

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,400

Open access books available

118,000

International authors and editors

130M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# 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, synthesizing 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 synthesized [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 *PSSs* [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]:

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

where  $\sigma$  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  $\ln a_2$  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<sub>2</sub>O 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.

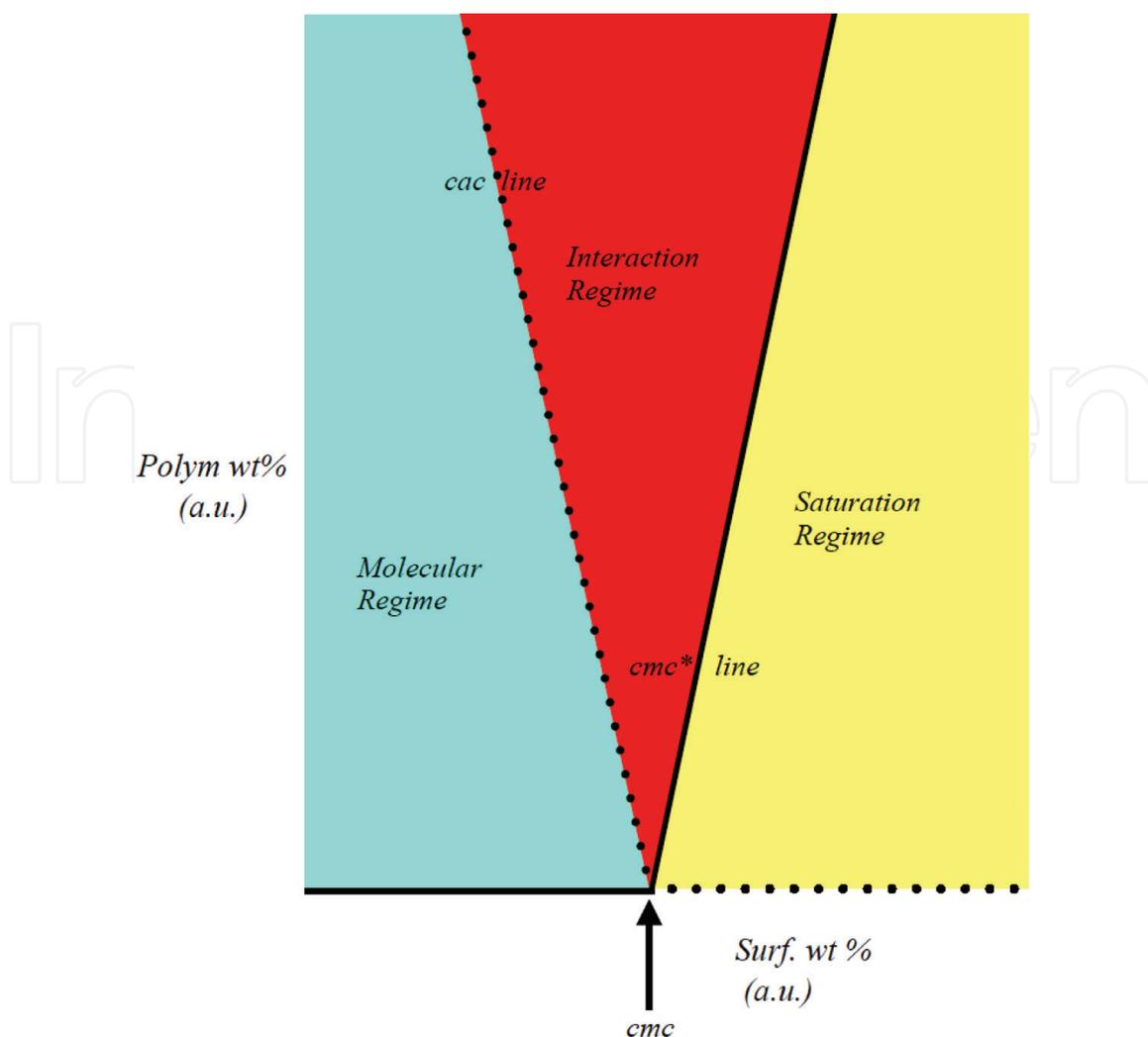
To unify the above features, that is, surface activity and solvent capacity, in a whole definition, we assume that the point at which surface activity ends and micelles begin to form is a “pseudo” phase separation threshold, indicated as critical micellar concentration or *cmc* [18, 19]. The definition “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:



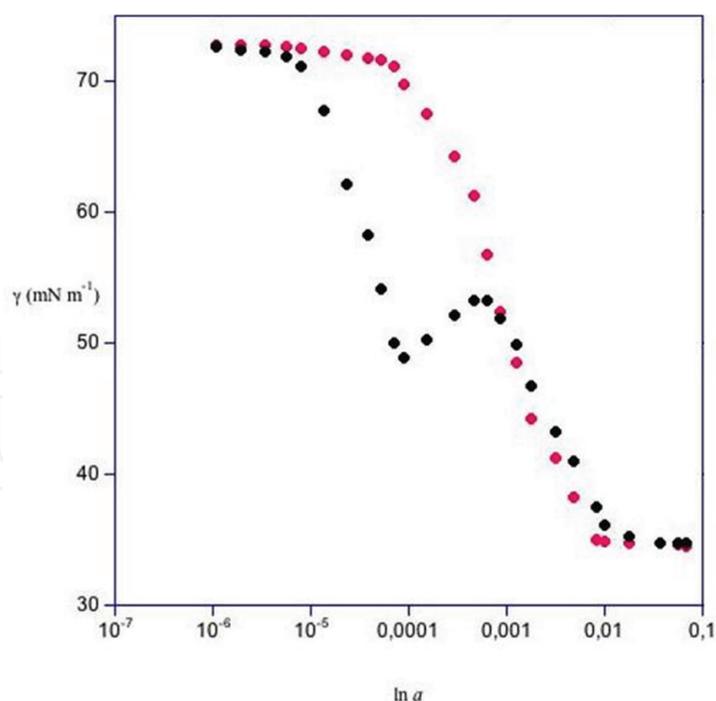
**Figure 1.**

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 from 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

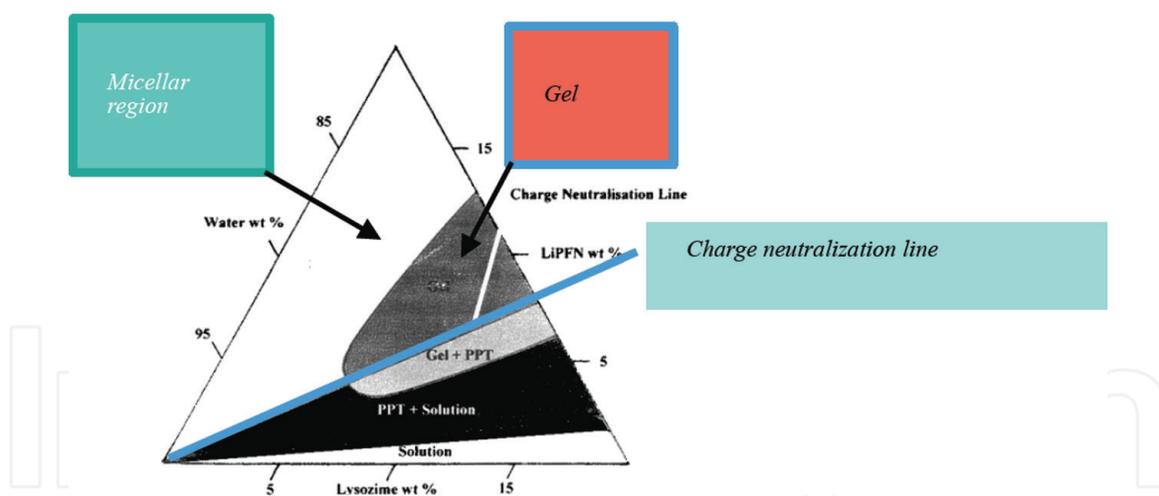


**Figure 2.** Plot indicating how to get the *cac*, the first minimum, and the *cmc*<sup>\*</sup>, at surface saturation, for a given amount of polymer vs. surfactant content. Black points refer to data in presence of polymer, the red ones to the surfactant alone.

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*<sup>\*</sup> 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].

