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ORIGINAL ARTICLE

Review on Anionic/Cationic Surfactant Mixtures

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Abstract It is commonly known that cationic and anionic surfactants cannot be mixed without the risk of precipitation or instability. However, many studies have shown that not only is it possible to combine cationic and anionic surfactants, but also that this combination can present synergic properties. Mixtures of anionic and cationic surfactants have many unique properties that can be very useful when used properly. The aim of this report is to present relevant information concerning the interaction between anionic and cationic surfactants. A bibliographic review on anionic/cationic mixtures is presented here in order to better understand their properties and possible synergic effects, as this is of practical importance for the chemical industry.

Keywords Anionic surfactants · Application of surfactants · Cationic surfactants · Detergent formulation · Non-ionic surfactants

Introduction

The term surfactant is a blend of “Surface Active Agent”. Surfactants are usually amphiphilic organic compounds (normally possessing a hydrophobic tail and a hydrophilic head), which allows them to change the interfacial properties of liquids in which they are present.

Surfactants are commonly classified into four categories, according to the formal charge present in their hydrophilic head: anionic (negatively charged), cationic (positively charged), nonionic (uncharged) and amphoteric (presents both positive and negative charges at an intermediate pH). For each classification, it is possible to sub-classify according to the functional group of the hydrophilic head. For the household industry, the most common anionic surfactants are those with a sulfate, sulfonate, or carboxylate (soap) group attached to them. For the cationic surfactants, the quaternary ammonium groups are widely used, and are by far the most common. The nonionic surfactants are mainly derived from the reaction of alcohols, alkylphenols and amines with ethylene oxide and/or propylene oxide. Finally, the amphoteric surfactants, also known as zwitterionic surfactants, are represented mainly by acyl ethylenediamines and alkyl amino acids. A common misunderstanding is the classification of alkyl betaines as amphoteric surfactants, as they have a permanent positive charge and can present a negative charge at high pH. However, as they never present a single negative charge, they cannot be considered zwitterionic surfactants.

There are many examples of surfactant mixtures in the household market. Since it is a well-established idea that cationic and anionic surfactants cannot be present in the same formulation, mixtures are generally between anionic/anionic, cationic/cationic, nonionic/nonionic, amphoteric/amphoteric, anionic/nonionic, cationic/nonionic or amphoteric/nonionic. However, synergism increases with the degree of charge difference [1, 2] meaning that synergism between anionic/anionic or nonionic/nonionic is less than that between anionic/nonionic or cationic/nonionic, which, in turn, is less than that between cationic/anionic. Consequently, the higher synergism is obtained by mixing anionic and cationic surfactants, and therefore, a better understanding of that system may broaden the horizon for household formulations.

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Anionic/Cationic Complexes

When small amounts of either anionic or cationic surfactants are added to an aqueous solution, they exist only as monomers in solution. When the concentration is increased and reaches the cmc (critical micelle concentration), micelles start to form. If, however, the concentrations of both the anionic and cationic monomers exceed the solubility product, precipitation will occur. As precipitation generally renders the surfactant ineffective in solution, it is important to understand that system. Precipitation of anionic surfactants [3–5] and mixtures of anionic/nonionic surfactants [6] has been previously successfully modeled, and the behavior and physicochemical properties of mixtures of a highly branched cationic and sodium alkyl sulfate have been widely studied by Zhi-Jian Yu and co-workers [7–9].

K.L. Stellner and co-workers decided to study mixtures of anionic and cationic surfactants [10] over a wide range of concentrations in order to develop a model that could provide complete phase boundaries for that system.

Figure 1 shows a schematic diagram of the equilibrium proposed by Stellner.

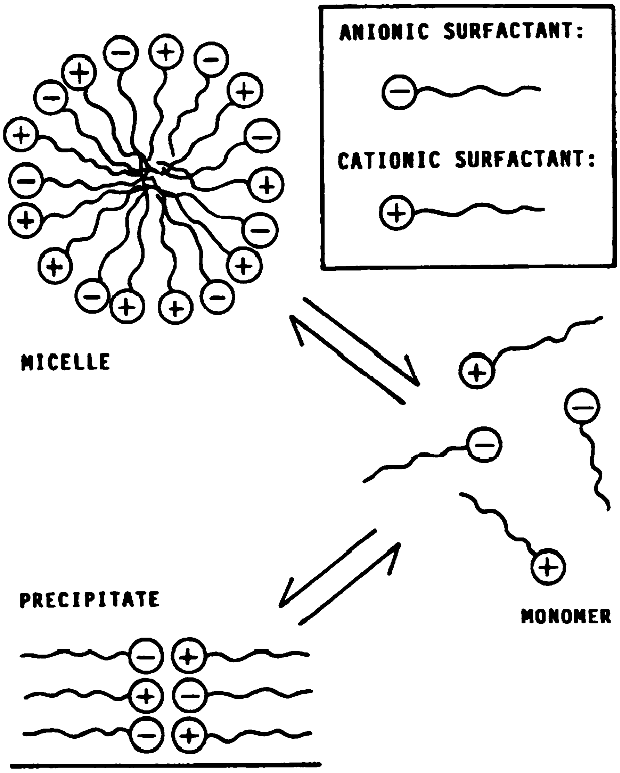


Fig. 1 Schematic diagram of basic equilibrium in a cationic/anionic system. Reprinted from [10], with permission from Elsevier

According to Fig. 1, the surfactants can be present in three different environments: as monomers, incorporated in mixed micelles and as precipitate. The formation of precipitate can be represented by:

$$\mathrm{DS^-(aq) + DP^+(aq) \rightleftarrows DSDP\ (s)}$$

where DS^- stands for dodecyl sulfate anion and DP^+ is dodecylpyridinium cation, and DSDP is the precipitate formed in the reaction. This reaction can be described by the following solubility product:

$$K_{sp} = [DS^-]_{mon}[DP^+]_{mon} f_{\pm}^2$$

where K_{sp} is the solubility product, $[DS^-]_{mon}$ and $[DP^+]_{mon}$ are the respective monomer concentration, and $f_{\pm}$ is the activity coefficient, which can be estimated by using an extended Debye-Hückel equation proposed by Davies [11]:

$$\log f_{\pm} = -0.5139|z_+ z_-| \times \left\{ \sqrt{I} \Big/ \left(1 + \sqrt{I}\right) - 0.3I \right\}$$

where I is the ionic strength. As the idea is to calculate the precipitation phase boundaries, we can assume that all the surfactants on the boundary are present in monomers or mixed micelles. Therefore, we can consider:

$$C_{NaDS} = [DS^-]_{mon} + [DS^-]_{mic}$$

$$C_{DPCl} = [DP^+]_{mon} + [DP^+]_{mic}$$

where C_{NaDS} and C_{DPCl} are the total concentration of NaDS and DPCl in solution, and the concentration of each surfactant in mixed micelles is given by $[DS^-]_{mic}$ and $[DP^+]_{mic}$.

