Application Report

Characterization of surfactant mixtures

Application report: AR204e
Industry section: Chemical
Author: CR
Date: 01/1996

Force Tensiometer – K12

Method:

Keywords: Surfactant, micelle, surface tension, CMC, spray atomization, surfactant synergism, SDS, DTAB

Synergistic aspects of surfactant mixtures

The anionic surfactant sodium dodecyl sulfate and the cationic surfactant dodecyl trimethylammonium bromide

Background

Surfactants are compounds which are structurally heterogeneous. Each surfactant molecule consists of a hydrophobic end (commonly referred to as the "tail") and a hydrophilic end (commonly referred to as the "head"). This heterogeneous nature is what makes surfactants so useful in industrial and commercial formulations. Surfactants are primary components of products such as cleansers, degreasers, emulsifiers, dispersants, and foamers and defoamers. In each of these products, surfactants perform a specific function, and that function is only possible due the heterogeneous nature of surfactant molecules. For cleansers and degreasers the function is to remove hydrophobic material from a solid substrate. For emulsifiers and dispersants the function is to stabilize either a hydrophobic or a hydrophilic material in a liquid medium which is of the opposite nature. For foamers and defoamers the function is either stabilization or destabilization of gas bubbles in a liquid medium.

However, heterogeneity is only the beginning of the surfactant story. Aggregation is the remainder. In many surfactant based products, including most of those described above, surfactant molecules do not act individually to perform their functions. Rather, they act as aggregates. Aggregation of surfactant molecules in solution occurs because either their head group or their tail group is not soluble in the bulk solvent.

This application note focuses largely on surfactants in aqueous solution. In aqueous solution, it is a surfactant's hydrophobic tail group that is insoluble. The tail group is insoluble not because it dislikes water (as the misnomer "hydrophobic" implies), but because it is thermodynamically unfavorable for water molecules to associate with it.[i] It is, however, favorable for water molecules to associate with a surfactant's head group. Therefore, a certain thermodynamic conflict of interest is established on the part of water with regard to surfactants. The most favorable solutions to this conflict are ones which allow water molecules to interact with head groups of surfactant molecules and not interact with tail groups.

One thermodynamically favorable solution is for the solvent to drive a fraction of the surfactant molecules to the solution's boundaries. The size of this fraction is dictated by considerations of chemical potential, which are governed by the structural makeup of the surfactant and the solvent in question, as well as the concentration of surfactant in solution. Aggregation of surfactant molecules at a solution's boundaries can be loosely viewed as form of phase separation (surface phase separation if you will). The two dimensional surface phase of a surfactant solution consists of a disproportionate concentration of surfactant molecules relative to the bulk solution phase. Aggregation of surfactant molecules at a solution's surface is also referred to as monolayer formation. Monolayer formation is the first type of surfactant aggregation considered in this note because, when one starts with pure solvent and augments surfactant concentration, it is generally the first to occur.

For aqueous surfactant systems, as a surfactant monolayer is established, surface tension of the solution decreases. This decrease in surface tension can be monitored as a function of bulk solution surfactant concentration by a number of methods. One typical method is the Wilhelmy plate method. Figure 1 shows data pertaining to decreases in surface tension due to increases in bulk surfactant concentration for a simple system containing only water and a nonionic alcohol ethoxylate. The Wilhelmy plate method with a platinum plate, and a Krüss model K12 Tensiometer equipped with an automated dosing accessory, was used to obtain this data. (A complete description of Wilhelmy plate techniques is beyond the scope of this text. Those interested in such a description are referred to the Krüss K12 brochure.) Region 1 of figure 1 corresponds to the region of surfactant concentrations over which surface tension is logarithmically dependent on bulk surfactant concentration. Such a logarithmic dependence is a common result of the chemical potential which causes adsorption of surfactant at solution boundaries.

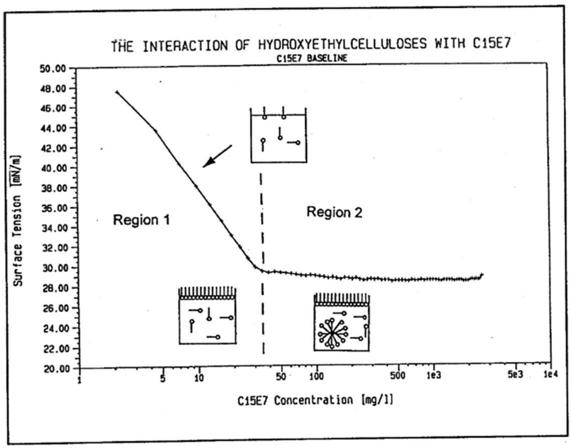

Figure 1

Throughout the range of concentrations of region 1, monolayer formation at the solution's boundaries is incomplete. Monolayer formation becomes complete at a critical point in surfactant concentration. This concentration corresponds to the boundary between region 1 and region 2 in figure 1. It is commonly termed the critical micelle concentration or "CMC" of the surfactant. Please note that the words "complete" and "incomplete" is the last few sentences are not to be taken as absolute terms. To your author, "complete" gives the conceptual idea that <u>every</u> molecule at the boundary of a solution is a surfactant molecule. This is most often not the case. Due to considerations of solvation of the head groups of the surfactant, some solvent is typically interdispersed with surfactant molecules in the monolayer, even at what has been termed here "complete" monolayer formation. Therefore, by "complete monolayer" I mean only to express that a solution's boundaries are saturated with surfactant to the point that it becomes more thermodynamically favorable for interactions between the tail groups of a surfactant and the solvent to be diminished by other means. For most aqueous surfactant systems, this "other means" takes the form of aggregation of surfactant molecules in the bulk solution to form what are termed "association colloids".[ii] Once the necessary surfactant concentration is reached such that formation of association colloids begins, further increases in the solution's bulk surfactant concentration cause very minor further increases in the concentration of surfactant in the solution's surface phase. This corresponds to very little further decrease in surface tension at the solution's boundaries, as is indicated in region 2 of figure 1.

