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Chapter

Surfactant Mixtures: Performances vs. Aggregation States

Camillo La Mesa and Gianfranco Risuleo

Abstract

The focus of this chapter is on bio-intended procedures based on mixing surfactants with polymers and biopolymers, or surfactants among them (provided they are oppositely charged). In the first case, polymer-surfactant and protein-surfactant systems are dealt with. Both are characterized by the splitting of the solution phase into, at least, three regions having peculiar properties. At first, surfactant nucleation onto polymers takes place; this implies large modifications in properties with respect to the starting materials. The formation of gels is possible in some instances. As to mixtures of oppositely charged surfactants, it is indicated how they form cat-anionic vesicles if mixed in nonstoichiometric amounts. Vesicle sizes are modulated by the charge ratio. These systems are excellent vectors for biomedical purposes.

Keywords: ionic surfactant mixtures, size and shape, surface charge density of micelles and vesicles, polymer-surfactant systems, protein-surfactant systems

1. Introduction

The certified history of surfactants and detergents goes back to the Mesopotamian and Egyptian ages. In the Roman period, authors contemporary of Julius Caesar described the procedures in use from Gauls and Belges to produce soaps from the alkaline hydrolysis of beef fat [1]. They were horribly shocked for the excessive use of soaps that Gauls consumed in hair cleaning. Such procedures are still in use in the preparation of niche products as Marseille soap. In much more recent times, new procedures largely improved the preparation of surface-active products, synthetizing alkyl sulfates. These studies date back to the 1930s of the last century [2]. Later on, nonionic surfactants of the alkyl-polyoxyethylene family, as Triton TX-100, or zwitterionic ones were worked out and synthetized [3]. This induced chemists to prepare new classes of solid or liquid formulations, with better performances in terms of surface activity and solvent capacity. These efforts allowed preparing chemicals capable to operate in all working conditions, irrespective of pH, the presence of calcium, and ionic strength of the dispersant [4–6].

Nowadays, focus is on surfactant mixtures, improving the intrinsic quality of formulations and allowing applications to much more cases than those originally intended for. Applications of surfactant-based systems are much more versatile with respect to canonical laundry and personal body care formulations that were exploited until now. Current research lines focus on unexpected fields, as applications in biomedicine and in the feminine personal hygiene formulations. We do not consider, in this review, the adjuvant action played by cosurfactants, as long-chain

alkanols, glycerol, sterols, perfumes, softeners, bleaching adjuvants, and so forth. We mainly focus on the addition of species increasing the surface activity and solvency of existing surface-active/cleaning formulations and in applications thereof. In particular, the synergistic properties that are observed in surfactant mixtures [7, 8] are discussed.

Cases of interest span from mixtures of ionic species of the same charge, to ionic/nonionic ones, and to mixtures of species having oppositely charged polar head groups. Relevant are also the cases where polymers, enzymes, and proteins are added. We discuss separately all the above fields taking into account the reasons underlying such research lines. In turn, focus is on the following aspects:

i. addition of polymers/biopolymers, referred to as *PSS*s [9]; and

ii. use of mixtures made of oppositely charged surfactants, defined as *Cat-An* systems [10].

The above items are more strictly interconnected than one could think at a first glance. In both the organizing role played, surfactants are crucial both on small or medium size scale (for polymer/surfactant systems) and on a much larger size scale, in case of surfactant mixtures. Both classes of formulations are biomimetic, and the efficiency is related to biopolymer modifications induced by surfactants and to surfactant-driven vesicle formation, respectively.

As a starting point, we report the essential details on the physical meaning of surface activity and solvent capacity; both requisites are necessary to understand biomimicry, surfactancy, and detergency on solid grounds. For more details, the interested reader is referred to pivotal books and reviews that have dealt with that field [11–14]. In many aspects, we follow the "main street" that is suggested in a seminal book, which allowed scientists to unify in a whole field the formation of both micelles, vesicles, and biological membranes [15].

