Literature Review

Optimizing the Surface-Active Performances of Cat-Anionic Mixtures: A Short Review

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Abstract: Mixtures of oppositely charged surfactants are used for applications requiring extensive foaming. This holds true for cat-anionic systems. Their bulk behavior is known in detail, when surface, or interface, properties do not attract the same attention. The thermodynamic features of such systems and the strategies interrelating the behavior in bulk to that at surfaces are outlined. Such systems are strongly not ideal. So, the interaction parameters for bulk and surface phases, β_{surf} and β_{mic}, respectively, are introduced. Efforts to connect the two quantities were made. The definition of interaction parameters comes from the regular solution theory. Originally applied to micelle formation, it was later extended to the saturation of fluid surfaces. In this context, the interaction parameters were applied to the surface properties of selected cat-anionic systems and their links with bulk ones discussed.

Keywords: Surfactants, Cat-Anionic Mixtures, Bulk Properties, Surface Properties, Non-Ideality of Interaction

Introduction

Surfactants and fatty acids spread on fluid surfaces. This is the reason why Greek sailors threw olive oil all around their boats, in case of violent storms. Spread oil forms a thin, elastic, fluid layer on seawater and minimizes the possibility of forming waves and ripples. Maybe you noticed from craftsmanship vases that Greek "triérēis" (triremes) often have an eye painted on their fores to observe and control, the onset of storms, Fig. 1. The "magic eye" informed sailors on the way out to follow; it also ensured Poseidon on the crew's religious attitudes. This legend is in the Odyssey and, several centuries later, was reported by Plinius the Elder, who described the best procedures capable of reducing ripple amplitude around boats when stormy weather was approaching.

Surfactants and olive oil have hydrocarbon moieties covalently linked to polar groups; the coexistence of such features in a single species imparts them a sort of "molecular schizophrenia". This old definition indicates that surfactants orient at interfaces, with polar groups staying in the bulk and a-polar ones facing toward the air (Murray and Hartley, 1935). More precisely, the polar part tends to be in polar media: The reverse holds true for apolar ones. Such behavior implies that surfactants are "molecular dipoles", orienting along a dielectric constant gradient, which crosses the air-water interface, Fig. 2.

The surface tension lowering due to surfactants depends on apolar moieties (be they hydrocarbons, or the much less common fluorocarbons), polar head groups (anionic, cationic, non-ionic, zwitterionic), T, cosolutes, and ionic strength of the solvent. Matching such properties tunes the system performances, controlled by the nature of polar head groups, net charge, and sometimes counter-ions. Other limits come from the bulkiness of the apolar parts. The surface tension of surfactant solutions is the result of a complex balance, which depends on the molecular details of the species in action and on intrinsic conditions at work. The effect of composition and co-solutes, is drawn in Fig. 3. In addition, it depends on the species in action.

Surface activity has some points in common with the organization in supra-molecular aggregates (Israelachvili *et al.*, 1976; Dill and Flory, 1981). The similarities and differences existing among bulk and surface properties are:

1. Fluid surfaces on which surfactants adsorb are flat and the motion of alkyl chains therein finds an analogy with anchored whips. In aggregates, chain motion is restricted and normal to the micellar surface The surfactant a-polar parts dislike contact with water and tend to minimize it. This holds true in both phases. The tendency is due to the "hydrophobic effect" (Tanford, 1980; Long *et al.*, 2015)

2. The packing density in both phases depends on composition and reaches a maximum when the local surfactant concentration increases