In order to calculate the monomer concentration, it is necessary to model the equilibrium monomer-micelle. Applying the regular solution theory [12] and considering that micelles are a surfactant pseudo-phase, we have:

$$[DS^-]_{mon} = X_{DS}\mathrm{cmc}_{DS} \exp\left\{(1 - X_{DS})^2 W/RT\right\}$$

$$[DP^+]_{mon} = (1 - X_{DS})\mathrm{cmc}_{DP} \exp\left\{(X_{DS})^2 W/RT\right\}$$

here cmc_{DS} and cmc_{DP} are the cmc values of the pure surfactants, W is the interaction parameter, R is the ideal gas constant, and T is the absolute temperature.

The X_{DS} (and $X_{DP} = 1 - X_{DS}$) is the mole fraction of the surfactant in the micelles:

$$X_{DS} = [DS^-]_{mic} \big/ \left\{[DS^-]_{mic} + [DP^+]_{mic}\right\}$$

If K_{sp}, W/RT, cmc_{DS} and cmc_{DP} are known, all the equations can be simultaneously solved for C_{DPCl}, $[DS^-]_{mon}$, $[DP^+]_{mon}$, $f_{\pm}$, I, X_{DS}, $[DS^-]_{mic}$ and $[DP^+]_{mic}$. Therefore, the model developed by Stellner can predict the precipitation phase boundaries.

Considering $\mathrm{cmc}_{DS} = 7.7 \times 10^{-4}$ M, $\mathrm{cmc}_{DP} = 4.0 \times 10^{-3}$ M, $K_{sp} = 2.24 \times 10^{-10}$ and $W/RT = -8.62$ [10], the precipitation boundary was calculated and the results are in Fig. 2. It is clear that, as the precipitate-monomer

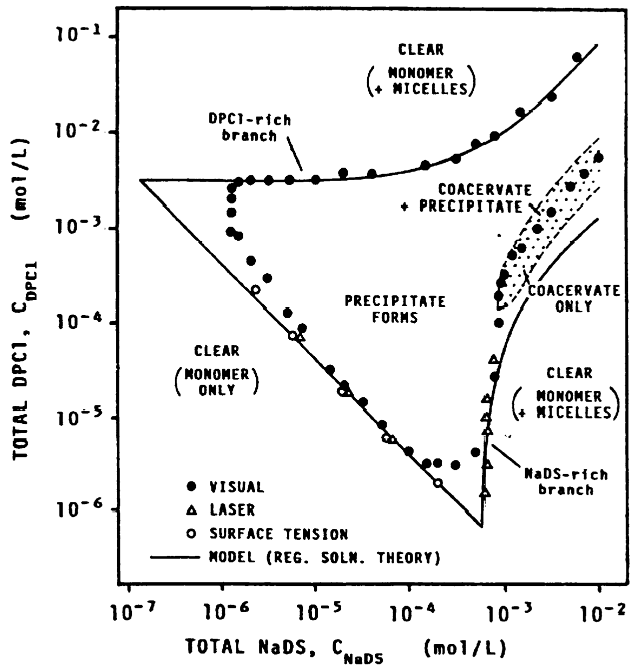


Fig. 2 Precipitation phase boundary with predictions using regular solution theory. Reprinted from [10], with permission from Elsevier

line approaches the cmc values of each surfactant, significant changes occur in the solution. The sharp breaks are indicative of the formation of micelles in solution. From these points, the boundary extends in two branches, a NaDS-rich and a DPCl-rich. It is interesting to note that at the NaDS-rich branch, the experimental data deviates significantly from the model. This is probably due to the formation of coacervates, which are small droplets in solution that are rich in surfactants. These coalesce over a period of time so that the original solution separates into two isotropic liquids: one is rich in surfactant and therefore usually viscous, and the other contains little surfactant. Figure 2 shows that in some of the solutions studied only coacervate forms, while in other solutions both coacervate and precipitate form, and the precipitation boundary lies within the region where coacervate may form. Indeed, in some solutions it is difficult to determine the presence of precipitate due to turbidity caused by coacervate that has not settled out of solution [10].

Joel C. Amante and Bor-Jier Shiau have studied the influence of some variables, such as pH, temperature, chain length [13] and addition of nonionics [14], on Stellner's model. They have used the theory to draw the phase boundaries and have conducted many experiments to corroborate them.

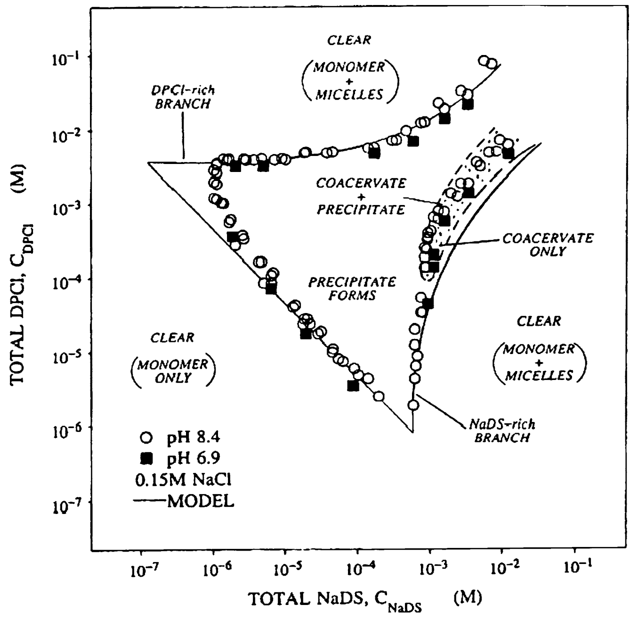


Fig. 3 Effect of the pH on the precipitation phase boundary. Reprinted from [13], with permission from Elsevier

Figure 3 shows the influence of pH on the precipitation boundaries. At the tested pH range (6.9–8.4), no influence on precipitation is observed. In addition, pH does not significantly influence the cmc of the tested surfactants, and the influence of electrolytes added for pH adjustment is negligible.