2. Solvent capacity and surface activity

The term surface active, or surfactant, refers to substances capable to lower significantly and permanently the surface tension of water, i.e., to decrease the work required increasing the surface area of a liquid. In terms of the classical Gibbs surface adsorption equation valid for aqueous binary mixtures, we define as surface active all species fulfilling the equation [16]:

$$d\sigma = -G_2 dRTd\ln a_2 \quad (1)$$

where σ is the surface tension and a_2 is the solute activity. G_2, the surface excess concentration, indicates as to whether the surface tension will decrease, or increase, upon addition of a given solute. G_2 is defined with respect to the concentration of the given chemical in the bulk and depends on its modulus. That is the rationale underlying the meaning of the term "surface active." When $d\sigma = 0$, there is no more room for adsorption, and the surface is saturated. In addition, if $d\ln a_2$ is zero, the solute activity is constant and a new phase is being formed. This is the basis for the so-called phase separation approach to micelle formation [17], discussed later on.

The solvent capacity arises from a more subtle behavior and is univocally related to micelles onset. The organization of surfactant molecules arises from the "schizophrenia" that such molecules suffer from. They associate in micellar entities whose interior, mostly composed of alkyl groups, is capable to dissolve

nonpolar (i.e., hydrophobic) molecules. The polar groups facing outward the bulk guarantee thermodynamic stability to the aggregates so formed. In words, the solubilizing capacity toward oils and fats starts to occur only when micelles do form. For this reason, micelles are swelling units which grow in size upon addition of fats and oils.

From a thermodynamic viewpoint, micelle formation is mainly entropy-driven. This is a rather counterintuitive behavior, if we consider that several molecules associate in a given entity. The reason underlying the entropy-based statement is that water molecules hydrophobically interacting with alkyl chains are released during micelle formation [15]. This substantially increases the number of degrees of freedom for H_2O and those of the chains, as well. It is also worth noticing that an increase in temperature increases the number of rotational degrees of freedom of geometrically constrained surfactant alkyl chains, which are free to move into micelles. This is the main reason why micelle interior is assumed to be in a "liquid-like" form.

To unify the above features, that is, surface activity and solvent capacity, in a whole definition, we assume that the point at which surface activity ends and micelles begin to form is a "pseudo" phase separation threshold, indicated as critical micellar concentration or *cmc* [18, 19]. The definition "critical" indicates the steep discontinuity in many thermodynamic quantities (molar volumes, dilution enthalpies, activity coefficients, and so forth) observed in close proximity of the *cmc*.

For a given class of surfactants, such as alkali metal alkylsulfates, alkyltrimethylammonium halides, polyoxyethylene glycol alkyl ethers, etc., the two features jointly depend on the length of alkyl chains. The longer the latter are, the lower is the *cmc*, the steeper is the decrease in surface tension, and the more efficient is solvent capacity. We do not enter in more details about micelle sizes, shape, and polydispersity and assume, in a first approximation, that such aggregates are spheroidal colloids. For these reasons, they scatter light, have much lower diffusion coefficients than molecules from which they are made of, and their solutions can be moderately or significantly viscous. At high concentrations, they form ordered phases known as lyotropic liquid crystals [20, 21]. More aspects, such as the role of salts and cosolvents in micelle formation, shall be introduced when the need of "ad hoc" information will be necessary.

3. Addition of polymers or biopolymers

Studies on additives as salts and cosolvents have been widely investigated in the past and will not be reported, unless this is strictly necessary. Conversely, studies on systems containing synthetic polymers or biopolymers are still a matter of debate and investigation and will be discussed in this section. The first efforts along this line go back to the 1950s and were essentially dealing with protein separation from biological membrane lipids. These efforts were led to convergence in a classical textbook of the early 1990s [22]. This induced many scientists to focus on new and, sometimes, controversial fields [23–25].

