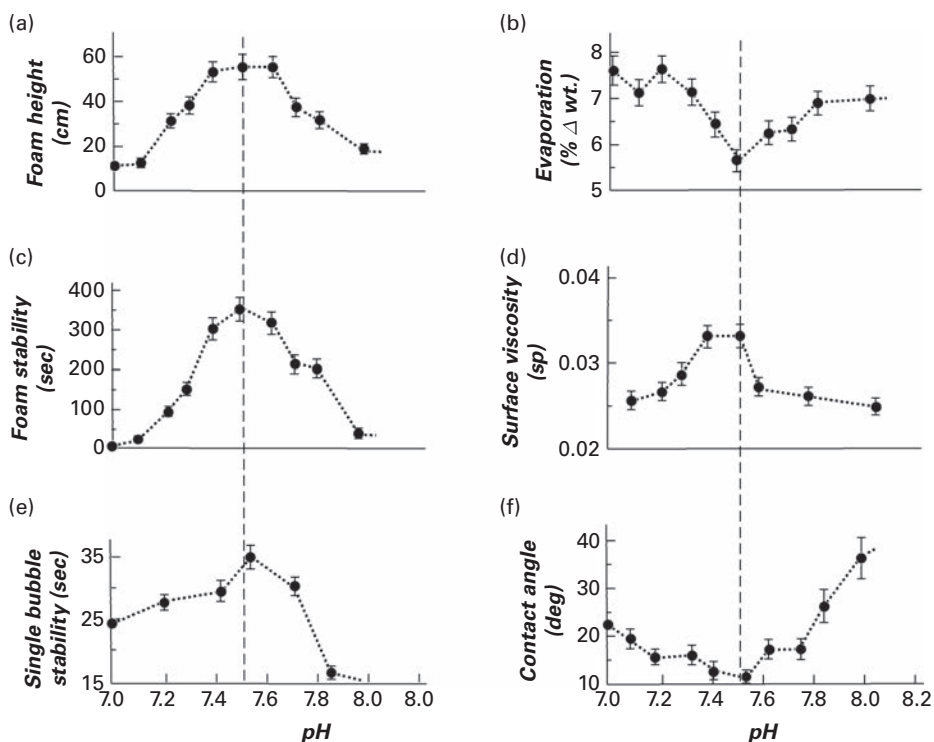


Fig. 2.15 The maxima and minima in various interfacial properties with respect to pH for sodium laurate solution pK_a 7.5. From ref (13).

lauric acid/sodium laurate solution are shown in Fig. 2.15. This type of research is clearly important for many technological processes which involve fatty acids.

2.9 Mixed surfactants

Later studies by Patist and coworkers (14) showed that interfacial packing compatibility was particularly influential on the foaming performance of strongly ionized mixed surfactant systems. For example, the addition of low concentrations of a cationic surfactant (tetra-alkylammonium chloride, such as tetra-ethylammonium chloride, TC₂AC) to an anionic surfactant (sodium dodecyl sulfate, SDS) solution causes a decrease in electrical repulsion, since the TC₂AC adsorbed below the SDS monolayer neutralized the charge and increased the packing and foamability. However, at higher concentrations, the TC₂AC was found to penetrate into the SDS monolayer, decreasing the intermolecular distance (area per molecule) and the foaming. The molecular packing arrangements for these systems are illustrated in Fig. 2.16.

The overall effect of the critical surfactant ratio on the bubble stability, foam lifetime (stability), foam volume (foamability), foam half-lifetime, surface viscosity and the

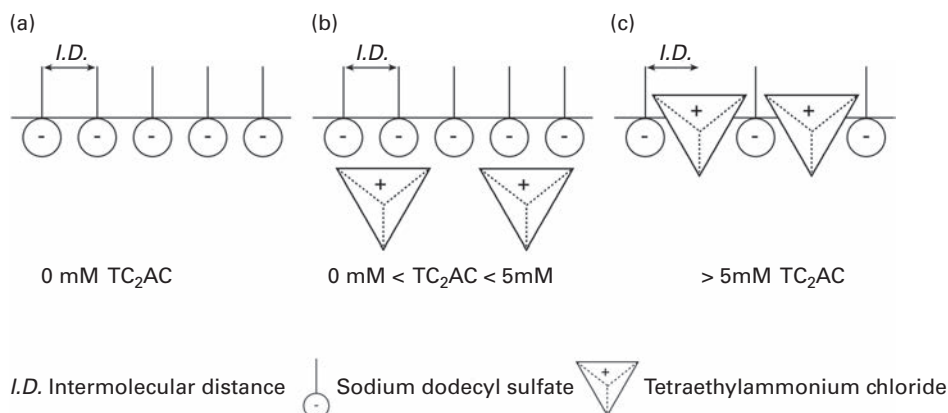


Fig. 2.16 Schematic diagram showing the effect of tetra-alkylammonium chlorides on the SDS molecular packing: (a) pure SDS, (b) decrease in electrical repulsion due to adsorption of TC_2AC below the SDS monolayer results in a smaller area per molecule, (c) penetration of TC_2AC into the SDS monolayer increases the area per molecule. From ref (14).

surface tension is shown in Fig. 2.17. Similar trends were also reported for the effects of long chain alcohols on sodium dodecyl sulfate (15).