Prior to discussing surfactant association colloids however, it may be instructive to briefly discuss at least one industrial application in which monolayer formation is a fundamental reason for the addition of surfactants to a formulation. A good example of this is the addition of surfactants to spray formulations. One of the large considerations in developing a product which is applied as a spray is "atomization". The term atomization relates to how well a liquid spray product disperses into droplets as it leaves a sprayer and travels through the atmosphere to a substrate at which it meant to be applied. In most cases, it is desirable for spray droplets to be as small as possible prior to contacting a substrate. At spray manufacturing companies, many engineers work diligently at establishing spray nozzle designs and optimizing sprayer back pressure to achieve better atomization of their sprays. Better atomization means smaller, more uniform sized, droplets. The dispersion of a solution into droplets in a spray application is governed by many effects which are difficult to model mathematically. These include Bernoulli effects, Rayleigh-Taylor instabilities, and Kelvin-Helmholtz instabilities. However, one of the fundamental factors governing atomization is surface tension of the solution being sprayed. Surface tension is the force necessary to create a new atmosphere/solution surface per unit area of surface created. Surfactant monolayer formation lowers a solution's surface tension. As a result, surfactants are often added to spray formulations for the purpose of forming complete (or even partial) monolayers on the surfaces of spray droplets, thereby allowing them to disperse into small droplets more easily. This concept is shown schematically in figure 2.

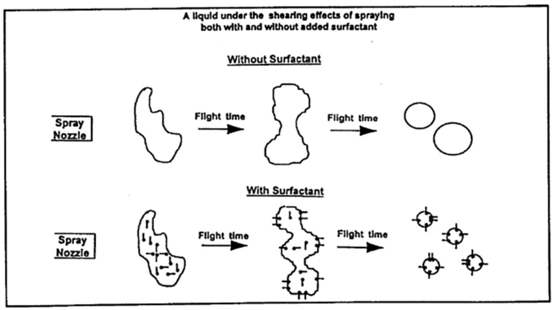

Figure 2

Be aware that in some ways figure 2 presents an oversimplified explanation of the use of surfactants in spray formulations, because spraying is an application which is dynamic in nature. Therefore, in deciding the proper surfactant type and concentration for a spray formulation, it is often necessary to also study the dynamics of surfactant monolayer formation. A discussion of such a study is beyond the scope of this text. However, for those interested, Krüss does offer a dynamic surface tension instrument (the Bubble Pressure BP2) for these studies, and we do have some expertise in this area.

Sprays are only one industrial application in which surfactants are added to a formulation because they tend to aggregate at solution boundaries. Many others exist. However, the purpose of this background section is not to focus on any one set of applications for surfactants. Rather, it is to lay the ground work for a discussion of the idiosyncracies of multiple surfactant systems, by providing the reader with a working level of understanding of the use of surfactants in general. Therefore, it is important to proceed to a discussion of surfactant "associative colloids" and their utility in industrial and commercial product formulations. Recall that surfactant associative colloids begin to form in aqueous surfactant solutions as a secondary means of diminishing interactions between water and surfactant tail groups.

The most widely studied surfactant associative colloids are spherical micelles. This is because, in many surfactant systems, they are the first type of associative colloid to form as bulk solution surfactant concentration is augmented beyond what is necessary to "complete" a monolayer at the solution's boundaries. A schematic of a surfactant micelle in aqueous solution is shown in figure 3. Be aware that this schematic is meant to represent a cross section of a spherical entity.