The underlying phenomenology can be understood by looking at **Figure 1**. In the plot the behavior of a ternary system containing water, surfactant, and polymer is reported. If the relative *wt%* of the latter substances is much lower than water, the ternary phase diagram can be simplified in a pseudo-binary one. As can be seen in **Figure 1**, a pseudo-phase behavior occurs in absence of polymer; the *cmc* is the point separating the micellar from the molecular regime. Added polymer induces the splitting of the solution phase into three regions. For finite amounts of polymer, the following areas are observed, from the left:

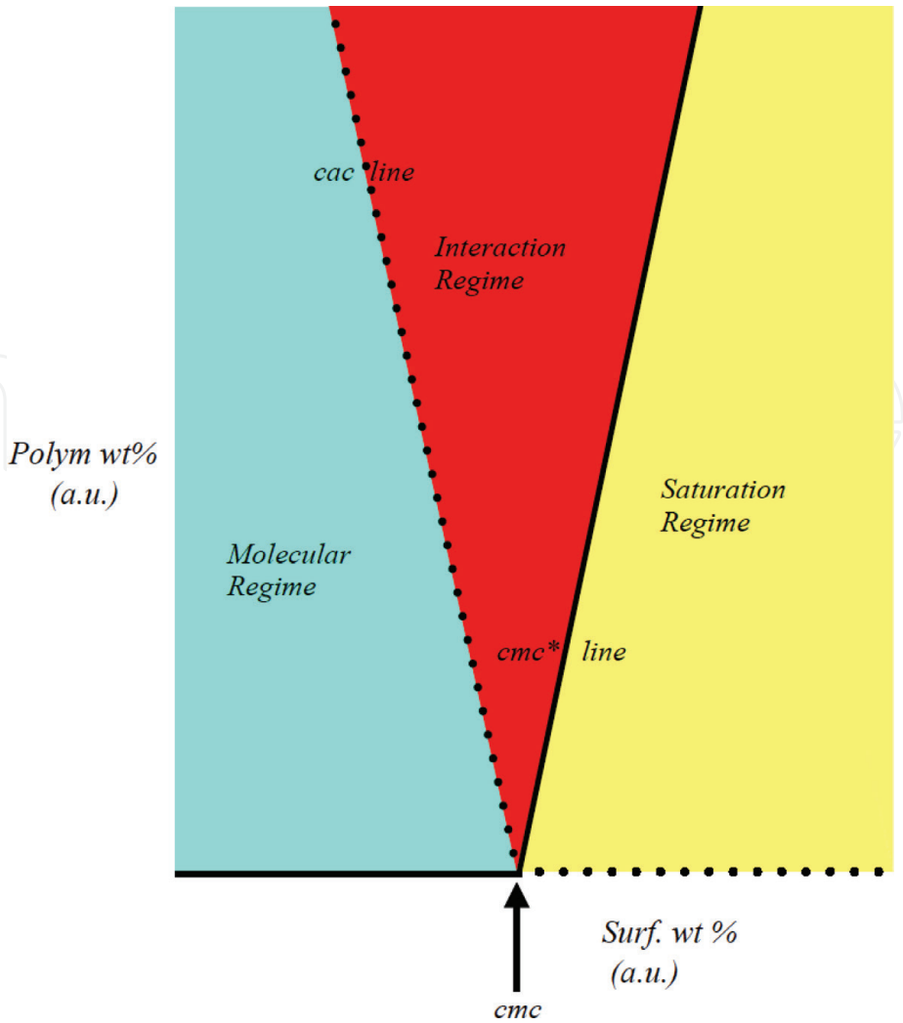

Figure 1.
The surfactant behavior in presence of a nonionic polymer. The black line in the left bottom of the figure indicates the molecular solution region and the dotted one the micellar regime. The turquoise area indicates the molecular regime and is limited by the cac, above which the surfactant starts to interact with the polymer. The red area indicates the interaction regime; the yellow one, the saturation regime, occurs when the polymer is saturated. The line separating the red and yellow regions is indicated as cmc line.*

i. a molecular solution region, ***I***;

ii. a polymer-surfactant one, ***II***; and

iii. a region where free micelles coexist with polymer-surfactant adducts, ***III***.