As seen in Fig. 4, an increase in temperature generally results in the reduction of the precipitation boundaries. For the studied system, the higher the temperature, the higher

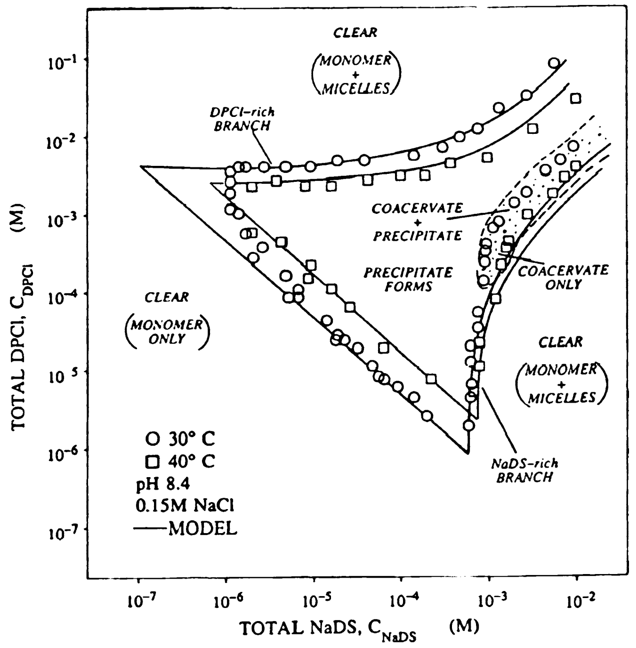


Fig. 4 Effect of the temperature on the precipitation phase boundary. Reprinted from [13], with permission from Elsevier

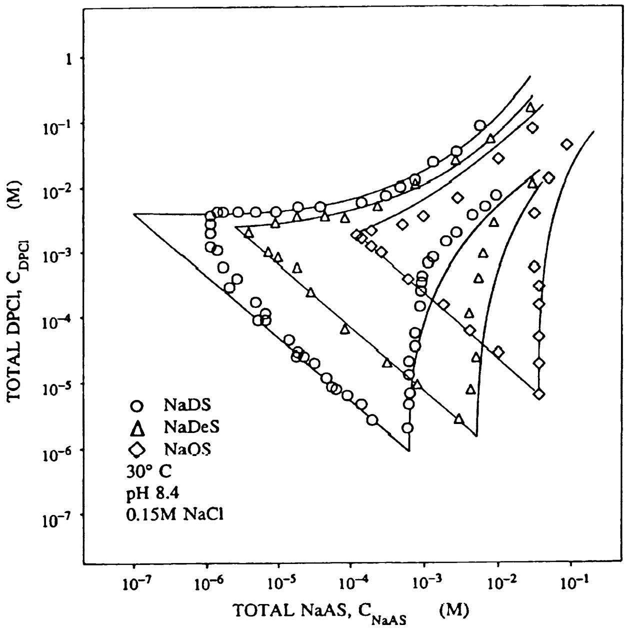


Fig. 5 Effect of the chain length of the anionic on the precipitation phase boundary. Reprinted from [13], with permission from Elsevier

the surfactant concentration that is needed to obtain precipitation below the cmc and below the DPCl-rich branch.

From Fig. 5 one can conclude that, as the chain length of the NaAS decreases, precipitation requires a higher NaAS concentration to occur.

Again, for all three studies, the experimental data deviates from the model when there is formation of coacervate.

The addition of a nonylphenol ethoxylate with 10 mol of EO (NP(EO)$_{10}$) to the cationic/anionic system was studied by Bor-Jier Shiau [14], and leads to a new equilibrium, shown in Fig. 6.

The model, based on the equilibrium above, was able to predict the effect of the addition of NP(EO)$_{10}$ to the system, as shown in Fig. 7.

As seen in the graphic, the higher the concentration of NP(EO)$_{10}$, the shorter the precipitation area, that is, the increase in nonionic concentration shrinks the precipitation boundaries. Shiau has concluded that this can be understood by considering the influence of nonionic surfactants on the cmc of the surfactant mixture. His model was able to predict the shrinkage of precipitation domains when NP(EO)$_{10}$ was added into the anionic/cationic surfactant system by accounting only for the lowering of the cmc of the system. The low cmc of NP(EO)$_{10}$ tended to enhance mixed micellization. If a nonionic surfactant with a high cmc had been used, the extent to which the precipitation domain shrank would have been less because mixed micellization would not have been so enhanced.

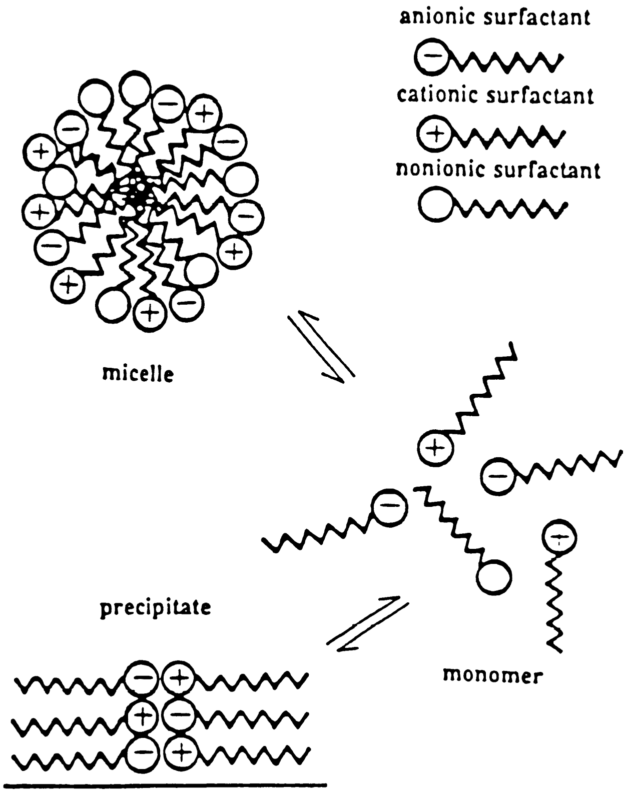


Fig. 6 Schematic diagram of basic equilibrium in a ternary surfactant mixture. Reprinted from [14], with permission from Elsevier