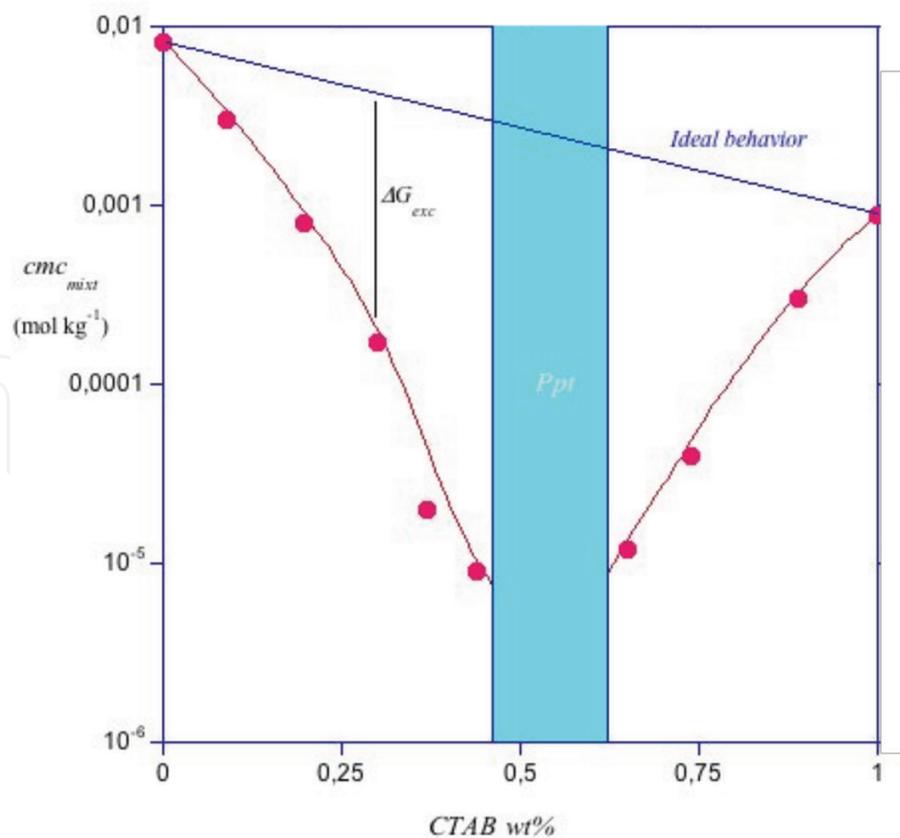
$$(1/cm_{mixt}) = [(X_2/\gamma_3 cmc_3) + (1 - X_2)/\gamma_2 cmc_2] \quad (2)$$

where  $\gamma_2$  and  $\gamma_3$  are the activity coefficients of the surfactants, having  $cmc_3$  and  $cmc_2$  as the corresponding critical values.  $cm_{mixt}$  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].

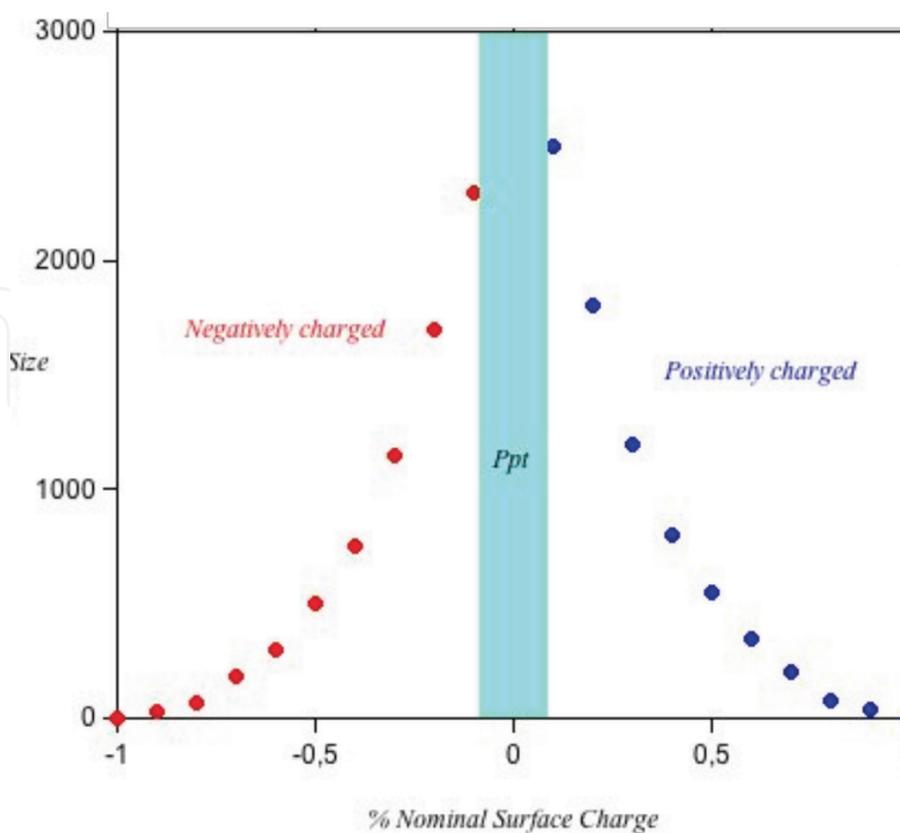
$$b = \Delta G_{exc,mixt} [(X_2^2 + X_3^2)/(X_2^2 X_3^2)] \quad (3)$$