To build up the phase map, surface tension values are measured for a number of polymer *wt%* (**Figure 2**). There splitting of surface tension values in three regimes is evident. *Cac* and *cmc** are easily determined form these and other experiments, as well [22].

On thermodynamic grounds, the line separating region ***I*** from ***II*** indicates the points above which polymer/surfactant interactions start to occur; the line position depends on polymer content and nature. There is an ensemble of critical points, whose location in the phase map depends on the polymer amount. Once the process has occurred, the surfactants located on the polymer backbone act as nucleation sites for the binding of more surface-active species. Thus, entities similar to micelles (*emi-micelles*) aggregate thereon: a sort of "pearl necklace" is formed [26]. Thus, the polymer backbone is decorated by a series of small aggregates, whose number is dictated by its length; the interacting polymer sections, the so termed "polymer

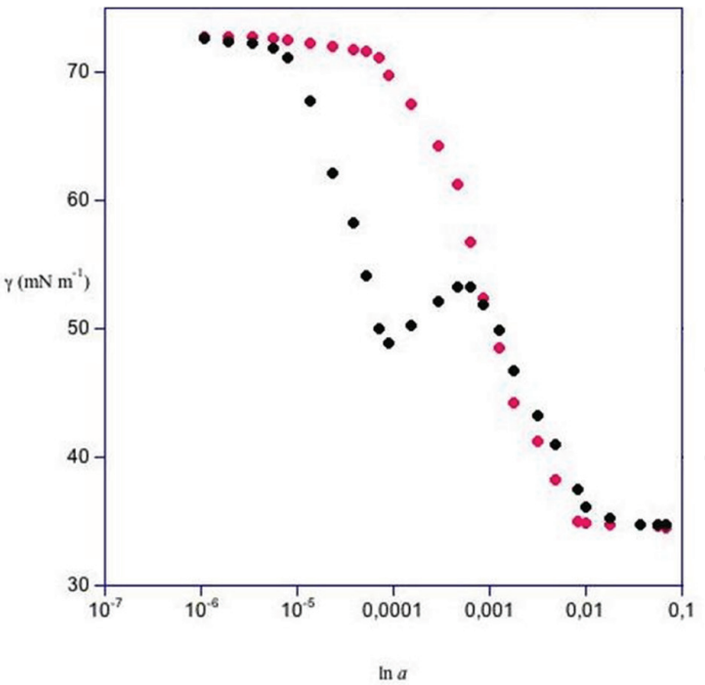

Figure 2.
Plot indicating how to get the cac, the first minimum, and the cmc, at surface saturation, for a given amount of polymer vs. surfactant content. Black points refer to data in presence of polymer, the red ones to the surfactant alone.*

binding sites", are a few kdalton long. Surfactant nucleation thereon continues until all possible sites are saturated. In consequence of that, the polymer tends to assume a different conformation with respect to the native one, with subsequent changes in viscosity. This is the reason why polymer/surfactant systems act as "viscosity modulators" [27, 28]. Another important consequence is the fact that they are "kinetic buffers" as to matter exchange with the bulk is concerned [29].

Ancillary effects are concomitant to the mentioned behavior. First, micelles of smaller size compared with free ones are formed; they behave as a whole kinetic entity with the polymer (i.e., the binding energy is significant). This is a feature similar to those occurring in biological systems, as in the binding of molecules to the protruding parts of a receptor. The line separating the two regions is defined as "critical aggregation concentration" or *cac* line. The nucleation of fat droplets on a cotton string is a pertinent example for the formation of polymer-surfactant adducts; their location thereon is energetically more favored than in free form. The *cmc** one, conversely, is a polymer saturation threshold, above which there is no room for binding. As a consequence, free micelles do form and coexist with polymer-adsorbed ones. Technological applications find place in formulation. The viscoelastic properties that such systems exhibit are used in shampoos, eye-drop fluids, etc. [30, 31]. Viscoelasticity is simply detected by abruptly rotating the fluid-containing vials, with transient formation of ellipsoidal bubbles or, in a more quantitative way, by rheology [27, 28]. An alternative simple procedure requires pressing drops of these formulations between glass slides and looking by a polarizing microscope, to detect the preferred orientation that polymer-surfactant adducts assume during the flow.