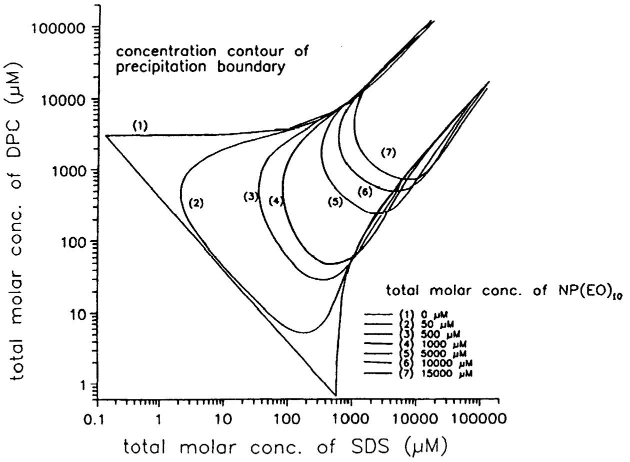


Fig. 7 Effect of nonionic concentration on precipitation phase boundaries. Reprinted from [14], with permission from Elsevier

Micelle to Vesicle Transition

Mixtures of cationic and anionic surfactants may present different properties and structures. Bergström and coworkers have studied the formation of many of those structures in cationic/anionic surfactant systems using the small-angle neutron scattering technique [15–17]. The formation of vesicles, which are single-bilayer closed shells that encapsulate an aqueous interior, in the specific sodium dodecyl sulfate/didodecyl dimethylammonium bromide system was studied by Marques and co-workers [18, 19].

Eric W. Kaler and co-workers [20–23] have studied the phase behavior and structures of mixtures of oppositely charged surfactants. For those studies, measurements of conductivity, cryo-transmission electron microscopy, video-enhanced microscopy, time-resolved fluorescence quenching, and/or quasielastic light scattering were used.

Mixtures of anionic and cationic surfactants present many unique properties: they have much lower critical aggregation concentrations (cac) than do single pure surfactants; they are usually more surface active than either pure surfactant; and they can produce microstructures not formed by pure components (such as vesicles and rod-like micelles). They can also decrease the concentration at which liquid crystalline phases form.

These properties can be exploited in many ways. The cac may be useful in detergency applications, and the vesicles could eventually be used for controlled drug release, microreactors and model membranes [21].

It was found that the extent of the vesicular phase depends on the surfactant structure: when both surfactants are linear and symmetric in chain length, the precipitate phase dominates the phase behavior and micelles and vesicles are observed only at higher concentrations. Vesicular phases are stable when the surfactants are branched and/or contain a bulky substituent in the tail group.

Figure 8 shows a ternary phase diagram for a CTAT/SDBS/water (cetyl trimethylammonium tosylate / branched sodium dodecyl benzene sulfonate / water) mixture. As seen in the graphic, it has a large vesicular phase, mainly in the water-rich corner and precipitation occurs only at the equimolar line.

As the vesicular phases all present mixed surfactant bilayers, a question that arises is why do mixed surfactants form bilayers, when pure surfactants form only micelles, multilayers or exist as monomers in solution? One of the possible theories to explain the formation of vesicles says that the packing of surfactant molecules is ruled by a “surfactant number” $v / a_0 l_c$ [24–26] where v is the volume of the hydrophobic portion of the surfactant, l_c is the length of the hydrophobic group, and a_0 is the area of the hydrophilic head group. According to the theory, when the surfactant number is less than 1/3, spherical micelles are preferred. Cylindrical micelles form when it is between 1/3 and 1/2, and when it is greater than 1/2, curved bilayer vesicles are formed. As the surfactant number goes to 1, flat bilayers are formed. For anionic/cationic surfactant mixtures, one can assume that there is a formation of a pseudo double-tailed zwitterionic surfactant, meaning that there is a decrease in the effective size of the head group and an increase in the volume of the hydrophobic portion. This will dramatically affect the surfactant number, leading to a transition from the spherical or cylindrical micelles that exist in the pure component to vesicles or multilayers in the mixed surfactant system.

Another experiment by Herrington has proven the impact of surfactant geometry on the anionic/cationic system [21]. Figure 9 shows a ternary phase diagram for a DTAB/SDS/water (dodecyl trimethylammonium bromide / linear sodium dodecyl sulfate / water) mixture.

This ternary phase is rather different from the previous one. The micellar phase is far more extensive at the SDS side and the precipitate appears above a mixing ratio of

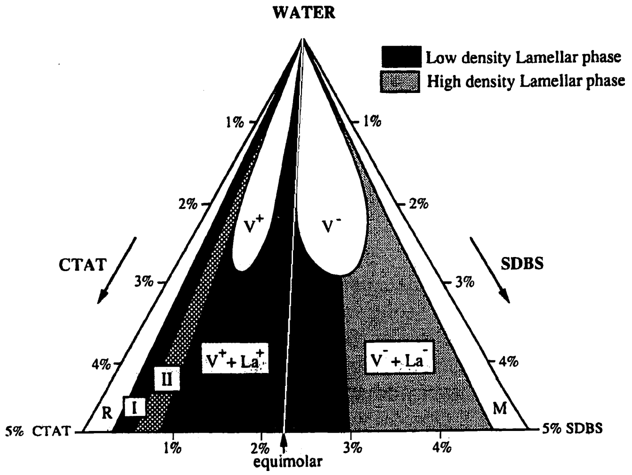


Fig. 8 Ternary phase diagram for CTAC/SDBS/Water. (*V*) vesicles, (*La*) lamellar phase, (*M*) micelles, (*R*) rod-like micelles, (*I* and *II*) multi-phase region, precipitate is along the equimolar line. Reprinted with permission from [20], American Chemical Society