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  $\text{mol kg}^{-1}$ ) on cetyltrimethylammonium bromide, CTAB, mole fraction for SDS-CTAB mixtures, at  $25^\circ\text{C}$ . 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  $\text{nm}$ ) for SDS-CTAB mixtures, at  $25^\circ\text{C}$ , 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.

### Author details

Camillo La Mesa<sup>1\*</sup> and Gianfranco Risuleo<sup>2</sup>

<sup>1</sup> Department Chemistry, Sapienza University, Rome, Italy

<sup>2</sup> Formerly at Department Biology, Sapienza University, Rome, Italy

\*Address all correspondence to: [camillo.lamesa@uniroma1.it](mailto:camillo.lamesa@uniroma1.it)

### IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

## References

- [1] *Historia Naturalis*. Old Plinius. 1582 Italian version. In: Gamba C, Vidali G, editors. 1992
- [2] The phase behavior of dodecyl sulfonic acid and of its alkali salts with water, Vold MJ. *Journal of the American Chemical Society*. 1941;**63**:1427-1432
- [3] Hiemeland LM. A nondenaturing zwitterionic detergent for membrane biochemistry: Design and synthesis. *PNAS*. 1980;**77**:6368-6370. N.B. The mentioned product is of current use in the formulation of mild detergents. See also Ref. 8
- [4] Shinoda K, Takeda H. The effect of added salts in water on the hydrophile-lipophile balance of nonionic surfactants. The effect of added salts on the phase inversion temperature of emulsions. *Journal of Colloid and Interface Science*. 1970;**32**:642-646
- [5] Mancuso JR, McClemens DJ, Decker EA. The effects of surfactant type, pH, and chelators on the oxidation of salmon oil-in-water emulsions. *Journal of Agricultural and Food Chemistry*. 1999;**47**:4112-4116
- [6] Baviere M, Bazin B, Aude R. Calcium effect on the solubility of sodium dodecyl sulfate in sodium chloride solutions. *Journal of Colloid and Interface Science*. 1983;**92**:580-583
- [7] Hua XY, Rosen MJ. Synergism in binary mixtures of surfactants: I. Theoretical analysis. *Journal of Colloid and Interface Science*. 1982;**90**:212-219
- [8] Rosen MJ, Zhu BY. Synergism in binary mixtures of surfactants: III. Betaine-containing systems. *Journal of Colloid and Interface Science*. 1984;**99**:427-434
- [9] Hoff E, Nystroem B, Lindman B. Polymer-surfactant interactions in dilute mixtures of a nonionic cellulose derivative and an anionic surfactant. *Langmuir*. 2001;**17**:28-34
- [10] Jurassic DD, Segota S, Cadez V, Selmani A, Sikirc MD. Recent advances in cationic mixtures. In: Najjar R, editor. *Application and Characterization of Surfactants*. Rijeka: IntechOpen; 2017
- [11] Rosen MJ. *Surfactants and Interfacial Phenomena*. New York: Wiley and Sons; 2004
- [12] Porter MR. *Handbook of Surfactants*. New York: Springer; 1991
- [13] Schramm LL, editor. *Surfactants. Fundamental and Applications in the Petroleum Industry*. Cambridge: Cambridge University Press; 2009
- [14] Laughling RJ. *The Aqueous Phase Behavior of Surfactants*. London: Acad. Press; 1994
- [15] Tanford C, editor. *The Hydrophobic Effect: Formation of Micelles, Vesicles and Biological Membranes*. Vol. II. New York: Wiley; 1980
- [16] Everett DH. *Basic Principles of Colloid Science*. Roy. Soc. Chem., Cambridge; 1994. Chapt. V, pp. 63-75
- [17] Shinoda K, Hutchinson E. Pseudo-phase separation model for thermodynamic calculations on micellar solutions. *The Journal of Physical Chemistry*. 1962;**66**:577-582
- [18] Ruckenstein E, Nagarajan R. Critical micelle concentration. Transition point for micellar size distribution. *The Journal of Physical Chemistry*. 1975;**79**:2622-2626
- [19] Palladino P, Ragone R. Ionic strength effects on the critical micellar concentration of ionic and nonionic surfactants: The binding model. *Langmuir*. 2011;**27**:14065-14070