There is no significant difference when polyelectrolytes replace nonionic polymers. In cases like such, precipitation may also occur; cases are known [32], mostly as to biopolymers are concerned [33–36]. In mixtures containing proteins, precipitates or, eventually, two-phase regions are usually met. As a rule, these are centered around the charge neutralization line, where precipitates or gels may coexist (**Figure 3**). In such systems relevant are the modifications observed in

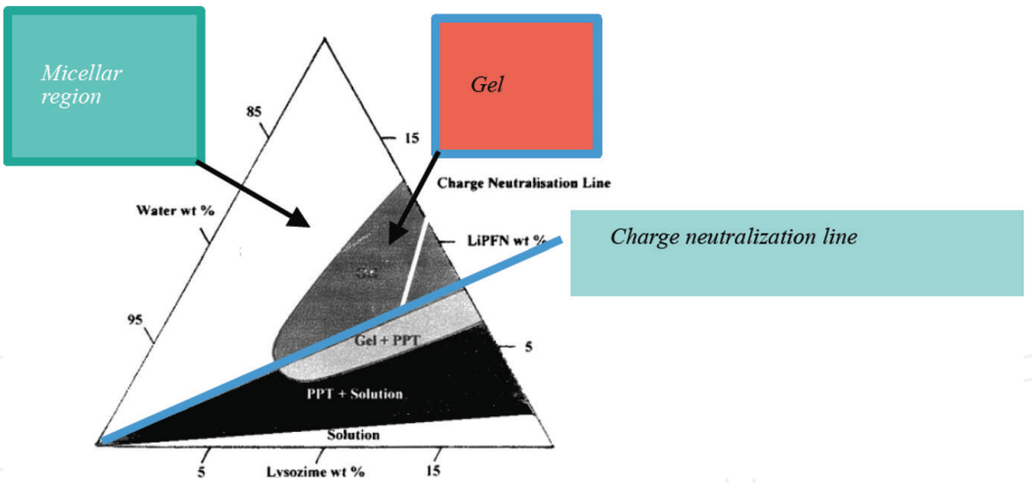

Figure 3.
Partial phase diagram for the system water-lysozyme-lithium perfluorononanoate (a stiff, fully fluorinated surfactant), at 25°C. The coexistence of a solution and precipitate occurs in the black area, whereas a pure gel, in dark gray, and one empty of particles, in light gray, are met. The charge neutralization limit is indicated as a blue line. This is the point at which all nominal charges on the protein, at the given pH, are fully neutralized. Partly redrawn from Ref. [26].

protein conformation. Changes in the relative amounts of alpha-helix, beta-sheet, and random coil conformations are concomitant to protein-surfactant interactions in a wide part of the interaction regime. Such changes are responsible for significant variations in protein activity and three-dimensional structure of the "adducts" that are formed. All these systems are characterized by a not univocally defined stoichiometry, and the definition of "adduct" is more correct with respect to that of "complex." The rationale underlying that behavior finds origin in the fact that alkyl chains are essentially located in the protein hydrophobic tasks. Many possible locations are available in cases like such. The above statements are quite well acquainted from experiments on albumins and, more generally, on protein denaturation strategies [37]. Thus, biopolymer/surfactant systems offer the opportunity to prepare proteins in pure form from extensive dialysis of the corresponding mixtures. For these reasons they find extensive use in biochemically intended procedures.