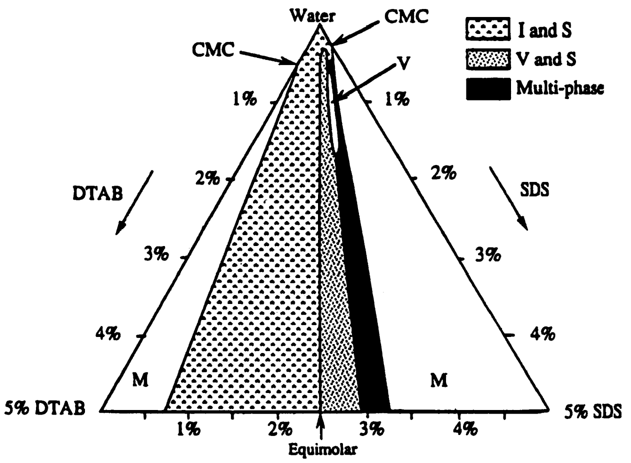


Fig. 9 Ternary phase diagram for DTAB/SDS/Water. (*M*) micelles, (*I*) clear liquid, (*V*) vesicles, (*S*) precipitate. Reprinted with permission from [21], American Chemical Society

85:15 DTAB/SDS at the cationic-rich mixture and 40:60 DTAB/SDS at the anionic-rich mixture.

When comparing both ternary phase diagrams, it is possible to conclude that when the surfactants are branched and/or contain a bulky substituent (e.g., benzene group) the precipitate region is reduced relative to that of the micelles and the vesicles. It is also possible to note that the more symmetrical the anionic/cationic system (cationic and anionic surfactants with the same carbon chain), the wider the precipitation region. This explains why there are large regions of vesicular phase and small precipitation areas in the first ternary phase diagram.

Based on the second ternary phase diagram, a path to the micelle-to-vesicle transition was proposed: SDS-rich micelles grow as the DTAB concentration is increased. Above the mixing ratio of 20:80 DTAB/SDS, long rod-like micelles start to form. DTAB is added until vesicles and multilamellar vesicles appear. The transition from rod-like micelles to vesicles is not very sharp. There is a multiphase region between the two phases.

A third experiment by Yatcilla and co-workers [22] corroborates the conclusions above. A ternary phase diagram of CTAB/SOS/water (cetyl trimethylammonium bromide / sodium octyl sulfate / water) is shown in Fig. 10.

As seen in the graphic, mixtures of asymmetrical surfactants promote the formation of vesicles relative to multilamellar structures or precipitates. This is probably due to the fact that asymmetrical chain lengths cannot pack efficiently into the crystalline lattice, limiting the formation of precipitates. It is also possible to confirm the assertion that whenever the tail lengths are different, the extent of the vesicle region is larger for mixtures rich in the shorter-tailed surfactant.

Söderman and co-workers have tested the influence of the counterion on the vesicle formation [23]. A comparison between DTAB (dodecyl trimethylammonium bromide) and DTAC (dodecyl trimethylammonium chloride) was made, and a partial phase diagram with the results is shown in Fig. 11.

As seen in the graphic, when chloride is the counterion the vesicle phase is smaller. According to Söderman, the extent of the vesicle phase depends on how closely packed the vesicles are. When intervesicle interactions are stronger, the vesicles begin to feel crowded at lower surfactant concentrations and the extent of the vesicle lobe decreases. Thus, the chloride ions, being more hydrated than bromide ions, are less effective in shielding the charge of the surfactant aggregate. This leads to a stronger interaction between them and thus decreases the vesicle region.

Brasher and co-workers have tested the influence of electrolytes in these systems [27] since aggregation is apparently driven by electrostatic interactions between the oppositely charged surfactants. He has found that the addition of salt dramatically reduces the range of surfactant concentrations at which vesicles can form.

B. Jönsson and co-workers studied the phase behavior and microemulsions of what he called catanionic surfactants [28–31], which are basically equimolar mixtures of anionic and cationic surfactants. They have developed a

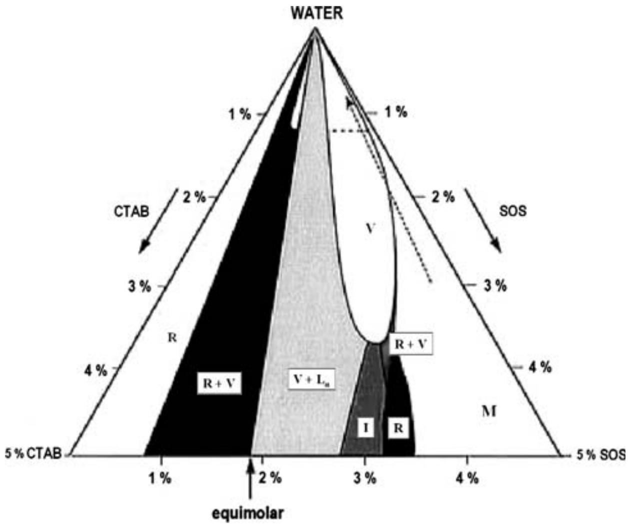


Fig. 10 Ternary phase diagram for CTAB/SOS/Water. (*V*) vesicles, (*R*) rod-like micelles, (*M*) micelles, (L_α) lamellar phase, (*I*) multiphase region, precipitate is along the equimolar line. Reprinted with permission from [22], American Chemical Society