- [20] Hiltrop K. Lyotropic liquid crystals. In: Stegemeyer H, Mehret H, editors. *Liquid Crystals. Topics Phys. Chem. Book Ser.* 1993, Vol. 3, Chapt IV. pp. 143-171
- [21] Ekwall P. Composition, properties and structures of liquid crystalline phases in systems of amphiphilic compounds. In: *Adv. Liq. Cryst. Vol. I. Chapt. I.* New York & London: Acad. Press; 1975. pp. 1-142
- [22] Goddard ED, Ananthapadmanabhan KP. *Interactions of Surfactants with Polymers and Proteins.* Boca Raton, FL: CRC Press; 1993. The whole book contains information on the most relevant points inherent to such systems
- [23] Bell CG, Breward CJW, Howell PD, Penfold J, Thomas RK. Macroscopic modeling of the surface tension of polymer-surfactant systems. *Langmuir.* 2007;**23**:6042-6052
- [24] Chatterjee S, Prajapati R, Bhattacharya A, Mukherjee TK. Microscopic evidence of “Necklace and Bead”-like morphology of polymer–Surfactant complexes: A comparative study on poly(vinylpyrrolidone)-sodium dodecyl sulfate and poly(diallyldimethylammonium chloride)-sodium dodecyl sulfate systems. *Langmuir.* 2014;**30**:9859-9865
- [25] La Mesa C. Polymer-surfactant and protein-surfactant interactions. *Journal of Colloid and Interface Science.* 2005;**286**:148-157
- [26] Sesta B, Gente G, Iovino A, Laureti F, Michiotti P, Paiusco O, et al. Supramolecular association in the system water-lysozyme-lithium perflorononanoate. *The Journal of Physical Chemistry. B.* 2004;**108**:3036-3043
- [27] Tsianou M, Alexandridis P. Control of the rheological properties in solutions of a polyelectrolyte and an oppositely charged surfactant by the addition of cyclodextrins. *Langmuir.* 1999;**15**:8105-8112
- [28] Roversi M, La Mesa C. Rheological properties of protein–surfactant based gels. *Journal of Colloid and Interface Science.* 2005;**284**:470-476
- [29] D’Aprano A, La Mesa C, Persi L. Polymer-surfactant interactions: An ultrasonic relaxation study. *Langmuir.* 1997;**13**:5876-5888
- [30] Kalantar TH, Tucker CJ, Zalusky AS, Boomgaard TA, Wilson BE, Ladika M, et al. High throughput workflow for coacervate formation and characterization in shampoo systems. *Journal of Cosmetic Science.* 2007;**58**:375-383
- [31] Dubald M, Bourgeois S, Andrieu V, Fessi H. Ophthalmic drug delivery systems for antibiotherapy: A review. *Pharmaceutics.* 2018;**10**:1-31
- [32] Goddard DE. Polymer-surfactant interaction: Part II. Polymer and surfactant of opposite charge. In: Goddard ED, Ananthapadmanabhan KP, editors. *Chapt. IV Interactions of Surfactants with Polymers and Proteins.* Boca Raton: CRC Press; 1993. pp. 123-1170
- [33] Reynolds JA, Tanford C. Binding of dodecyl sulfate to proteins at high binding ratios. Possible implications for the state of proteins in biological membranes. *Proceedings of the National Academy of Sciences of the United States of America.* 1970;**66**:1002-1003
- [34] Turrro NJ, Lei X-G. Spectroscopic probe analysis of protein-surfactant interactions: The BSA/SDS system. *Langmuir.* 1995;**11**:2525-2533
- [35] Kelley D, McClements DJ. Interactions of bovine serum albumin with ionic surfactants in aqueous solutions. *Food Hydrocolloids.* 2003;**17**:73-85