4. Mixtures made of oppositely charged surfactants

Pioneering studies in the field are due to Wennerstroem [38], who focused on the synthetic analogues of lipids and suggested that stoichiometric mixtures of oppositely charged surfactants could be good substitutes of lipids. The original hypothesis dealt with systems of 1–1 stoichiometry, in terms of charge. There, the electrostatic interactions between polar groups mimic charge separation among entities bound on a glycerol backbone, which is also joining two alkyl chains. The above systems are models of swelling, lamellar domains. The first experimental results were discouraging; in fact, these mixtures often show thermotropic rather than lyotropic behavior [39], due to the high "Krafft point" [40] of alkyl chains in such mixtures. Later work demonstrated that nonstoichiometric *Cat-An* mixtures were more promising. It was noticed there the presence of vesicular entities [41, 42]. Debates occurred on the stability of largely polydispersed in size vesicles. It is actually accepted that they are kinetically stable entities although thermodynamic stability is demonstrated in some cases [43, 44].

The phenomenology of such systems, defined by the acronym "cat-anionic," is extremely appealing from a bio-intended viewpoint. In the phase diagram, in particular, the vesicular areas are located in proximity of micellar ones and are clearly

distinguishable from them. The observation is in favor of a significant modification in the micellar structure induced by the second surfactant. Cat-anionic mixtures, hereafter termed *Cat-An*'s, are characterized by a bluish color and may turn to yellowish or opalescent appearance when vesicle sizes exceed some 100 nms. They are both positively and negatively charged. This fact gives the opportunity to use *Cat-An* vesicles as vehiculating/binding agents of DNA (for positively charged ones) and proteins. In the latter eventuality, both positively and negatively charged vesicles may be used, depending on the demand dictated by protein charge.

Debates questioned on the possible protein denaturation that could be induced by the surfactants present in *Cat-An* formulations, until it was realized that the surfactant in molecular form is solely responsible for protein denaturation [45]. The amount of such species is orders of magnitude lower than in solutions of the single surfactants.

The above behavior is supported by the following thermodynamic considerations. The mutual interactions between polar head groups and alkyl chain packing play a key role in such systems. The observed behavior is different from that expected if ideality of mixing holds. In words, when fluid chains are presumably miscible in all proportions, the effect of surface charges modulates the area on which alkyl chains insist and determines their optimal packing. This results in a strong nonideality of mixing. It is not surprising, therefore, that the *cmc* for an aggregate of given stoichiometry can be orders of magnitude lower than expected from primitive considerations. To quantify such effects, it was assumed the validity of regular solution theory, and it was imposed, accordingly, that "the free monomer has an activity coefficient of unity" [46]. This is an oversimplified viewpoint, since surfactant solutions are strongly nonideal even below the *cmc*. To proceed along, we assume that the concentration above which added surfactant preferentially enters into aggregates (disregarding their size and shape) is the saturation threshold for the molecular species. In this way, the difference in composition between molecular and micellar form is immaterial. In two-component surfactant mixtures, thus, the *cmc* of the mixed system is defined according to the relation [47].

$$(1/cmc_{mixt}) = \left[(X_2/\gamma_3 cmc_3) + (1 - X_2)/\gamma_2 cmc_2)\right] \tag{2}$$

where γ_2 and γ_3 are the activity coefficients of the surfactants, having cmc_3 and cmc_2 as the corresponding critical values. $cmcmix_t$ is the critical concentration of the mixed system. *X*'s are the mole fraction of the given surface-active species. In the limits dictated by the regular solution theory [48], the solute-solute interaction parameter, *b*, results to be [47].

$$b = \Delta G_{exc,mixt}\left[\left(X_2^2 + X_3^2\right)/\left(X_2^2 X_3^2\right)\right] \tag{3}$$

The underlying rationale is as follows. Micelles are in fluid state with freely moving polar head groups. They may change position, adsorb/desorb counterions, and so forth. The constraints acting on alkyl chains are such that polar head groups close each other attract/repel. In consequence of that, mixed systems show strong deviations from the ideal behavior. This tendency is quantified by the mentioned *b* parameter. The effect is substantial (**Figure 4**) and explains why the amount of both surfactants in molecular form is orders of magnitude lower than expected. In words, *Cat-An*'s are in equilibrium with their own counterions and with tiny amounts of free surfactants, as well. This is the basis for using cat-anionic vesicles as cargos for proteins and DNA [49–51].