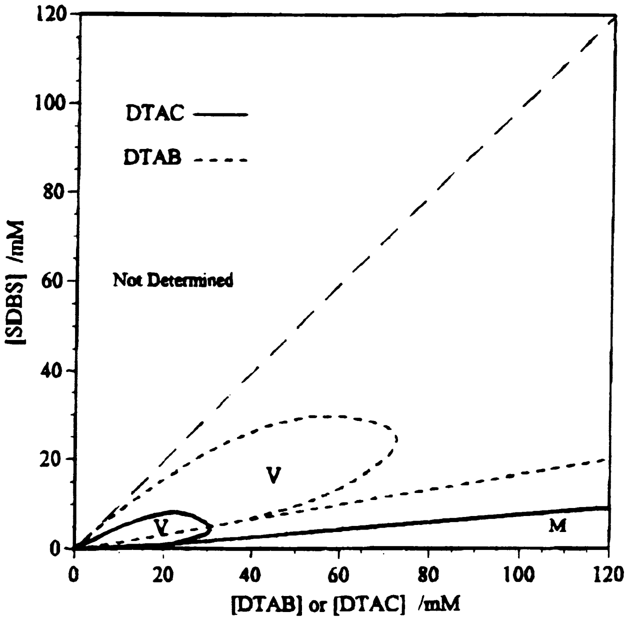


Fig. 11 Partial phase diagram for aqueous mixtures of SDBS with either DTAB or DTAC. (*V*) vesicle, (*M*) micelle. Reprinted with permission from [23], American Chemical Society

model that gives a description of the thermodynamics and phase equilibria in ionic surfactant-water systems, where they considered the cationic/anionic complex as a zwitterionic (or amphoteric) surfactant, the difference being that in catanionics the distance between the two opposite charges is not fixed [28]. They have found that the catanionic surfactant-water systems show similar phase behavior as lecithin/water systems, where a lamellar phase is in equilibrium with almost pure water [29]. In both cases, the swelling of the lamellae is assumed to be due to the hydration force interactions between the bilayers. The experimental results show that the strength of the hydration force is more dependent on the size of the polar headgroups than the specific chemical composition of them. They have also studied ternary systems such as sodium octanoate-octylammonium octanoate-water [30] and dodecyl ammonium dodecanoate-dodecanol-water [31], developing equilibrium diagrams for each system and showing size and stability of the different possible phases that may appear.

N. Filipović-Vincenković and co-workers have also studied the transition from catanionic salt to mixed cationic/anionic vesicles [32]. He has confirmed the experiments of Kaler [20], showing that there is a region in the intermediate concentration of the surfactants where crystalline and liquid crystalline phases coexist, the latter consisting of small and large vesicles.

Andrea J. O'Connor and co-workers pictured a more detailed model for the micelle-to-vesicle transition [33]. Figure 12 illustrates that model.

Synergism

Synergism of mixtures of surfactants increases with the degree of charge difference between them [42], which means that mixtures of anionic and cationic surfactants present the highest level of synergism. Many studies were conducted in order to better understand this.

Milton J. Rosen and co-workers have studied the synergism in binary mixtures of surfactants [1, 34–38]. By using the Regular Solution Theory [12] to calculate a parameter β called Molecular Interaction Parameter, Rosen was able to quantify the synergism of different surfactant mixtures.

Lucassen-Reynders and co-workers studied the surface tensions of several mixtures of SDS (sodium dodecyl sulfate) and DTAB (dodecyl trimethylammonium bromide) [39]. Figure 13 shows the relationship between surface tension, concentration and mixing ratios (SDS/DTAB).

From the graphic, it is clear that a strong synergism occurs in the cationic/anionic mixtures. For instance, to reach a surface tension of 50 mN/m, a concentration of 4.5 mol/m^3 of SDS alone is required. However, to reach the same surface tension only 9×10^{-3} mol/m^3 of the equimolar mixture is needed.

According to Lucassen-Reynders, and considering that R is the surfactant with the respective formal charge, the basic idea is that only electroneutral combinations of ions can take place. Therefore, in a mixed system NaR$^-$/R$^+$Br, there are four possible combinations. The combination NaBr is singularly non surface-active and it is demonstrated that the

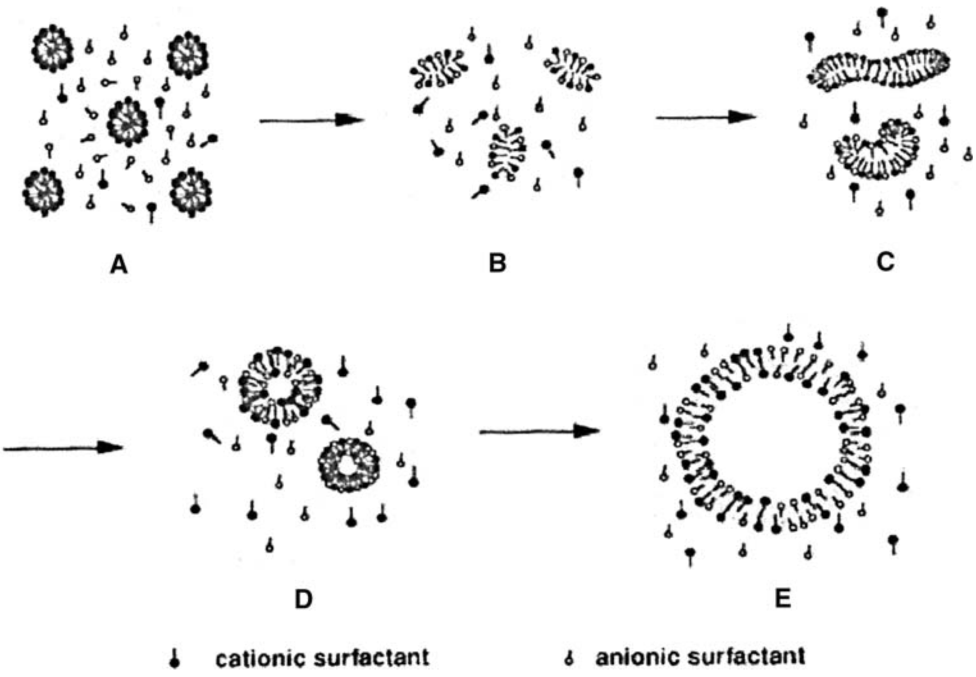


Fig. 12 Possible intermediate states during micelle-vesicle transition. *A* SOS (sodium octyl sulfate) monomers and CTAB (cetyl trimethylammonium bromide) micelles. *B* nonequilibrium mixed micelles. *C* floppy, irregularly shaped mixed micelles. *D* nonequilibrium vesicles. *E* final vesicles. Reprinted with permission from [33], American Chemical Society