- [36] Otzen D. Protein–surfactant interactions: A tale of many states. *Biochimica et Biophysica Acta*. 2011;**1984**:562-591
- [37] Ciurleo A, Cinelli S, Guidi M, Bonincontro A, Onori G, La Mesa C. Some properties of lysozyme-lithium perfluorononanoate complexes. *Biomacromolecules*. 2007;**8**:399-405
- [38] Jokela P, Jonsson B, Wennerstroem H. Phase equilibria in systems containing both an anionic and a cationic amphiphile. A thermodynamic model calculation. *Progress in Colloid and Polymer Science*. 1985;**70**:17-22
- [39] Jokela P, Jonsson B, Khan A. Phase equilibria of catanionic surfactant-water systems. *The Journal of Physical Chemistry*. 1987;**91**:3291-3298. To our knowledge this is the first article on which the term Catanionic is accounted for
- [40] La Mesa C, Ranieri GG, Terenzi M. Studies on Kraft point solubility in surfactant solutions. *Thermochimica Acta*. 1988;**137**:143-150
- [41] Shioi A, Hatton TA. Model for formation and growth of vesicles in mixed anionic/cationic (SOS/CTAB) surfactant systems. *Langmuir*. 2002;**18**:7341-7348
- [42] Marques EF, Regev O, Khan A, Miguel MDG, Lindman B. Vesicle formation and general phase behavior in the catanionic mixture SDS-DDAB-water. The anionic-rich side. *The Journal of Physical Chemistry. B*. 1998;**102**:6746-6758
- [43] Safran SA, Pincus P, Andelman D. Theory of spontaneous vesicle formation in surfactant mixtures. *Science*. 1990;**248**:354-356
- [44] Segota S, Tezak D. Spontaneous formation of vesicles. *Advances in Colloid and Interface Science*. 2006;**121**:51-75
- [45] Stenstam A, Khan A, Wennerström H. Lysozyme in catanionic surfactant mixtures. *Langmuir*. 2004;**20**:7760-7765
- [46] Evans DF, Wennerstroem H. Chapt. IV The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet. New York: VCH; 1994. pp. 131-185
- [47] Muzzalupo R, Gente G, La Mesa C, Caponetti E, Chillura-Martino D, Pedone L, et al. Micelles in mixtures of sodium dodecyl sulfate and a bolaform surfactant. *Langmuir*. 2006;**22**:6001-6009
- [48] Takasugi K, Esumi K. Micellar surface charge modification for regular solution theory: Application to mixed systems of cationic fluorocarbon-nonionic hydrocarbon surfactants. *The Journal of Physical Chemistry*. 1996;**100**:18802-18807
- [49] Bonincontro A, Falivene M, La Mesa C, Risuleo G, Ruiz-Pena M. Dynamics of DNA Adsorption on and release from SDS-DDAB cat-anionic vesicles: A Multi-technique study. *Langmuir*. 2008;**24**:1973-1978
- [50] Letia C, Andreozzi P, Scipioni A, La Mesa C, Bonincontro A, Spigone E. Protein binding onto surfactant-based vesicles. *The Journal of Physical Chemistry. B*. 2007;**111**:898-908
- [51] Russo L, Berardi V, Tardani F, La Mesa C, Risuleo G. Delivery of RNA and its intracellular translation into protein mediated by SDS-CTAB vesicles: Potential use in nanobiotechnology. *BioMed Research International*. 2013;**2013**:1-6
- [52] Lozano N, Pinazo A, La Mesa C, Perez L, Andreozzi P, Pons R. Catanionic vesicles formed with arginine-based surfactants and 1,2-dipalmitoyl-sn-glycero-3-phosphate monosodium salt. *The Journal of Physical Chemistry. B*. 2009;**113**:6321-6327

[53] Andreozzi P, Funari SS, La Mesa C, Mariani P, Ortore MG, Sinibaldi R, et al. Multi- to unilamellar transitions in cationic vesicles. The Journal of Physical Chemistry. B. 2010;**114**:8056-8060

[54] Pucci C, Scipioni A, La Mesa C. Albumin binding onto synthetic vesicles. Soft Matter. 2012;**8**:9669-9675

[55] Bonincontro A, La Mesa C, Proietti C, Risuleo G. A biophysical investigation on the binding and controlled DNA release in a cetyltrimethylammonium bromide-sodium octyl sulfate cat-anionic vesicle system. Biomacromolecules. 2007;**8**:1824-1829

IntechOpen