Sizes of *Cat-An* vesicles strongly depend on the formulation stoichiometry. As mentioned above, 1–1 mixtures form indefinitely large smectic crystals; on both sides of this threshold, sizes depend regularly on composition and approach values

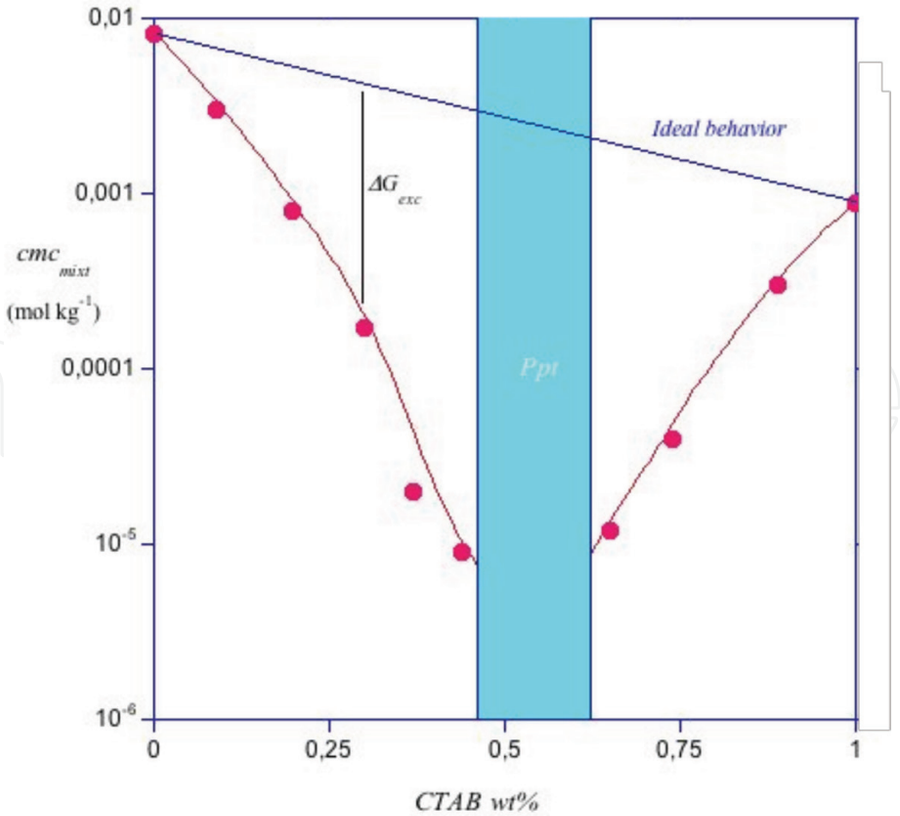

Figure 4.
Dependence of the cmc (in mol kg^{-1}) on cetyltrimethylammonium bromide, CTAB, mole fraction for SDS-CTAB mixtures, at 25°C. The red line is for visual purposes; the full on the top refers to ideal mixing and the vertical to the nonideality of mixing. The blue area indicates the precipitation regime.