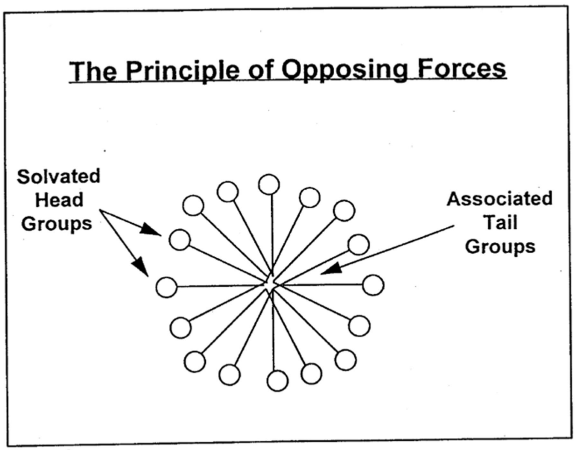

Figure 3

Micelles are generally spherical due to two opposing forces. The first force, which causes surfactant tail groups to associate, has to do with the entropic and enthalpic unfavorability of the association of water molecules with hydrophobic moieties. This principle was discussed previously. The second force, the one which gives a micelle its spherical nature, has to do with interactions between the head groups of surfactant molecules in a micelle, and with solvation effects. In general, the spherical shape of micelles is due to the thermodynamic favorability of keeping the head groups of surfactants solvated, even when surfactant molecules are associated due to their tail groups. This is the same effect that causes surfactant "monolayers" at solution boundaries to not be completely devoid of solvent molecules. The spherical conformation allows space for water molecules to solvate the surfactant head groups of a micelle. The region of surfactant head groups in a micelle (or other surfactant associative colloid) is termed the "palisade layer". The nature of developed palisade layers is perhaps the most significant factor in determining how associative colloids are developed in aqueous surfactant solutions. Ironically, it is, in many cases, much more important than the nature of a particular surfactant's hydrophobic tail, which is, after all, the portion of the surfactant that causes colloidal associations to be developed. We shall consider this concept in some detail shortly, since the main focus of this application note is surfactant synergy. The synergistic effects observed in many multi-surfactant systems are due to advantageous interactions between the head groups of surfactant molecules in palisade layers. However, before we discuss synergistic effects, it is instructive to briefly expand our discussion of surfactant association colloids to include important aggregations which are of a higher order than spherical micelles.

An abbreviated list[iii] of relevant surfactant association colloids that may exist in aqueous surfactant systems is provided in figure 4. For each type of association a schematic of the structure of the colloid is provided.

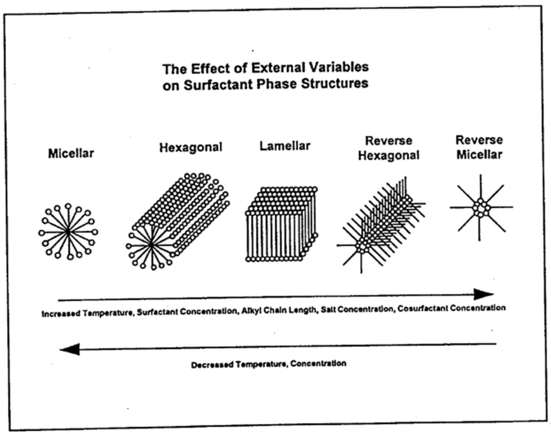

Figure 4

Please make particular attention to the descriptions at the bottom of figure 4, which pertain to variables that can cause transitions between phases. These descriptions only represent general trends and are not necessarily to be regarded as absolute. As we will see in a moment, even "simple" single surfactant aqueous solutions can have complex phase diagrams which are dependent on these variables. Nonetheless, our discussion to this point has followed the trend of increasing surfactant concentration. With that in mind, note that, according to figure 4, increasing surfactant concentration will generally promote spherical micelles to be reformed into hexagonal phase association colloids, and then into lamellar phase associations. In a hexagonal phase, the head groups of surfactant molecules are closer packed (in the palisade layer) than they are in spherical micelles. In the lamellar phase, head groups are even closer packed in the palisade layer.

Why do these association colloids become thermodynamically favorable in surfactant solutions, even in light of the fact that micelles have a spherical shape to provide for solvation of surfactant head groups? The answer is that, once the concentration of surfactant in a solution becomes high enough, the formation of spherical micelles is no longer an efficient way to eliminate contacts between surfactant tails and the water structure. There are just so many tails that need to be associated that more efficient packing becomes favorable. This means making the thermodynamic sacrifice of forcing surfactant head groups into close proximity (often diminishing their solvation sheafs), for the thermodynamic gain of associating more tail groups. At what point in concentration does this spherical micelle to hexagonal or lamellar phase transition occur? This is largely dependent on how compliant or resistant the head groups of the surfactant are to being close packed. For some surfactant systems these transitions never occur. In others they occur at low concentrations just above (or even at) the CMC of the surfactant. It depends largely on the nature of the palisade layer that would be developed if the colloid was formed.

Shown below is a rough phase diagram for the nonionic surfactant polyoxyethylene(8) cetyl ether (chemical structure: $C_{16}H_{33}(OCH_2CH_2)_8OH$) in water.

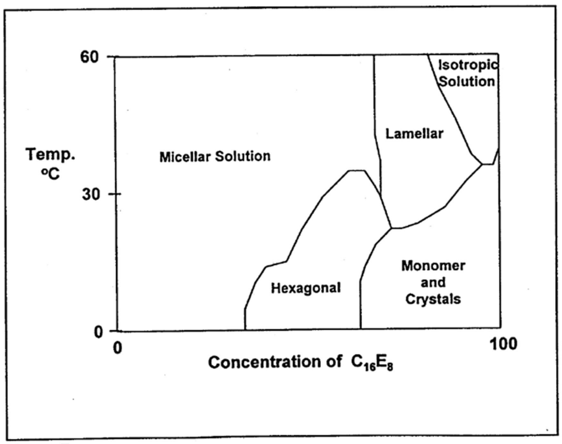

Figure 5

This phase diagram shows the general trends discussed above, although the transitions between regions based on changes in surfactant concentration and temperature are complex as promised. The region labelled "isotropic" in this diagram is most likely a reverse micellar region. (It may also be a cubic phase, the description of which is beyond the scope of this text.) Reverse micelles occur at extreme surfactant concentrations in aqueous solutions. In fact, when they occur the solution is phase inverted and oil continuous. The region labelled "monomer and crystals" may also contain some reverse hexagonal phase. A reverse hexagonal phase is also an oil continuous phase. The other labelled regions have been discussed previously.