3. The transfer of polar parts to air, or to micelles, minimizes the Gibbs energy. The driving force for the two processes is the same
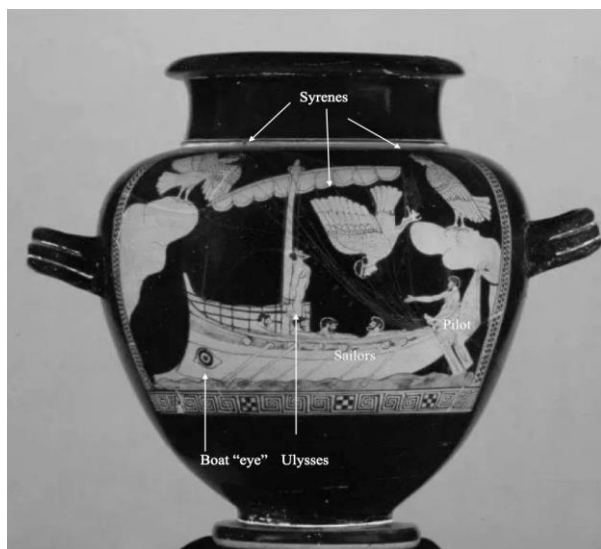

Fig. 1: Ulysses is tied to his boat's must, avoids being captured by Sirens, but is curious to hear their voices. Sailors and pilots are deaf because of the wax and cotton in their ears. Note the magic "eye", on the boat's low left side. Such vases were common in Italy, Greece, Etruria, or the black sea area. Image redrawn from a craftsmanship of the Vth century B.C
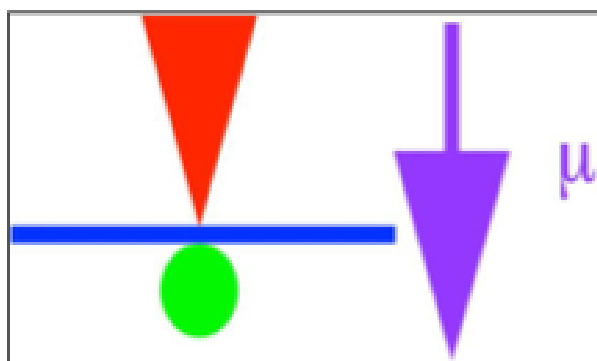

Fig. 2: Surfactant orientation at interfaces. The air-water one is indicated as a blue line. The green sphere is the polar head group in the bulk, and the red triangle is the apolar part of the molecule. The triangle is solid with apolar chains inside. The violet arrow and the Greek symbol indicate that a "chemical dipole" crosses the interface so that the polar part is anchored in the bulk, and the polar one freely moves on the surface, depending on the local concentration of chains. They act as anchored whips. In aggregates, chain motion is restricted, and normal to the micellar surface
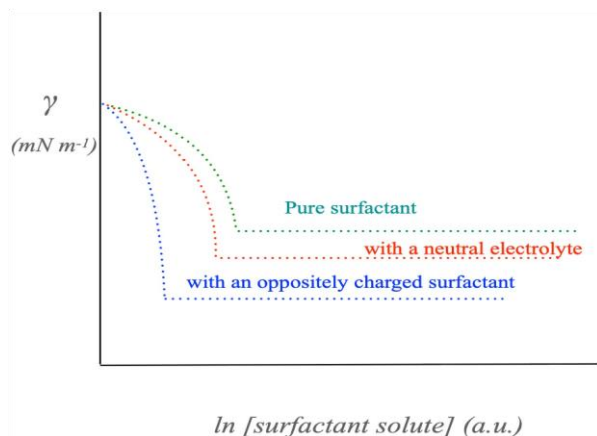

Fig. 3: Surface tension of ionic surfactant solutions at 25°C. Neutral electrolytes, in red, shift the *cmc* to a lower concentration. The same holds true with oppositely charged surfactants. The intersection point of the low-low-concentration curves with flat segments indicates the critical micellar concentration (*cmc*). At that point surface activity ends, $d\gamma = 0$, and micelles begin to form. Below the *cmc*, the surface area that surfactants occupy, $1/\Gamma_i$, is inversely proportional to the tangent of the curve