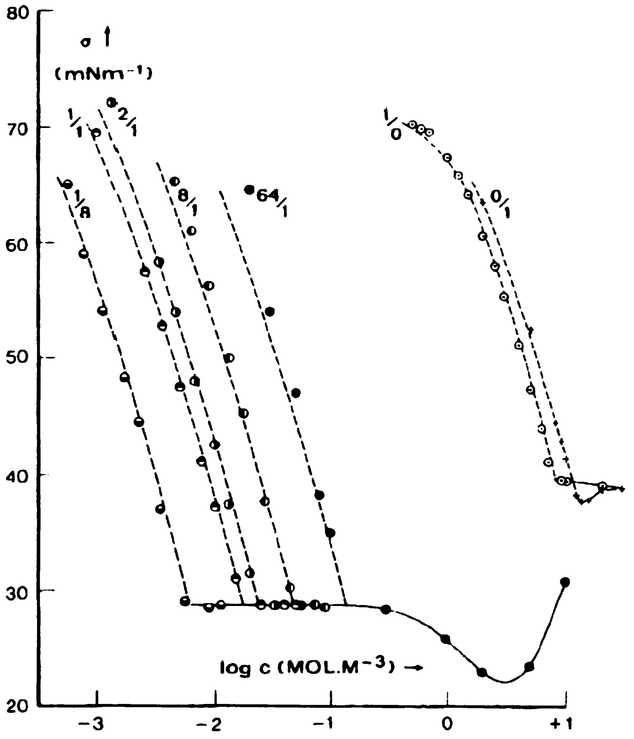


Fig. 13 Surface tension for mixtures of SDS/DTAB. Mixing ratios 1:8, 1:1, 2:1, 8:1, 64:1, 1:0, 0:1, respectively. Reprinted from [39], Copyright (1981), with permission from Elsevier

electroneutral combination R^+R^- is far more surface active than either NaR^- or R^+Br [40]. Thus, adsorption of R^+R^- will be much higher than that of either NaR^- or R^+Br at a given concentration. This higher adsorption leads to a much lower surface tension.

Similar results to Lucassen-Reynders work on surface tension were obtained by Z.-G. Cui and J.P. Canselier [41]. Figure 14 presents the curve of surface tension versus concentration of DTAB (dodecyl trimethylammonium bromide) in the mixture TADPS (triethanolammonium dodecylpoly (oxyethylene) sulfate)/DTAB. For $\alpha = 0$, the solution is cationic only and for $\alpha = 1$ it is anionic only. Again, the concentration to reach any surface tension is smaller for any mixture than for both pure solutions.

Mehreteab and co-workers studied the formation of water-soluble pseudo-nonionic complexes of anionic and cationic surfactants [42]. They found that such complexes can present a cloud point temperature, a typical nonionic characteristic. Cloud point in nonionic surfactants, especially in polyoxyethylenated ones, is believed to be due to micellar aggregation. Hydrated oxyethylene head groups oppose that aggregation, thus preventing the turbidity. However, as the temperature is increased, the oxyethylene groups become dehydrated, leading to micellar aggregation, and consequently, to turbidity and cloud point. Considering that, it is reasonable that ionic surfactants do not have a cloud point, as the electrostatic repulsion between their charged micelles is higher than the forces needed to aggregate them. For mixtures of anionic/cationic surfactants, at a molar ratio of 1:1, the charge on the micelle is close to zero, thus eliminating the electrostatic repulsion between their micelles, forming the so called pseudo-nonionic micelles. And, as expected, as the concentration of one of the surfactants is increased, the cloud point also increases. Figure 15 shows the results for a mixture of AEOS (alkylpolyoxyethylene sulfate) and TTAB (tetradecyl trimethylammonium bromide), at a total fixed surfactant concentration of 0.05 M. As seen in this

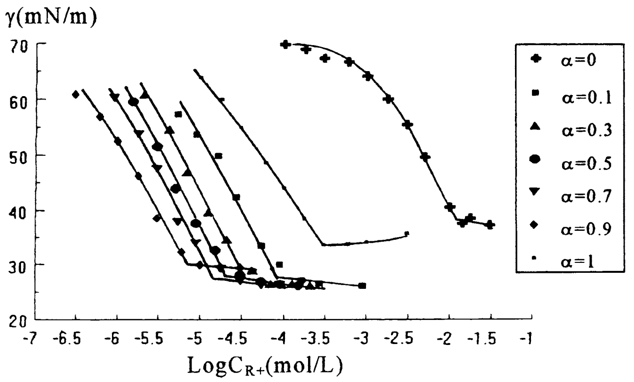


Fig. 14 Surface tensions of TADPS/DTAB system at 25 °C (for $\alpha = 1$, $c = c_{TADPS}$). Springer [41], Fig. 1, Copyright Springer-Verlag 2001, is given to the publication in which the material was originally published, by adding: “With kind permission from Springer Science and Business Media”

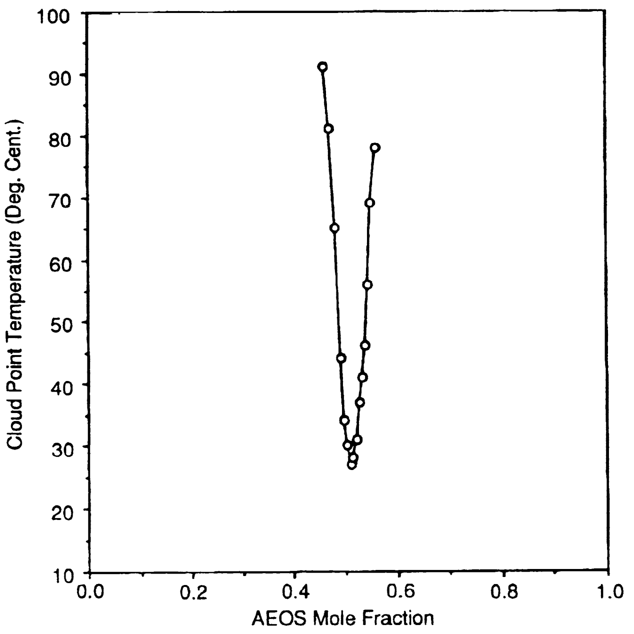


Fig. 15 Cloud point temperature of AEOS/TTAB solutions (total surfactant concentration = 0.05 M). Reprinted from [42], with permission from Elsevier