Industrial and commercial products are formulated in each of these associative colloidal phases, and one basic reason for using mixtures of surfactants in a formulation is to promote the development of one or more of these phases. Micelles act as stabilizers for disperse oils and colloids. The hydrophobic oils and/or particles simply reside in the interior of micelles with the surfactant tail groups. This is useful for products such as detergents, emulsifiers, and dispersants. The hexagonal phase is also capable of disperse phase stabilization, by basically the same mechanism. However, in addition, the hexagonal phase tends to close pack as shown in figure 4. This provides rheological properties which are often desirable in cosmetics and other products. Lamellar phases are similarly important as cleaners and stabilizers, but have much different rheological properties than the hexagonal phase. Lamellar sheets tend to slip pass one another if the structure is sheared. Lamellar phases are also, in general, the best foam stabilizers. The reverse hexagonal phase is used for degreasers, and also in cosmetics. It typically has rheological properties analogous to those of the hexagonal phase. Reverse micelles are used to stabilize hydrophilic materials in a hydrophobic medium. Figure 6 illustrates some of these applications.

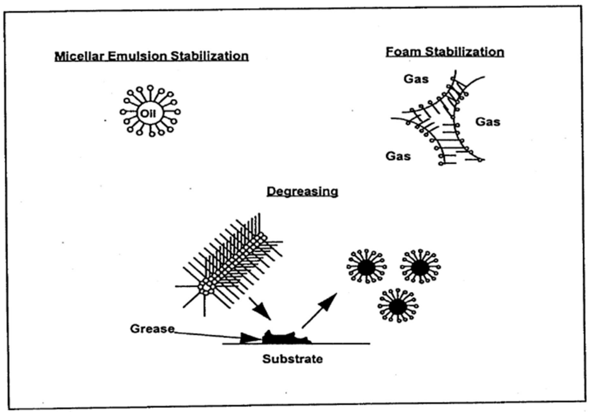

Figure 6

As was stated previously, the nature of palisade layers is often key to determining the type of colloidal associations that will occur in a solution containing surfactants. In order to consider placide layers further, let's consider figure 7 in light of some literature data pertaining to micelles of various surfactants.

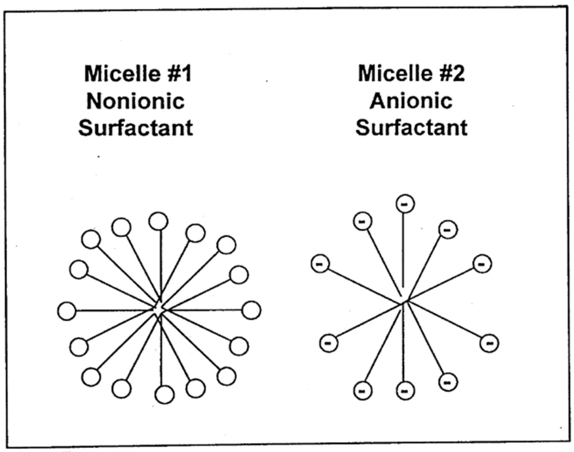

Figure 7

The schematics in figure 7 represent two very different micelles. Micelle #1 has a typical spherical shape, with well solvated surfactant head groups. For purposes of illustration we will say that it is composed of nonionic surfactant molecules. Micelle #2 is comprised of a hypothetical surfactant with the exact same tail group as the surfactant used to make micelle #1. However, the surfactant in micelle #2 is anionic. Its head group contains an ionic bond which dissociates in aqueous solution to render the surfactant head group negatively charged. The cation to the surfactant diffuses some distance from the micelle due to Donnan equilibrium effects.[iv] Ionic surfactant head groups not only need to be solvated by water (as do nonionic head groups), but they also repel each other coulombically. If you think of each surfactant head group occupying a certain surface area on the spherical micelle, ionics take up more surface area per head group versus nonionics as result of columbic repulsion. This is, of course, assuming a single surfactant system in which all of the head groups have like charges. Further, for ionic surfactants, columbic repulsion tends to resist the formation of micelles. Remember that the hydrophobic effect and the association of surfactant tails is what drives micelle formation. The palisade (head group) layer is forced to form as a consequence.

Shown below is data pertaining to formation of micelles for some select ionic and nonionic surfactants. All data was obtained from literature and pertains to the surfactants in aqueous solution near room temperature.

Surfactant	Structure	CMC (Micro molar)	Aggre gation Number
Sodium Dodecyl Sulfate	$C_{12}H_{25}SO_4^- Na^+$	8200[v]	64[vi]
Dodecyl Trimethyl ammonium Bromide	$C_{12}H_{25}N^+(CH_3)_3 Br^-$	16000[vii]	55[4]
Tetradecyl Trimethyl ammonium Bromide	$C_{14}H_{25}N^+(CH_3)_3 Br^-$	3600[viii]	70[4]
Hexadecyl Trimethyl ammonium Bromide	$C_{16}H_{25}N^+(CH_3)_3 Br^-$	920[ix]	89[4]
Polyoxyethylene(6) Dodecyl Ether	$C_{12}H_{25}(OC_2H_4)_6OH$	87[x]	400[xi]
Polyoxyethylene(8) Dodecyl Ether	$C_{12}H_{25}(OC_2H_4)_8OH$	100[xii]	123[xiii]

Based on the explanations put forth above, pertaining to figure 7, it might be expected that an ionic surfactant would have a higher CMC and a lower number of molecules per micelle (aggregation number) than a nonionic surfactant with the same size hydrophobic tail group. The data above supports this. The CMC's of both sodium dodecyl sulfate and dodecyl trimethylammonium bromide are approximately two orders of magnitude higher those of the nonionic polyoxyethylene dodecyl ethers listed. Comparing the same surfactants, aggregation numbers at the CMC are at least twice as large for the nonionics as they are for the ionics.