2.10 The influence of the CMC on foaming

In accordance with Gibbs adsorption theory (Chapter 1), it has been well established that the foaming performance of surfactants in dilute solution (below the CMC) increases with the concentration; this correlates with the decrease in surface tension and increase in surface activity. In fact, usually a linear relationship between the concentration of surfactant in solution and the initial foam height has been reported. However, at concentrations close to the CMC, a maximum in foamability is reached and then often remains constant at higher surfactant concentrations. Experiments carried out by Badwan and coworkers (16) illustrate this behavior. In this study, data were recorded from three different types of foaming test: the Ross–Miles test, a rotation (or stirring test) using a commercial mixer and a foaming column with a sintered base. The foam volume was measured at a range of concentrations on two series of purified surfactant samples: (a) a cationic surfactant, triethanolamine, and (b) an anionic surfactant, sodium alkyl sulfate, shortly after generating the foam. The CMC of the surfactants was determined by surface tension measurements and conductivity. The results for the series of triethanolamine alkyl sulfate surfactants in which the alkyl chain length of the linear alkyl group varied from $n = 10$ to 18 versus the concentration of surfactant (expressed in terms of the CMC) are shown in Fig. 2.18.

For the different higher alkyl chain length surfactants in this series, maximum foaming corresponds to the CMC in all cases and then remains constant at concentrations above the CMC. In addition, the highest foaming performance corresponds to C_{10}

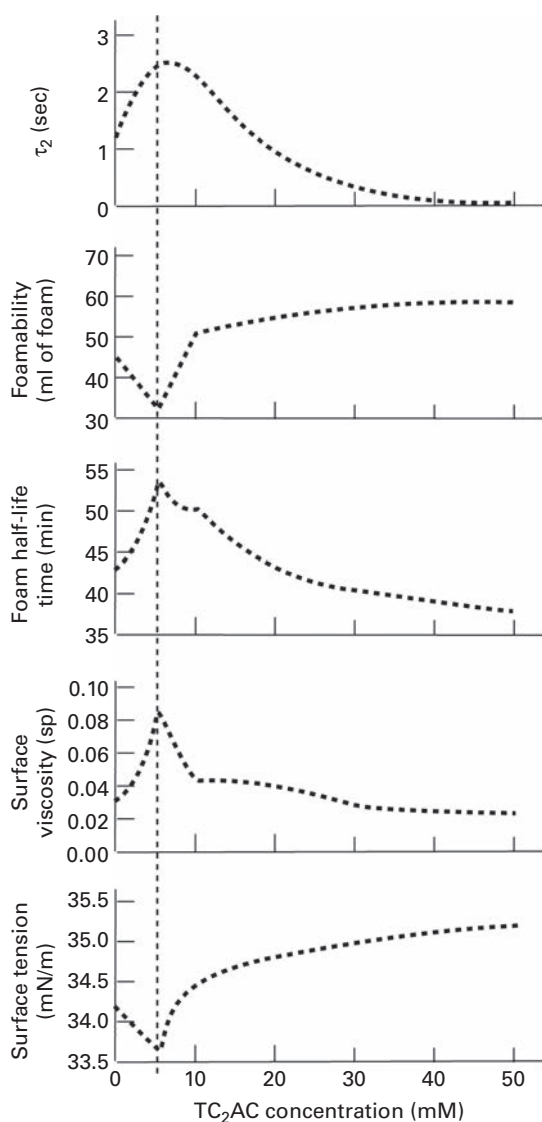


Fig. 2.17 The effect of tetra-alkylammonium chloride (TC_2AC) on the foaming properties of sodium dodecyl sulfate (SDS) solution (150 mM). From ref (14).

and then decreases with increase in chain length to C_{18} . Similar results were found for the sodium alkyl sulfates which were in agreement with earlier experiments by Dreger and coworkers (15). Generally, surfactants with lower CMC values are known to be more effective foamers at lower concentrations. Therefore, additives (inorganic and organic) which lower the CMC act as foam boosters. For example, addition of an inert electrolyte such as sodium chloride may increase foaming. In addition, increase in the temperature usually results in lowering the CMC, and this causes foaming to occur at lower concentrations.

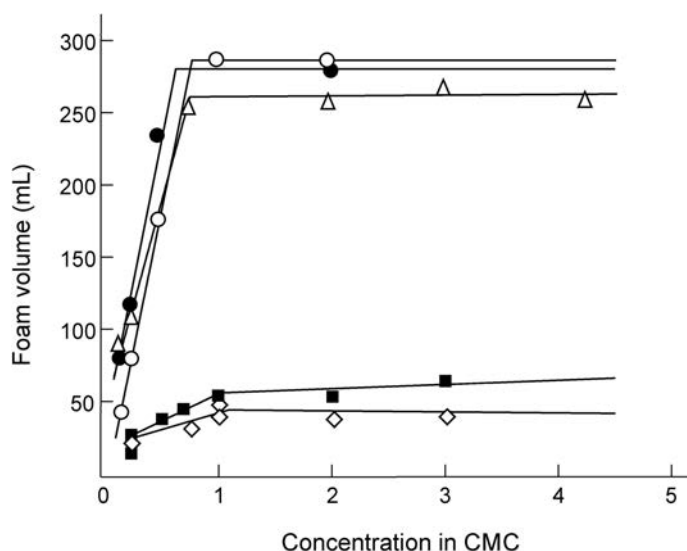


Fig. 2.18 The foam volume versus concentration (expressed as CMC) of triethanolamine Cn sulfate as determined by the Ross–Miles test, where $n = 10$ (○), $n = 12$ (●), $n = 14$ (△), $n = 16$ (■), $n = 18$ (◇). From ref (16).