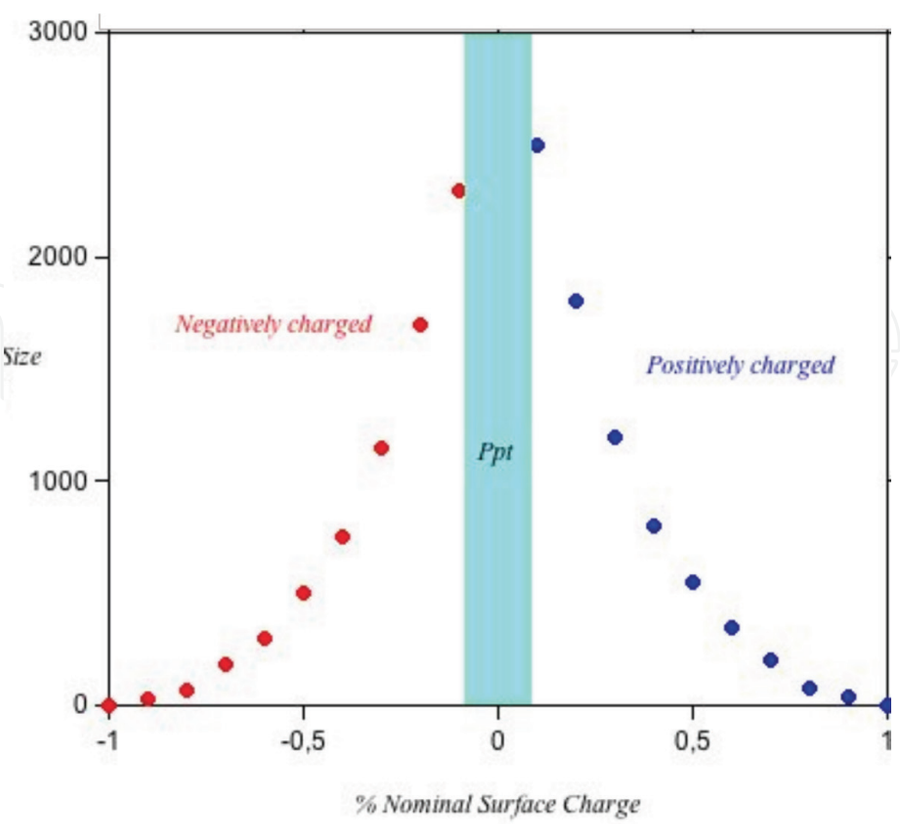

Figure 5.
Vesicle size (in nm) for SDS-CTAB mixtures, at 25°C, vs. the nominal surface charge excess of the vesicular aggregate. The light blue area in the center of the figure refers to the precipitation regime.

pertinent to the pure surfactant aggregates. In words, the excess surface charge determines vesicles sizes (**Figure 5**). It is worth to note that similar trends are also observed in mixtures of oppositely charged lipids [52]. The surface charge versatility is reminiscent of statements based on the relations between particles size and surface charge density. The higher the former, the lower the latter. This fact has important consequences on the links between (nominal) surface charge density and sizes. It is a sort of charge-based size tailoring and is quintessential in choosing the proper particles for transfection technologies. Another pertinent possibility along this line arises from thermal cycling procedures, which allow getting stable particles of proper size by raising the temperature above a certain value (which depends on the composition of the *Cat-An* mixture [53]. Thermally quenched vesicles obtained accordingly retain their size for indefinitely long times.

Sound procedures based on the combination of the above features allow getting vesicles of the desired size and surface charge density. This allows using them for DNA transfection technologies and protein immobilization onto vesicles [54]. An interesting feature is that vesicles of a given composition are destroyed by adding amounts of surfactant required for the complete neutralization of the *Cat-An* mixture. In consequence of that, the biopolymer which is eventually bound onto vesicles is released in its pristine form [55]. This is a terrific possibility for bio-intended technologies.

5. Conclusions

This contribution focuses on the possibilities offered by surfactants and their mixtures in selected bio-intended applications. The mentioned systems are niche fields, but are becoming of relevant impact in a lot of practical purposes. Think, for instance, that applications in shampoos and similar products almost always include silk proteins as adjuvants of hair state and health. Transfection, conversely, is quite appealing for biochemistry and molecular biology applications. In many aspects, thus, both fields of research are on the same line as those originally intended in the pre-Christian age. It is as if we were moving back to the roots of surfactancy. Luckily, we have much more knowledge in the field, and this allows us to exploit applications on more conscious grounds.

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