Data pertaining to tetradecyl trimethylammonium bromide and hexadecyl trimethylammonium bromide are also included for comparison with the dodecyl trimethylammonium bromide data. This series shows the effect of increasing the size of a surfactant's tail group while holding the head group constant. As expected, the effect is that CMC decreases and aggregation number increases. More hydrophobe equals more thermodynamic drive toward association. However, this data also suggests that the effects of increasing a surfactant's tail length by four alkyl units are only to decrease CMC by a little more than an order of magnitude and increase aggregation number by less than a factor of two. This justifies previous statements that the head group of a surfactant, and the nature of the palisade layer, can have even more influence on aggregation properties of the surfactant than does the nature of the surfactant's tail group.

This background section has focused largely on aggregation properties of single surfactants in aqueous solution. It has been mentioned that many industrial and commercial systems contain multiple surfactants for the purpose of tailoring their properties to the system's application. As a result, effective formulators of multi-surfactant systems understand, not only the information presented thus far, but also that if more than one surfactant is present in a solution, then the surfactant association colloids formed can be quite different from those formed with any of the surfactants individually. Mixing just two surfactants can produce surfactant associations in concentration and temperature regimes wherein such associations are not possible for either of the surfactants individually. This concept is generally known as "surfactant synergism". As an example of surfactant synergism, we have recently studied micelle formation in aqueous solutions containing the anionic surfactant sodium dodecyl sulfate and the cationic surfactant dodecyl trimethylammonium bromide.

Experimental

Both sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) were obtained commercially in powdered form. Each surfactant had a reported purity of 99%, and each was used without further purification.

Thirteen aqueous solutions were prepared from dry surfactant powders. Each was prepared in distilled water. The total concentration of surfactant in each of these solutions was varied as necessary by dilution with pure distilled water. However, each solution contained a specific molar ratio of SDS relative to the total amount of surfactant in the system (SDS + DTAB). The following SDS/surfactant molar ratios were studied.

Solution #	Molar Ratio (SDS/Total Surfactant)
1	0.00
2	0.01
3	0.05
4	0.10
5	0.25
6	0.40
7	0.50
8	0.60
9	0.75
10	0.90
11	0.95
12	0.99
13	1.00

Solution #1 was of course an aqueous solution containing only DTAB, while solution #13 was an aqueous solution containing only SDS.

Solutions #1 and #13 were used, individually, as dosing solutions to determine CMC values for SDS and DTAB, by the Wilhelmy plate method. The Krüss Processor Tensiometer model K12 with an automated dosing accessory and a roughened platinum Wilhelmy plate was used for this and all of the remaining CMC work reported in this text. The initial solution in both cases was pure water. (Those who are unfamiliar with the operation of a K12 in the automated CMC mode are referred to the K12 brochure.)

The results of these initial experiments are shown in figures 8 and 9.

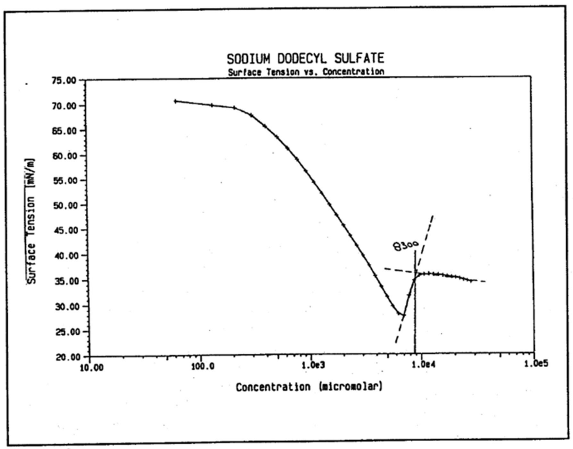

Figure 8

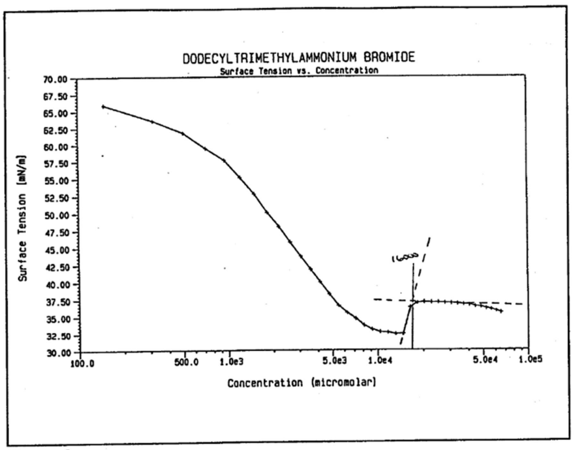

Figure 9

From these CMC curves, it is evident that both the SDS and the DTAB used contained some impurities. Impurities can cause pre-CMC dips in a surfactant's CMC curve, if the impurities are more surface active than the main surfactant. For example, the impurity in sodium dodecyl sulfate is most often the lauryl alcohol from which it is synthesized. It is often difficult to obtain a CMC value for a surfactant that is highly contaminated, but that was not the case with these surfactants. In order to avoid the impurity dips in these sets of data, the CMC for each surfactant was simply taken as the point in concentration at which each curve reached a plateau after the impurity dip. See figures 8 and 9. This method seems to work quite well. The CMC values obtained from figures 8 and 9 were 8300 and 16000 micromolar respectively. The literature values, as reported previously, are 8200 micromolar for SDS and 16000 micromolar for DTAB. Based on this data we were, I believe, justified in using the same CMC evaluation technique for data pertaining to solutions containing both SDS and DTAB.