2.11 Foaming above the CMC: the influence of the stability of the micellar self-assemblies

Foamability relies on rapid transport of the surfactant monomer to the bubble interface. At concentrations below the CMC, it is the concentration and size of monomer in solution which plays the primary role in the kinetics of diffusion, adsorption and foaming. In this low concentration range, the transport of surfactant is relatively slow, but as the concentration in bulk solution increases, the diffusion becomes rapid, allowing sufficient surfactant to adsorb at the interface to stabilize the foam. In the region of the CMC, the foamability reaches a maximum.

However, beyond the CMC, the nature of the micelles becomes important, since these aggregates are transient species which disintegrate and reform very quickly. For spherical micelles, this dynamic break-up process has been characterized by an overall relaxation time constant (τ) which can be determined by a range of experimental methods such as stopped flow, temperature jump, pressure jump and ultrasonic absorption. Further studies have shown that this relaxation process can be defined by two separate steps: (a) a fast relaxation process (τ_1) associated with the quick exchange of monomer and micelle in bulk solution (which occurs in the order of micro-seconds) and (b) a second relaxation time (τ_2) which is slower (in the order of milliseconds) and has been attributed to micelle formation and disintegration. These two dynamic processes are depicted in Fig. 2.19.

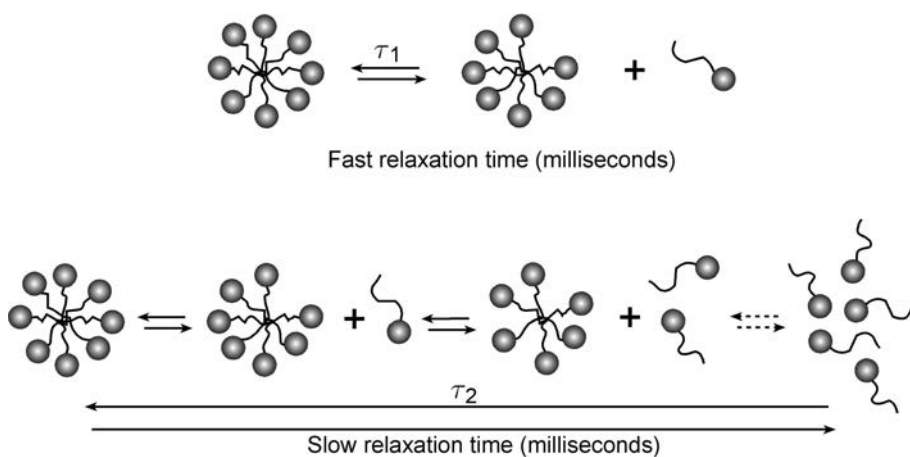


Fig. 2.19 Surfactant solutions above the CMC. The mechanism (a) relaxation time τ_1 which is attributed to the equilibrium between monomer in solution and the micelle and (b) τ_2 attributed to the micelle formation and disintegration of the micelle. From ref (17).

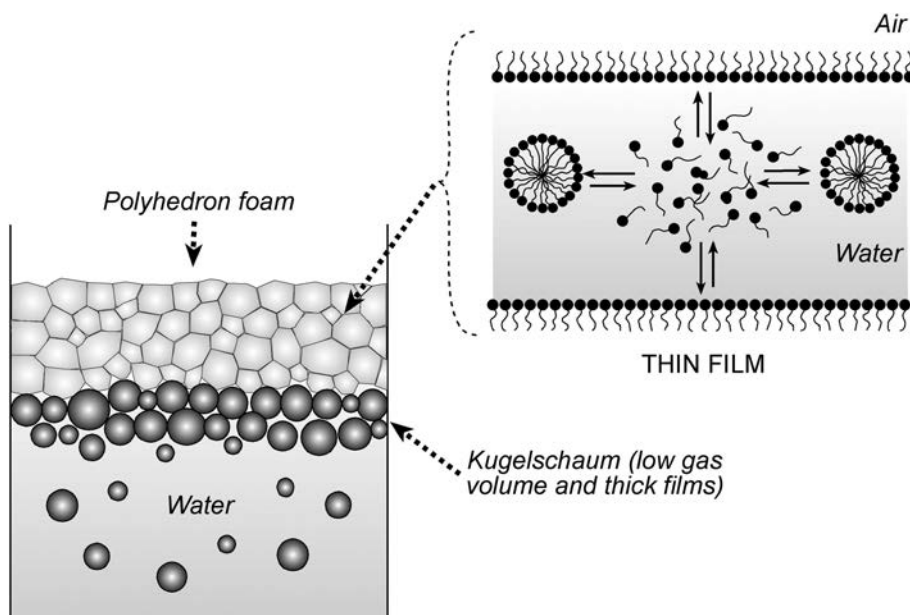


Fig. 2.20 Schematic representation of the adsorption of surfactant onto a newly created bubble interface due to disintegration of micelle during foam generation. From ref (17).