What is well acquainted for single surfactants holds true for their mixtures. The surface efficiency of blends is higher than that pertinent to the single species and synergism substantial. Among the many possible causes, I report on the cat- anionics, a class of mixtures. The acronym indicates that both cationic and anionic species jointly take part in association and surface activity. There are substantial differences compared to similar blends, mostly as to aggregation and phase separation. In the first, a substantial *cmc* reduction with respect to the mother species is met, even orders of magnitude. The second effect is because, at mole ratios close to full neutralization, no stabilization due to free charges is present and cat-anionics precipitate as layered solids. The precipitate stoichiometry is 1-1 in terms of charge. Upon mixing, the two surfactants exchange the respective counter-ions by metathesis. This "colloid titration" mode leads to a precipitation and/or re-dissolution, if one surfactant is in excess. The 1-1 precipitate is a thermotropic waxy solid, insoluble in water. When one species is in excess, solutions or dispersions occur. In what follows, the focus is on the second eventuality, when micelles or vesicles can be met. The differences among these organization modes are not considered here and have been reported in detail elsewhere (Marques *et al.*, 2003; Tondre and Caillet, 2001). Relevant are the links between average vesicle size, <R>, and surface charge density, σ. Low vesicle sizes imply a high surface charge density and vice versa; thus, σR = const (Pucci *et al.*, 2014). The organization in vesicles can be mono, multilamellar, or in character, depending on the preparation mode, or thermal treatment.

Thermodynamic Generalities

The area covered by a single surfactant at interfaces depends on composition, as indicated by the Gibbs adsorption isotherm, and reduces substantially when the solute concentration is raised. Increasing amounts of surfactant progressively saturate the interface, until there is no more room for adsorption. One may safely assume that because of the abnormal condition that atoms/molecules have at the surface of a solid or a liquid compared to that in the bulk, the surface of any phase is a seat of free energy.

The classical relation keeps the form indicated below and holds true at *P* and *T* constant:

$$dG = \sum_{i=1} \mu_i dn_i + \gamma dA \tag{1}$$

μ_i is the chemical potential of the ith component, the mole number concentration is n_i; γ the surface (interface) tension and dA is the change in the area on which measurements insist.

Equation 1 gives the interface area of the ith species, by integration and subsequent redifferentiation. In thermodynamic terms, $1/\Gamma_i$ is a partial molal quantity, the area covered at an interface (dA/dn_i), and depends on the composition. Accordingly, surface adsorption continues until there is no room for putting more species on the surface (Menger and Rizvi, 2011) and saturation is attained. Above that threshold γ remains nearly constant: These considerations imply that surfaces are independent phases, which saturate if there is no more room for surfactant uptake. In concomitance, micelle formation is considered in analogy to the onset of a (pseudo)-phase in the bulk (Shinoda and Hutchinson, 1962; Elworthy and Mysels, 1966).

Aqueous surfactant mixtures have moderate surface tension, almost never lower than 22 mN m⁻¹ (Menger *et al*., 2009). To reduce surface tension, formulators proceed according to a "trial and error" basis, to get species with noteworthy performances in highly saline media, in the presence of mud or sand, to extract (or denature) bio-macromolecules, dissolve fats and oils and so on. The demand required for formulators is, thus, very diversified, depending on whether laundry, dishwashing, body care, shampooing, paintings, minerals recovery, or other applications are needed. Laundry formulations contain zeolites, salts, enzymes, ion sequestrants (EDTA, as a rule), softeners, bleaching species, perfumes, and so on. The additives do not modify significantly the surfactant's efficiency. For each formulation, there are "niche products". Think about what is required to wash linen, cotton, or wool, ensuring a substantial softness to each tissue and to the many ad hoc devoted specialties one may find in the market!

Two more points deserve mention: One is the amount of surfactant to be added to reduce pollution; the second deals with an efficient modulation of surface tension. Formulators use surfactant blends and rely on synergism between more species. It is easy to get mixtures compatible with a given medium and there is no urgent need, therefore, to prepare new surfactants, if not specifically requested.