Therefore, by these techniques, CMC data was obtained from solutions #2 through #12. Figure 10 is one of the eleven resultant CMC curves, which is shown as an example. It shows that the CMC of an aqueous solution containing a 0.5 molar fraction of SDS to total surfactant is 120 micromolar.

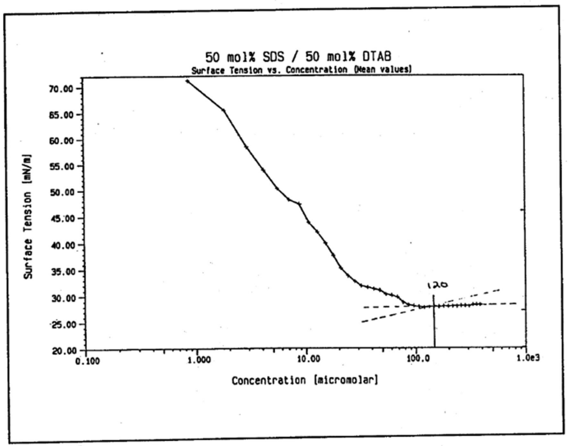

Figure 10

Results and discussion

Shown below, in both tabular and graphical form, is all of the CMC data obtained from the study.

Molar Ratio (SDS/Total Surfactant)	Critical Micelle Concentration (Micromoles of Total Surfactant)
0.00	16000
0.01	8000
0.05	1200
0.10	490
0.25	270
0.40	180
0.50	120
0.60	150
0.75	220
0.90	390
0.95	700
0.99	5000
1.00	8300

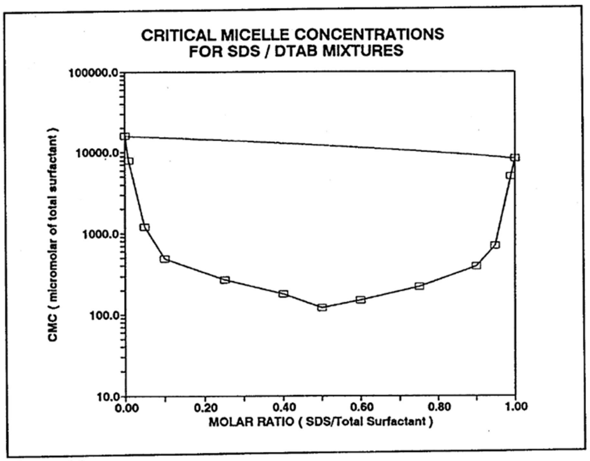

Figure 11

The dotted line in figure 11 represents CMC values which might be expected for SDS/DTAB mixtures if synergism did not occur. In other words, in the absence of synergism, the CMC of a surfactant mixture might be expected to simply be the average of the CMC values of the component surfactants weighted by their respective molar ratios within the mixture. It is evident that this is by no means the case for SDS/DTAB mixtures. The data shows a synergistic pattern, with all CMC data for the mixtures falling below the dotted line. The synergistic effects reach a maximum at a 0.5 molar ratio of SDS (and correspondingly a 0.5 molar ratio of DTAB) in the surfactant mixture. At this point the CMC is 120 micromolar of total surfactant, which is almost a full two orders of magnitude lower the CMC of either surfactant in pure form.

What causes this level of synergism? Quite simply the fact that mixed surfactant systems have the thermodynamic alternative to form micelles in which the head groups of the palisade layer are not repulsive. (In fact, for SDS/DTAB systems, they are attractive.) Recall our background discussion of how and why CMC values varied in nonionic versus ionic surfactants, and consider figure 12.

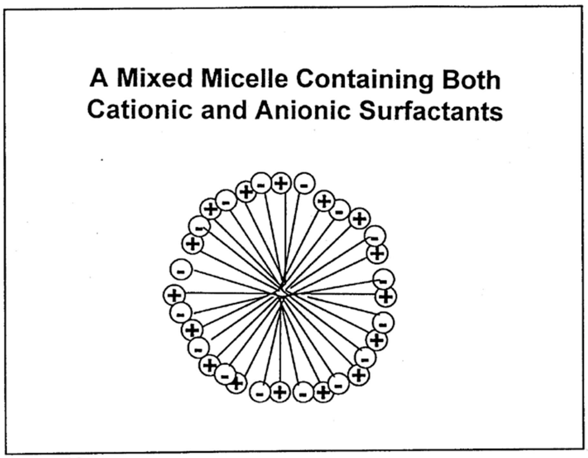

Figure 12

The micelle depicted in figure 12 is formed from a mixture of cationic and anionic surfactant molecules, like the SDS/DTAB systems we are discussing here. It is still favorable for head groups of such a micelle to be solvated, but the thermodynamic drive to keep them apart is greatly diminished by the fact that they can pack into an array such that they have columbic attraction between them. In other words, anionic molecule, cationic molecule, anionic molecule, etc… This large decrease in the thermodynamic unfavorability of palisade layer formation causes the CMC of SDS/DTAB surfactant mixtures to be lower than the CMC of either SDS or DTAB. The data presented above indicates that, even at mole fractions of 0.01 for either component, substantial synergistic effects take place.