The micelle disintegration associated with τ_2 has been shown to play a particularly important role in the foaming kinetics, since the micelle acts as a reservoir to supply monomer to the foam lamellae interface (17). This mechanism is illustrated in Fig. 2.20.

In fact, it is the kinetics of micellar break-up defined by the relaxation time τ_2 which governs the disintegration and release of monomer and which acts as a rate-determining

step in the generation of foam. The degree of stability of the micelle depends on the type and concentration of surfactant and the presence of other types of surfactants in solution. For example, nonionics and mixed surfactant systems can have τ_2 values of several minutes. These are fairly stable micellar systems due to the absence of ionic repulsion between head groups; for example, polyoxyethylene alkyl ethers such as Triton X-100. However, ionic micelles, (e.g. sodium dodecyl sulfate) exhibit short relaxation times, with τ_2 in the range of milliseconds to seconds, and also high foamability.

Patist and coworkers (17, 18) experimentally demonstrated that foamability is related to the presence of spherical micelles in surfactant solutions and found a direct correlation between the dynamic surface tension, micellar relaxation time and foaming. When air is blown through a surfactant solution, a substantial amount of interfacial area is created during the bubble generation process and molecules from bulk solution are required to diffuse and adsorb to this interface in order to reduce the surface tension. In systems with very stable micelles, monomer cannot be released rapidly, so the surface tension remains high, giving poor foaming performance. In the opposite case, for surfactant systems with less stable micelles, the interfacial tension is rapidly reduced, which assists foam generation.

Experimental foaming studies (17) were carried out with three nonionic commercial surfactants: Synperonic A7 (an alkanol ether, C_{12} – C_{15} (EO₇)); Brij 35, a lauryl alcohol ether (EO₂₃); and Synperonic A50 (an alkanol ether; C_{12} – C_{15} (EO₅₀)), with $\tau_2 = 150$ s, 80s and 40s equilibrium surface tension values corresponding to 29 mN/m, 38.7 mN/m and 49.5 mN/m, respectively. Foams were generated by two different methods: (a) by slowly blowing air through a single capillary, which was submerged in surfactant solution, and (b) by vigorous handshaking. The volume of foam produced by the different processes was then compared with the surface tension data (Fig. 2.21). In the single capillary bubble test, the foam volumes are shown to decrease according to the order Synperonic A7 > Brij 35 > Synperonic A50, and in this generation method, it is the break-up time of micelles which determines the flux of surfactant to the bubble interface, and hence its foamability. It can also be concluded that there was sufficient time for the more stable micellar system (Synperonic A7) with a lower equilibrium surface tension to release monomer to stabilize the bubbles and give low dynamic surface tension values. However, under high shear conditions (vigorous handshaking) where a large surface area was rapidly created, the opposite order of foamability was observed. In this case, the Synperonic A50, with the shortest micellar break-up time but higher equilibrium surface tension, yielded the greatest volume of foam while the more stable micellar Synperonic A7 with the higher equilibrium surface tension gave a lower foam volume. To summarize, it is the micellar break-up time in relation to the foam generation method which plays an important role in the foamability.

Patist and coworkers (17, 18) also suggested that foaming performance can be controlled by specifically designing the micellar structure (in order to control the break-up characteristics) by using mixed surfactants to change the relaxation time of the micelle. This concept was demonstrated using mixtures of anionic/nonionic (sodium dodecyl sulfate/dodecanol) and anionic/cationic (sodium dodecyl sulfate/alkyltrimethylammonium bromide) systems, as shown in Fig. 2.22, where the mixed micellar systems

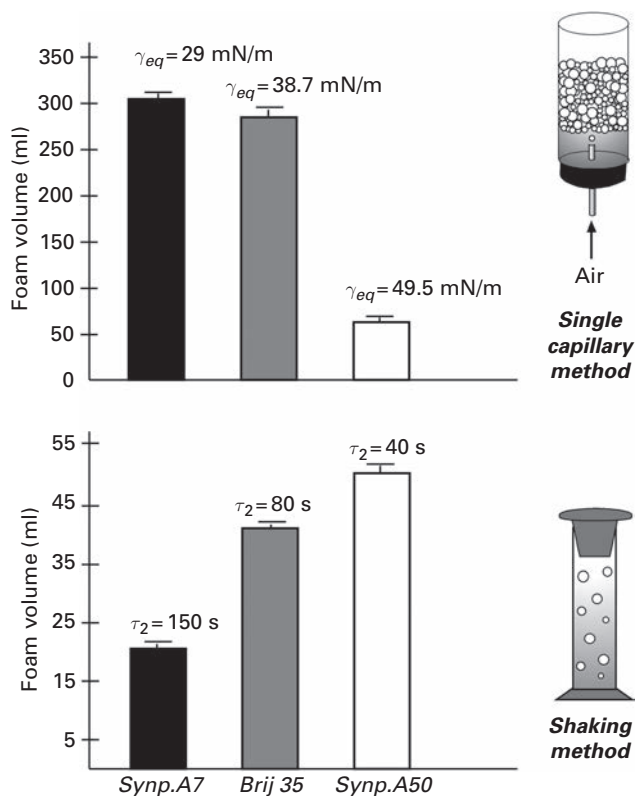


Fig. 2.21 The influence of the foaming method on the foamability of 2 mM solution of different nonionic surfactants – Synperonic A7, Brij 35 and Synperonic A50 – with different micellar lifetimes. From ref (18).