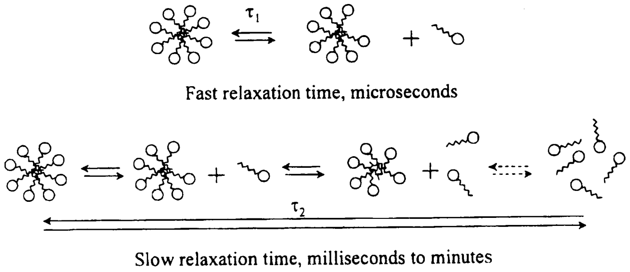


Fig. 16 Mechanism for two relaxation times, τ_1 and τ_2, for a surfactant above the cmc. Reprinted from [43], with permission from Elsevier

graphic, the lower cloud point is at the equimolar ratio of 0.5. Below 0.4 or above 0.6, no cloud point was observed even when heating to 100 °C.

Synergism is also observed in the stabilization of the micelle. Patist and co-workers have studied the relaxation time of the micelle [43]. Micelles are always in a dynamic equilibrium with the monomers in solution, continuously disintegrating and reforming. Figure 16 is a representation of this dynamic equilibrium.

There are two equilibriums in a micellar solution. The first one, with time constant τ_1, is fast and is associated with the exchange of monomers between micelles and the solution. The second one, τ_2, is much slower and is related to the formation and disintegration of the micelle. Therefore, by measuring the second constant, τ_2, it is possible to determine the stabilization of the micelle and compare it to many dynamic processes such as foamability, wetting time, bubble volume, emulsion droplet size and solubilization rate of benzene.

Figure 17 shows many properties and their relation to the micellar stability. For SDS (sodium dodecyl sulfate) solutions, a maximum relaxation time was found at 200 mM. The figure is interesting for showing the correlation between relaxation time and many dynamic processes such as foamability, wetting time, bubble volume etc.

Patist suggests that the micellar stability is directly correlated to Coulombic repulsions. He proposes that the minimization of the charge repulsion between micelles provides a considerable stabilization to the micellar structure. Filipović-Vinceković has also discovered that the addition of oppositely charged surfactant diminishes the surface charge density of the mixed micelles [44]. Based on that, one can affirm that there are many factors enhancing the micellar stability, thus enhancing detergency, and the addition of a surfactant of opposite charge is one of them [45]. Patist has measured the relaxation time of SDS micelles in the presence of long chain alcohols or cationic surfactants [46], and has found the following values:

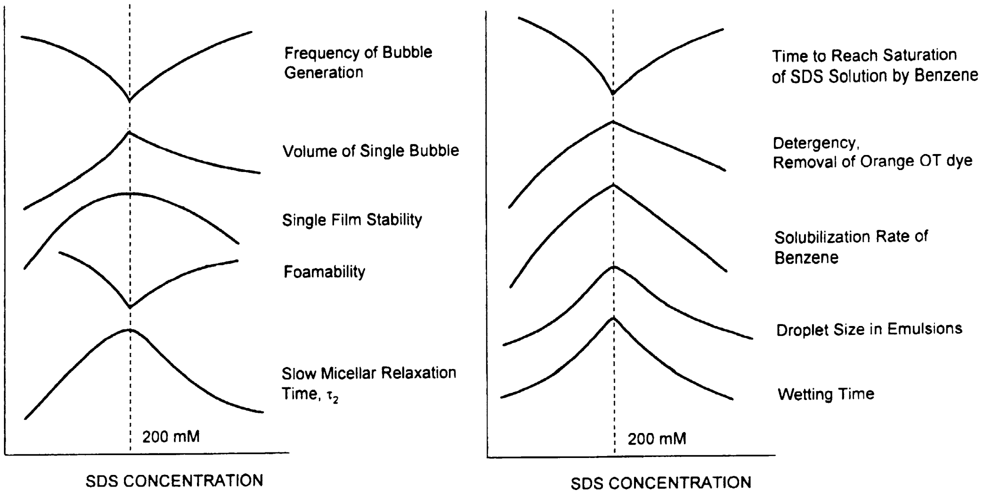
$$25\ \text{mM}\ \ \text{SDS}, \tau_2 = 1\,\text{ms}.$$

$$25\text{mM}\,\text{SDS} + 1.25\text{mM}\,\text{C}_{12}\text{OH}, \tau_2 = 230\,\text{ms}.$$

$$25\text{mM}\,\text{SDS} + 10\text{mM}\,\text{C}_{12}\text{TAB}, \tau_2 = 2000\,\text{ms}.$$

In other words, cationic surfactants, when used in concentrations that avoid precipitation of the formed complex and favor the formation of mixed micelles with anionic surfactants, can enhance the detergency properties of the anionics, as mixed anionic/cationic micelles present longer relaxation times, meaning they are more stable. In addition, they are more tightly packed and their interior is more hydrophobic, causing more rapid partitioning or solubilization of oily soils. This was proved by James-Smith and co-workers [47] who have determined that more stable micellar solutions lead to more efficient and effective detergency. This has been attributed to the following factors: stable micelles solutions have a lower concentration of sub-micellar aggregates, which are poor solubilizers;

Fig. 17 Liquid/gas, liquid/liquid and liquid/solid phenomena exhibiting minima and maxima at 200 mM. Reprinted from [43], with permission from Elsevier



stable micellar solutions have a higher concentration of micelles available to solubilize the oily stains; stable micelles can better solubilize oil stains because they are tightly packed; and stable micelles would minimize redeposition of soils as compared to unstable micelles.

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