Mixtures are made of non-ionic, ionic, and non-ionic, or only charged species. Cases relative to mixtures whose polar heads have the same net charge (as sulfates and sulphonate) are not very relevant when the reverse holds true for solutes with oppositely charged moieties. Among the more common ones, cat-anionic systems, hereafter termed cat-An, (to indicate that both cat-ionic and an-ionic species are present) are interesting. Investigation into these systems originated from the need to get neutral synthetic lipid analogs (Khan and Marques, 1997).

Mixing negative and positive species in stoichiometric amounts gets them; the counterions are released by metathesis and precipitates are obtained. The above behavior drastically changes if mixtures are not stoichiometric (Khan and Marques, 1999; Jönsson *et al*., 1991). Such possibility offers the opportunity to get aggregates of modulated curvature, as micelles or vesicles (Andreozzi *et al*., 2010). In most instances, vesicle sizes are inversely proportional to their net surface charge density (Pucci *et al*., 2014).

Moroi (1992); Kronberg (1997) described in some detail the thermodynamics of these systems. Not much is known about their surface properties (La Mesa and Risuleo, 2019), later rationalized by the regular solution theory and similar to that used for bulk phases. Reported below is a bird-flight view of cat-an systems in bulk and at surfaces. Efforts are made to determine the most relevant properties of the two phases. I will proceed, in turn, to examine the bulk and surface properties of cat-anionic systems and will try to relate them. The final goal is to find a way univocally and easily, to relate the properties of the surfactant in the bulk to the much less accessible interface ones. This strategy requires properly transforming the interaction parameters for the mentioned phases.

Bulk Properties

The critical concentration of an ionic surfactant, *cmc*, drastically decreases when it is partly mixed with an oppositely charged analog; in many aspects, the process finds an analogy with the addition of simple electrolytes. The bulk association features of catanionic mixtures are quite different from binary systems and *cmc*'s decrease of orders of magnitude: It can also be observed the occurrence of a precipitate when the (anionic/cationic) charge (mole) ratio, R, is unity. The above behavior is due to the metathesis of mobile counter-ions with long-chain

ones and the formation of hydrophobic ionic solids. These are layered and thermotropic, i.e., thermosensitive, in character. In some aspects, cat-An solids do not differ much from ionic liquids (Freemantle, 2010) and have a very low vapor pressure. Little is known about their solvent capacity, indeed. For the above reasons, they substantially differ from lyotropic cat-anionic systems and nonstoichiometric mixtures (Jurašin *et al.*, 2017).

I consider first dilute water-soluble systems and assume micelle formation to be a true phase separation. For systems containing three species, i.e., two surfactants and water, the *cmc* is defined as (Holland and Rubingh, 1983; Muzzalupo *et al.*, 2006):

$$cmc_{1,2\ mixt} = [(\Phi_1 cmc_1)(\Phi_2 cmc_2)]/[(X_1\Phi_1 cmc_1)(X_2\Phi_2 cmc_2)] \tag{2}$$

$cmc_{1,2\ mixt}$ is the critical value of the ternary mixture, cmc_1 and cmc_2 those of the surfactants, Φ_1 and Φ_2 their activity coefficients, X_i's the mole fractions. In the phase separation approach, I assume that:

$$(\Delta G_{mixt,mic}/RT) = cmc_{mixt,mic} = ln\ [(\Phi_1 cmc_1)(\Phi_2 cmc_2)/(X_1\Phi_1 cmc_1)(X_2\Phi_2 cmc_2)] \tag{3}$$