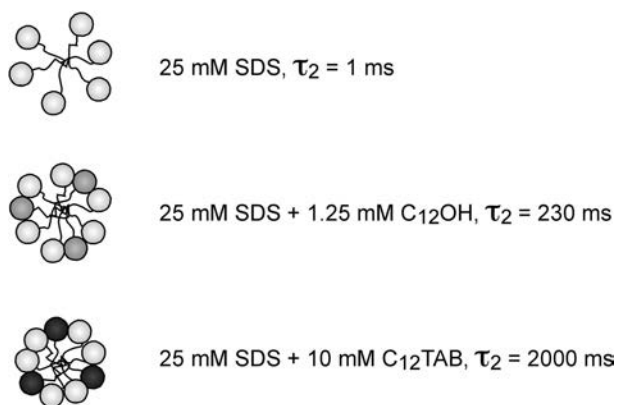


Fig. 2.22 Tailoring SDS micellar stability by the addition of 1-dodecanol (C₁₂OH) or alkyltrimethylammonium bromide (C₁₂TAB). From ref (17, 18).
The 25 mM SDS exhibits loosely packed micelles while the 25 mM SDS + 1.25 mM C₁₂OH and the 25 mM SDS + 10 mM C₁₂TAB exhibits more tightly packed micelles.

have longer break-up times compared to the sodium dodecyl sulfate/alkyltrimethylammonium bromide mixed micellar system which is the most stable.

Again, vigorous handshaking was carried out and differences in foaming performance were reported between pure SDS and the SDS/C₁₂OH mixtures, especially at low SDS concentrations, where the SDS/C₁₂OH and SDS/C₁₂TAB mixed systems produced much less foam than the single surfactant SDS system. This was again explained by the ability of micelles to break-up in order to provide monomers to stabilize the fresh interface. Very stable micelles cannot break-up fast enough to provide sufficient surfactant flux to stabilize the interface. All these studies emphasize the importance of the micelle break-up as the rate determining step in foamability.

A further example illustrating the relationship between aggregates' stability and foaming was demonstrated by Duer-Auster and coworkers (19) for the case of polyglycerol ester (PGE) surfactants. Above the CMC, these molecules were known to produce structural self-assemblies which consist of uni- or multi-lamellar vesicles, and at high concentrations, the amount of monomer in solution is restricted, so that an extended time is required to stabilize the interfacial film. However, it was found possible to break-up the self-assemblies by reducing the pH of the solution, which caused an osmotic shock, deforming the vesicles and causing partial exposure of the hydrocarbon core to the water phase. This process resulted in a rapid release of monomer into solution, increasing the adsorption kinetics and improving the foaming. This result suggests that destabilization of the vesicle dispersions can be utilized to increase the surface activity of the solution, and this concept was confirmed by comparing the dynamic surface tension of the PGE solutions at different pH values.

2.12 Influence of structure on foaming and low-foaming surfactants

As earlier discussed, it is the molecular structure and charge of the surfactant that determine the location, cohesive bonding and packing of the molecules at the gas/liquid interface, and these parameters also define the CMC and the foaming ability. Especially important aspects to consider are the branching and the location of the hydrophobic and hydrophilic groups within the molecule (central or terminal). Several trends have been observed in this respect. The foaming performance of surfactants with clearly defined structures has been quantified by the use of the Ross–Miles method, and this work has been discussed by Rosen (20) and may be summarized as follows:

- (a) A shift of the hydrophilic group to a more central position of surfactant molecule causes an increase in CMC and CPP with decreasing foamability.
- (b) Highly branched chain surfactants often give a higher CPP and lower foam heights than isomeric, straight-chain molecules. However, for many straight-chain compounds such as fatty acids, the length of the hydrophilic chain can become too long decreasing the solubility and reducing foaming performance (e.g. > 16 carbon atoms at 40°C).

- (c) For ionic surfactants, the foaming properties can also be strongly influenced by the nature of counterion and are also related to the packing at the interface. Generally, the presence of smaller counterions increases initial foam height and foam stability. For example, the foaming properties of the dodecyl sulfate series decrease with increasing size of the counterion in the order $\text{NH}_4^+ > (\text{CH}_3)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{C}_4\text{H}_9)_4\text{N}^+$.

At concentrations below the CMC, no significant change in foam stability has been reported when the counterions are changed. However, it is also important to consider the effect of counterions on interfacial and foaming properties of surfactants above the CMC. Foaming studies with anionic dodecyl sulfates were carried out by Pandey and coworkers (21) using shaking tests, and the performance were found to follow the order $\text{LiDS} > \text{NaDS} > \text{CsDS} > \text{Mg}(\text{DS})_2$. This result was explained by differences in micellar stability and diffusion of monomer.