The tendency for SDS and DTAB molecules to pack into a micelle in the basic one to one configuration which is suggested by figure 12 is actually quite strong. Based on the CMC data given above, and nonideal solution theory, the strength of this tendency can actually be calculated for each of the mixtures studied. From nonideal solution thermodynamics the following equation has been developed which pertains to surfactant synergism:[xiv,xv]

$$\frac{X_{SDS}^{2} \ln[\alpha\, C_{mix}|X_{SDS}\, c_{SDS}]}{[1-X_{SDS}]^{2} \ln[(1-\alpha) C_{mix}|(1-X_{SDS}) C_{DTAB}]} = 1$$

wherein X_{SDS} is the mole fraction of SDS molecules in the micelles, α is the mole fraction of SDS in the total surfactant used to make the solution, C_{Mix} is the CMC of the surfactant mixture, C_{SDS} is the CMC for pure SDS, and C_{DTAB} is the CMC of pure DTAB. The equation, as it is written above, has of course been conformed to the system SDS and DTAB. However, it can be analogously used for any surfactant pair.

The utility of this equation lies in the fact that, once the CMC of a surfactant mixture has been determined, it contains only one unknown (X_{SDS}, the mole fraction of SDS molecules in the mixed micelles). Of course, the nature of the equation is such that X_{SDS} must be solved for numerically. However, this is easily done.

The results pertaining to our SDS/DTAB system are shown below, both in tabular form and graphically.

Molar Ratio (SDS/Total Surfactant)	Micellar Molar Ratio (SDS/Total Surfactant
0.00	0.000
0.01	0.259
0.05	0.418
0.10	0.453
0.25	0.487
0.40	0.507
0.50	0.516
0.60	0.527
0.75	0.548
0.90	0.583
0.95	0.652
0.99	0.793
1.00	1.000

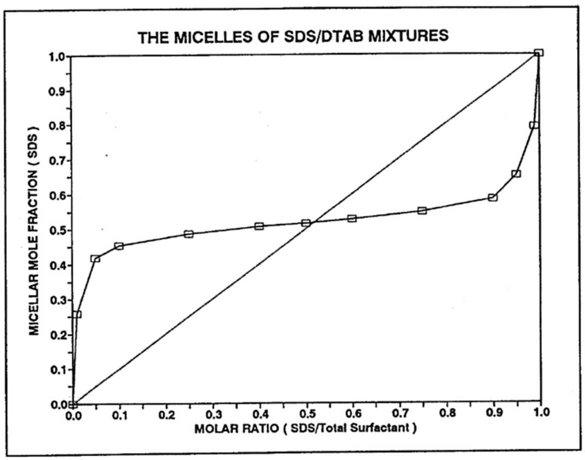

Figure 13

This data strongly supports the notion that SDS/DTAB mixed micelles have a strong tendency to form with a 0.5 molar ratio of each surfactant in the micelle. In other words, with a one to one ratio of SDS molecules to DTAB molecules. This in turn further supports the palisade layer based explanation of synergy between these two surfactants. Even when the surfactant mixture is comprised of only 1% SDS on a molar basis (0.01 mole fraction SDS/Total surfactant), 25.9% of the molecules in the mixed micelles are SDS molecules (0.259 micellar mole fraction SDS/total surfactant) due to the propensity for the palisade layer being developed in a one to one surfactant molecule ratio. Throughout the bulk of the molar concentrations studied the micellar ratios even more closely approached one to one (a 0.5 micellar molar ratio of SDS/Total surfactant). Note, however, that for the mixture containing only 1% DTAB (0.99 solution molar ratio of SDS) 20.7% of the molecules in the micelle where DTAB molecules. This ratio is somewhat lower than the 25.9% of SDS molecules that are found in mixed micelles if SDS is the 1% component. This is simply due the fact that SDS itself forms micelles more readily than DTAB. Recall that the CMC of pure SDS is 8300 micromolar, whereas that of DTAB is 16000 micromolar. This trend follows if you compare the 5% SDS mixture with the 5% DTAB mixture and so forth. In fact, for the mixture containing 50% SDS on a molar basis the mixed micelles contain 51.6% SDS molecules. This slight deviation from one to one surfactant incorporation in the mixed micelles also correlates with the difference in the CMC values of pure SDS and pure DTAB. The dotted line in figure one represents data for a hypothetical duel surfactant system in which there is no synergy and both of the surfactants have the same CMC in their pure forms. It is included for comparative purposes.

Conclusions

So far this application note has discussed many of the thermodynamic principles pertaining to the behavior of surfactants in aqueous solution. It has then used these principles as a basis for further discussion pertaining to synergistic properties of mixed surfactant systems, and shown a good example of synergistic properties between two commonly used ionic surfactants, sodium dodecyl sulfate and dodecyl trimethylammonium bromide. The note itself is particularly designed for individuals who work with products containing multiple surfactants. It is meant to teach, and also to inform such people that Krüss offers an instrument (the K12 Processor Tensiometer) which can assist them in their study of surfactant interactions in multi-surfactant systems. This brings up a couple of issues which require a bit of closure.

First, having read this application note, you may be thinking that we chose a relatively easy pair of surfactants with which to work. Once you understand the importance of the palisade layer in determining how surfactants aggregate in solution, you will realize that a cationic and an anionic surfactant are almost bound to have synergistic relations. This is, of course, completely true. In industry it is perhaps more common to deal with ionic/nonionic mixtures or even nonionic/nonionic mixtures. However, you might be surprised to find that these mixtures often have synergistic properties as well. For example, nonionics often form mixed aggregates with ionics because the presence of nonionic head groups in the palisade layers of aggregates buffers columbic repulsions between the ionic head groups. Rosen discusses the synergistic properties of a wide variety of surfactants in chapter 11 of his book entitled Surfactants and Interfacial Phenomena, which we highly recommend to those who have had their curiosity inspired by this application note.[xvi] There are also other means of causing surfactant systems to alter their aggregation properties aside from adding a cosurfactant. One of the most common is the addition of small molecule electrolytes (salts) to ionic surfactants solutions. This causes condensation of counterions onto the palisade layer of ionic surfactant aggregates, which in turn causes a phase transition toward a phase wherein the palisade layer less solvated (for example, a micellar to lamellar transition.) This effect is used by shampoo manufacturers as a thickening mechanism.

Second, you may be concerned by the fact that this note discusses a wide variety of surfactant colloidal associations and then promotes only the study of micelle formation as a technique for understanding the synergistic aspects of multiple surfactant systems. CMC studies are obviously directly helpful to formulators who wish to produce products in the micellar region. It is obvious that taking advantage of synergy can save surfactant cost and increase a product's performance to cost ratio for micellar based products. The data presented here shows that a small amount of either DTAB or SDS can save a large amount of the opposite surfactant, if micelle formation is the goal. However, the utility of CMC based studies to people who formulate products in hexagonal, lamellar, or other associative regions may not yet be completely clear.

The identification of hexagonal, lamellar, and many other associative surfactant phases is commonly done by polarized light microscopy. The phases are identified by characteristic diffraction patterns. However, the characterization of head group interactions in the palisade layers of these phases is quite difficult. In fact, no scientific technique has been established to routinely do so. The phases are discovered by the formation of phases diagrams, such as figure 5 shown above, in combination with polarized light microscopy identification. Prediction of concentration and temperature regimes in which certain phases will occur can be made based on nonideal solution thermodynamics and a thorough understanding of interactions between surfactant molecules.

CMC measurements do not directly provide information on associative colloids of higher order than micelles. However, they do a good job of characterizing interactions between surfactants in mixed surfactant solutions. This information can be used to predict how the phase diagram of a surfactant mixture will differ from phase diagrams of the component surfactants. Synergistic effects tend to shift a phase diagram to lower overall surfactant concentrations. In other words, the same synergistic effects that cause mixed micelles to form at lower surfactant concentrations also cause hexagonal and lamellar phases to form at lower concentrations. As a result, people who formulate surfactant systems, even in higher order phases than the micellar, rely on CMC measurements as predictors of surfactant phase behavior. Sorry, phase diagrams still need to be constructed. However CMC measurements can serve as a guide to which phase diagrams should be constructed and which are more likely to not be worthwhile. This is their utility.

References

[i.] Tanford, C.; The Hydrophobic Effect, Wiley, New York, (1980).

[ii.] Myers, D.; Surfaces, Colloids and Interfaces, VCH Publishers, New York, (1991).

[iii.] Mittal, K.L. and Lindman B., editors; Surfactants in Solution 1, Plenum Press, New York, (1984).

[iv.] Shaw, D.J.; Colloid and Surface Chemistry, Butterworth-Heinemann Ltd, Oxford, (1992).

[v.] Elworthy, P.H.; Mysels, K.J.; *J. Colloid Sci.*, 21, 331, (1966).

[vi.] Lianos, P.; Zana, R.; *J. Colloid Interface Sci.*, 84, 100, (1981).

[vii.] Klevens, H.B.; *J. Phys. Colloid Chem.*, 52, 130, (1948).

[viii.] Lianos, P.; Zana, R.; *J. Colloid Interface Sci.*, 88, 594, (1982).

[ix.] Czerniawski, M., *Roczn. Chem.*, 40, 1935, (1966).

[x.] Corkill, J.M.; Goodman, J.F.; Ottewill, R.H.; *Trans. Faraday Soc.*, 57, 1627, (1961).

[xi.] Balmbra, R.R.; Clunie, J.S.; Corkill, J.M.; Goodman, J.F.; *Trans. Faraday Soc.*, 58, 1661, (1962).

[xii.] Rosen, M.J.; Cohen, A.W.; Dahanayake, M.; Hua, X.Y.; *J. Phys. Chem.*, 86, 541, (1982).

[xiii.] Becher, P.; *J. Colloid Sci.*, 16, 49, (1961).

[xiv.] Rosen, M.J.; Hua, X.Y.; *J. Colloid Interface Sci.*, 86, 164, (1982).

[xv.] Rubingh, D.N. in Solution Chemistry of Surfactants, Mittal, K.L., ed., Vol. 1, Plenum, New York, (1979).

[xvi.] Rosen M.J.; Surfactants and Interfacial Phenomena, 2nd edition, John Wiley & Sons, New York, (1989).