Ionic surfactants in aqueous solution usually have a higher foamability than nonionic surfactants. In fact, it has been documented that structural effects are very important for PEO surfactants, and they generally produce less foam with less stability than anionic or cationic surfactants (11). This has been explained by the fact that the molecules are coiled and difficult to unpack at the air/solution interface occupying a lower surface area per molecule than linear molecules. Interestingly, the replacement of a straight alkyl chain hydrophobic group in POE nonionics by a cyclically or 1-alkylcyclohexyl group with the same number of carbon atoms produces little or no decrease in initial foam volume but a marked change in foam stability. Similar effects are produced when the single-alkyl chain hydrophobic group is replaced by two or three alkyl chains containing the same total number of carbon chains. The magnitude of the effect appears to decrease with increase in the number of carbon atoms in the hydrophobic portion and in the length of the POE chain (11).

In addition to anionic and nonionic surfactants, the foaming performance of cationic surfactants needs to be considered. With respect to this class of surfactants, the foaming data are controversial, and according to the earlier literature, cationics were generally described as poor or moderate foamers in aqueous solutions, but this may have been caused by adsorption of the positively charged cationic surfactant on the negatively charged silica on the walls of the glass-foaming apparatus. This causes the hydrophobic groups to orientate toward the aqueous phase causing foam rupture by dewetting. However, more recent studies have shown that many cationics, especially Gemini cationic surfactants, are fairly good foamers with low CMC values (22), and they have the added advantage of having germicidal characteristics. They are often used together with nonionic surfactants. Today, several modified cationics such as amine oxides are used in shampoo and detergent formulations, and alkanol amides are widely used as foam additives in handwash, detergents and shampoos.

Many manufacturing processes such as paper making, textiles, dyeing, etc., involve high-speed processes where a considerable amount of agitation occurs during the

movement of belts, stirring and mixing in tanks. Frequently, the material may pass through an aqueous bath where the surface activity is needed for wetting or coating, but high foaming is detrimental to the process. In these circumstances, low-foaming surfactants are needed, since high foaming may cause a reduction in speed and result in bubble adhering to material causing blemishing. Using the various structural concepts which relate structure to foaming, it becomes possible to design low-foaming surfactants. Changes in the molecular structure cause changes in the packing arrangements and configuration of the molecules at the interface which enables the foaming activity to be reduced. Also such changes in the molecular size usually lead to a change in the diffusion rates. Rapidly diffusing surfactants can destroy the film elasticity and thus prevent or reduce foaming. Slow diffusing surfactants are ineffective since they fail to build up sufficient elasticity. The following guidelines as presented by Rosen (20) and are summarized below:

- (a) The replacement of a large straight chain hydrophobic group with an isomeric branched chained group and positioning the hydrophilic group in a central rather than terminal positioning with respect to the molecule can reduce the foaming properties of the surfactant. This can be explained by the difference in diffusion rates of the molecules to the interface.
- (b) The structure of the molecule may be modified to give a large area/molecule on adsorption at the air/water interface. The idea is to produce a loosely packed coherent film that generates unstable foams. Structurally, this can be achieved by introducing a second hydrophilic group into the molecule some distance from the first one. Ideally, the configuration should involve the entire molecule between the two hydrophilic groups lying flat in the interface.
- (c) Alternately, a relatively short, highly branched or cis-unsaturated alkyl group can be chosen for the hydrophobic group rather than a long straight-chain saturated group. For example, a polyoxypropylene chain can be introduced as part of the hydrophobic group. However, it is important to point out that this type of modification may not be effective if the hydrophilic head already has a sizable cross-sectional area (as in POE nonionics).
- (d) A second hydrophobic group can be introduced into the molecule (preferably of different size or shape from that of the first hydrophobic group) at some distance from the first one. It can help to increase the surface area/mole of surfactant. For example, high-foaming POE nonionics can be converted to lower foaming surfactants by capping the $-OH$ of the POE with a short-chain alkyl group or by replacing the terminal $-OH$ group by $-Cl$. The capping of the $-OH$ or replacing it by $-Cl$ also decreases the cloud point of the POE nonionics, and above the cloud point this must result in the separation of a separate surfactant phase. Under these conditions the molecular species can act as a foam breaker.
- (e) The introduction of two bulky hydrophilic groups (e.g. POE chains) on the same carbon atom will cause the chain backbone to extend in different directions. This will also act to increase the area per molecule at the surface. In Table 2.1 the structures of several types of weakly foaming surfactants are listed.

Table 2.1 Structures of low-foaming surfactants in which foam disappears within a few minutes. From ref (20)

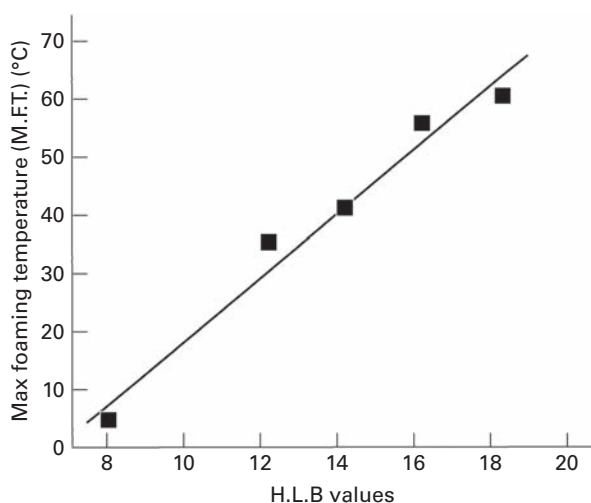
Structure	
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CHCH}_2\text{C}-\text{C} \\ \\ (\text{OC}_2\text{H}_4)_x\text{OH} \end{array} \equiv \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{C}-\text{CCH}_2\text{CHCH}_3 \\ \\ (\text{OC}_2\text{H}_4)_y\text{OH} \end{array}$	$x + y \leq 4$
$\text{RCH} \begin{cases} (\text{OC}_2\text{H}_4)_x\text{OH} \\ (\text{OC}_2\text{H}_4)_y\text{OH} \end{cases}$	$R < \text{C}_{11}, x = y \leq 5$
$\text{RN} \begin{cases} (\text{OC}_2\text{H}_4)_x\text{OH} \\ (\text{OC}_2\text{H}_4)_y\text{OH} \end{cases}$	$R = \text{C}_{10}, x = y \leq 3$
$\text{HO}(\text{C}_2\text{H}_4\text{O})_x(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_y\text{OH}$	$x + y \leq 12$
$\text{HO}(\text{C}_2\text{H}_4\text{O})_x(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_y(\text{C}_2\text{H}_4\text{O})_z\text{H}$	$y \leq 27, x + z \leq 82$
$\text{HO}(\text{C}_2\text{H}_4\text{O})_x \begin{array}{c} \text{CH}_3 \\ \\ \text{CHCH}_2\text{O} \end{array} \text{O}_y(\text{C}_2\text{H}_4\text{O})_z\text{H}$	$y = 35, x + z = 45$
$\text{C}_6\text{H}_{17} \begin{array}{c} \text{CH}_3 \\ \\ \text{OCHCH}_2 \end{array} \text{O}_x(\text{OC}_2\text{H}_4)_y\text{OH}$	$x = y \approx 10$

2.13 The application of the HLB (hydrophile–lipophile) balance concept to foaming

Devising a quantitative method of correlating chemical structure with surfactant performance has been the aim of formulation chemists for many years. One of the original concepts was to characterize surfactants according to a hydrophile–lipophile balance (HLB) value which was derived from their structure, and this method was originally developed for emulsions but later extended to foam systems, but with limited success. The HLB originally refers to the surfactant chemical structural HLB; it was originally derived by Griffin (23) for alkyl ethoxylate surfactants and was considered as an approximate measure of the partition coefficients of a surfactant between oil and water. The approach was later modified by Davies (24). HLB values were generally calculated on an empirical basis and are usually expressed on a scale from 0 to 20, with the low HLB having a high solubility in oil while the high HLB is extremely soluble in water. The equation derived by Davies (24) was expressed as

Table 2.2 Relationship between surfactant functionality and HLB

Functionality	HLB
• Foam breaking (insoluble)	1.5–3
• Emulsification	3–6
• Wetting/Spreading	7–9
• Medium foaming	8–18
Dispersion	13–15
Strong foaming	15–18
• (Solubilization)	15–18

**Fig. 2.23** Relationship between foaming and HLB for nonionics. From ref (16).

$$\text{HLB} = 7 + \left(\sum \text{hydrophilic group number} + \sum \text{lipophilic group number} \right)$$

Attempts to extend the HLB concept to include cationic, anionic surfactants (fatty acids or sulfates), where the hydrophobic or lipophilic (oleophilic) groups are usually considered to be large or straight chain hydrocarbons, have met with limited success. However, Table 2.2 shows a rough overview of the relationship between HLB and the functionality of the surfactant, with good foaming agents having more prominent hydrophilic groups in the mid-range and poor foaming surfactants and defoamers in the range of a HLB of 1.5–3.

Experiments carried by Badwan and coworkers (16) using a series of nonionic surfactants with HLB defined by Honeywell-Atlas HLB kit and where the foaming performance was expressed in terms of the maximum foaming temperature showed some degree of success. A plot of their results is shown in Fig. 2.23.

Also with polypropylene glycol surfactants of different molecular weight, mixed frothers (weak foamers) were prepared containing high HLB and low HLB components which were used to produce closely packed molecular cohesive films at the air/solution interface, giving greater surface elasticity and increased foamability (25). In a further study with nonionic frothers, the HLB value was used to represent the molecular structure which was related to the critical coalescence concentration of bubbles in a froth flotation cell (26). In the experiments, 36 surfactants were evaluated from three frother families, which were classified as (a) aliphatic alcohols, (b) polypropylene glycol alkyl ethers and (c) polypropylene glycols covering a wide range of alkyl groups and propylene oxide groups.

However, the HLB is due to many different types of structural and charged arrangements in a molecule, and it is unlikely it can be applied generally to anionic or cationic surfactant systems. In fact, Balson (27) concluded that HLB is probably more of a scientific curiosity than a useful concept to determine surfactant performance.

2.14 Temperature effects on surface tension and foaming

Both foamability and foam stability are affected by temperature. Surface tension is dependent on temperature and is a critical factor influencing foamability performance. Dynamic surface tension measurements on fatty acid soaps (sodium oleate solutions) at temperatures ranging from 20°C to 60°C are shown in Fig. 2.24, and it has also been demonstrated that an increase in temperature causes a considerable greater reduction in surface tension, particularly within the short-time scale range.

Following a rapid fall in surface tension, an increase in foamability can be predicted, and this appears to be in agreement with the work of Nakagaki and Shinoda (28), which showed that on shaking solutions of varying concentrations of fatty acid salts (potassium

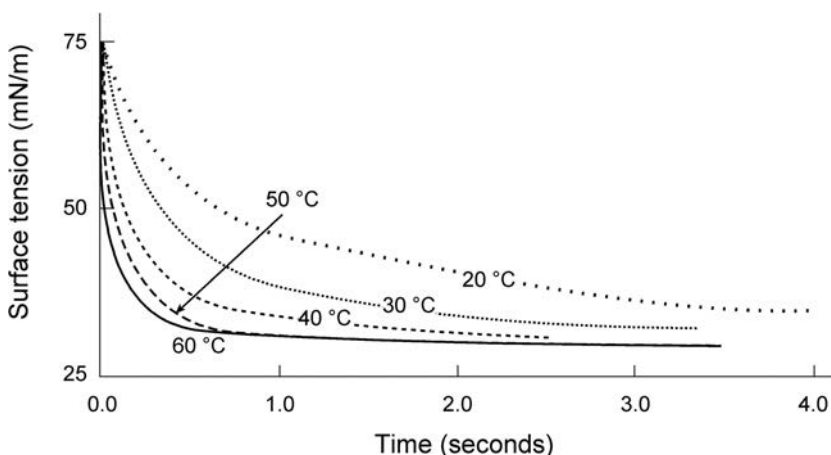


Fig. 2.24 Dynamic surface tension of oleic acid/sodium oleate solution at pH = 7 at a range of temperatures. From ref (3).

laurate and myristate), the foam heights were considerably higher at 35°C compared to 15°C. However, Gara and Szalmayer (29) showed that with sodium dodecyl sulfate and sodium dodecylbenzene sulfonate, although the foamability increased with temperature, the foam stability decreased. Generally, the decline in foam stability with increase in temperature can result from a number of different factors. Primarily, the drainage of the liquid will be increased due to the decline in viscosity (particularly in foams stabilized by gelatin-type thickening agents) and also an elevation in temperature can enhance evaporation of the volatile surface-active components. The surfactant may also decompose at higher temperature, and in the case of foams stabilized by proteins, denaturation of the molecules may occur.

Foaming experiments at different temperatures carried out with multi-component systems such as milk which involve interactions between lipids, caseins and possibly mineral salts are complex and difficult to resolve. Although temperature is well known to play an important role, the processing condition and fat content of the milk are also important. It was reported by Kamath and coworkers (30) that no correlation was observed between foaming and surface tension of whole milk in the temperature range of 15°C–45°C, which illustrates the complexity of the situation. It has been noted that milk foams to twice its volume when taken from a cold fridge but barely foams at all when heated, and this has been explained by the interaction of the enzyme (lipase) components with the casein. Essentially, it is the casein which is the protein which is adsorbed at the interface and stabilizes the bubbles, but as the temperature increases, the lipolysis fat components in the milk break-down into fatty acids and glycerol, which possibly weaken the casein structure or displace the casein from the air/water interface causing bubble collapse. To ensure good foaming, low fat milk is usually recommended (skimmed milk) so that the amount of fat decomposition is reduced and most of the adsorbed casein remains attached to the bubble interface and stabilizes the foam (31).

Ospanova and coworkers (32) used the Ross–Miles plunging jet procedure to compare the foaming performance of a strongly foaming anionic surfactant (sodium lauryl sulfate) with a less surface-active cationic surfactant (cetyltrimethylammonium bromide) in 10^{-3} M solution at temperatures up to 70°C. Both surfactants showed a reduction in foaming performance at higher temperature, particularly around 70°C, and the cationic surfactant was found to be less effective. Improved performance was achieved in the higher temperature range by adding gelatin to the surfactants, which increased the bulk viscosity and produced a surfactant/polymer complex that stabilized the bubbles. More generally, although surface tension plays a role, it is also important to take into account the influence of the solubility of the surfactant. In many cases, the foaming data can be related to the cloud points, particularly with nonionic surfactants: as the temperature increased above the cloud point, the surface tension is lowered and the foamability reduced. However, with other surfactants, the results are sometimes contradictory, since phase changes may result in the formation of crystalline phases which may act as defoamers. It is also important to consider the influence of the diffusion of gas between bubbles, which will increase with increase in temperature causing an additional foam

destabilization effect. To obtain reliable foaming data, control of temperature is very important, and according to Bikerman (33), solubility was one of the most important parameters that influences foaming behavior.

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