The latter term in Eq. (3) is a reference value for micelle formation. Equations (2-3) indicate the non-ideality of mixing for molecular and micellar forms. Combination with experiments gives the excess Gibbs energy of micelle formation, expressed as:

$$(\Delta G_{mixt,mic,exc}/RT) = ln\ [(\Phi_1\Phi_2)/(\Phi_1+\Phi_2)] \tag{4}$$
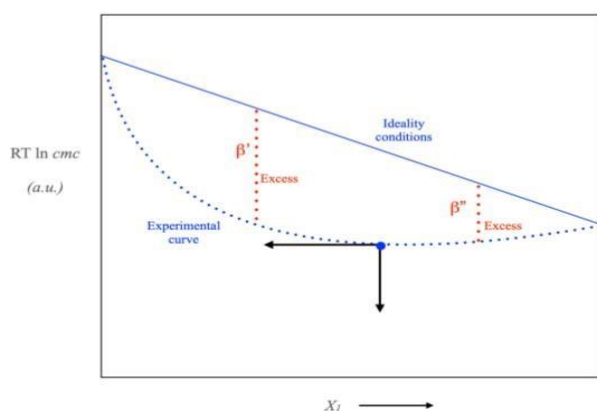

Fig. 4: Relation between energy terms, RT ln *cmc*, and mole fraction of one surfactant component in a cat-anionic mixture, X_1. The full blue line indicates ideality in micelle formation, i.e., $cmc_{1,2} = X_1\ cmc_1 + (1- X_1)\ cmc_2$: The dotted line experimental values. The red segment height depends on composition, indicating that β, the interaction parameter, may change

The relation relies on the "regular solution theory", RST, (Hildebrand *et al.*, 1970) and accounts for non-ideality. Accordingly, the activity coefficient of the ith solute, Φ_i, is defined as:

$$\Phi_i = exp\beta X_i^2 \tag{5}$$

where, β is the interaction parameter, which, as a rule, significantly depends on composition Thus:

$$\beta = \Delta G_{mixt,mic,exc}[(X_{1,1}+X_{1,2})/X_{1,1}X_{1,2}] \tag{6}$$

The quantity β, obtained by the RST, is strongly negative and scales with the non-ideality of mixing, Fig. 3. Examples are many: For instance, in the system sodium decylsulfate, SDeS, and decyltrimethylammonium bromide, DeTAB, we have β = -18.5 RT units (Moroi, 1992). Chain lengths of the surfactants are the same: Hence, the ionic interactions play a dominant role in controlling β. Note that β may depend on composition: In words, the transfer energy of cationic species into anionic-rich mixtures may not be equivalent to that observed in the reverse case. These considerations intuitively come from the shape of *cmc* curves versus the mole fraction of the first component, Fig. 4. The figure can be easily transformed in an excess function.

One may calculate β values in other ways, based on the regular solution theory. It is possible to obtain them using the dependence of $cmc_{1,2}$ from mole fraction in a partial molal approach, by deriving that quantity with respect to X_1. Another possibility relies on the link with *cmc s* (Rosen, 1989); it keeps the form:

$$a^{*,M} = [ln(cmc_1/cmc_2) + \beta^M]/2\beta^M \tag{7}$$

where, the meaning of symbols is known when a^*, M indicates the mole fraction of species 1 in the "total mixed surfactant in the aqueous phase" (Rosen, 1989). We consider two representative cases, that is:

$$a)\ cmc_1 = cmc_2$$

$$b)\ cmc_1 > cmc_2$$

Development of the equation for case a) implies a^*, $M = 1/2$. The relation is constant and the β^M value is immaterial. If a^*, $M = X^*$, M, (i.e., if the activity perfectly matches the mole fraction), solute 1 is ideal. However, the activity coefficients of ionic surfactants in the micellar form are hardly reconciled with ideality conditions (Burchfield and Woolley, 1984). Thus, the use of the equation is questionable.
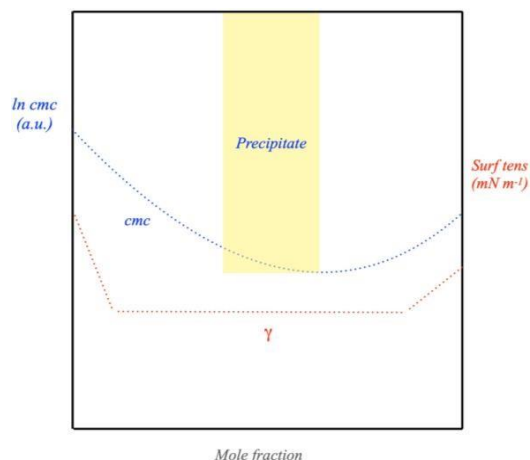
Fig. 5: The supramolecular association, expressed as *cmc* (in mole fraction units), and the surface tension, γ, (mN m^{-1}), vs. the mole fraction of the cationic surfactant in the mixture. The area in yellow indicates the possible location of a precipitate

The second condition was analyzed by rewriting the equation in the form:

$$\beta^M(2\,a^{*,M}-1) = ln(cmc_1/cmc_2) > 0 \tag{8}$$

We know that $\beta_M < 0$, as predicted by the RST theory. The same holds true for the term in parentheses. That is, the function is valid if the mole fraction of component 1, X_1, is $<1/2$. Thus, Eqs. (7, 8) cannot be extended to the whole concentration range.

Once that bulk properties are defined, let us proceed with interface ones. The reason for that is that β parameters developed for the surface phase are related to those of the bulk. Expectedly, the synergism met in mixed systems implies some changes in surface properties. What is more, bulk and surface parameters, β_{surf} and β_{mic}, are related to the interactions between species in micelles and monolayers. Both phases are mixed and one must ascertain whether synergism in the two phases is similar or not. It is conceivable, intuitively, that the above statement is not true. In addition, the *cmc* and the surface tension, γ, (mN m-1), vs the mole fraction of the cationic surfactant in the mixture overlap with the possible location of the precipitate, Fig. 5. It is well known that the RST, from which interaction parameters are obtained, is related to excess functions. It could be interesting to experience approaches accounting for the very nature of micellar systems, such as the small systems thermodynamic ones (Hill, 2013). In fact, an analysis of the energy terms could benefit from a detailed description of the forces effectively acting in cat-An aggregates, giving a reliable estimate of the energy of transfer from micelles (or whatever aggregates) to mono-layers.

Interface Properties

Pure cat-An solids spread at interfaces (Lozano *et al.*, 2011). The same behavior is expected to occur in non-stoichiometric catanionic mixtures (Tah *et al.*, 2011). The solutions are poorly air-permeable and find use in the area of foams (Barbetta *et al.*, 2014; Olechowska *et al.*, 2019). Synergism is concomitant to a high surface tension efficiency: This behavior, perhaps, was never observed. In cat-An mixtures, γ is never <25 mN m^{-1}; that of highly surface active fluorinated species is 20 mN m^{-1}, or less (Kunieda and Shinoda, 1976; La Mesa and Sesta, 1987). Fluorocarbon bulkiness (determined by their projection at air-water interfaces) is quite similar to that of two inter-twisted alkyl chains. It seems, therefore, that the lower surface tension limit is related to chain bulkiness. Cat-and-at-air-water interfaces may exist as interconnected chains since the interactions between hydrophobic ions tend to keep them close. It is not necessary, perhaps, that all surface chains located at surfaces do for couples.

β_{surf} and β_{mic} depend on interactions between species in micelles and monolayers in a yet undefined way. The investigation may allow us to determine if the surface properties of cat-anionic systems are synergistic. To clarify the validity of the theory at interfaces, one needs to know:

1. The surface tension vs. log c plots of the individual species close to their *cmc's*
2. The *cmc* of at least one component of the ternary mixture
3. The exact content of a mixture giving a surface tension close to that of individual surfactant

The structure and local environment determine β_{surf} and β_{mic} values. For this purpose, Rosen extended the RST, originally applied to the bulk, to surface phases (Liu and Rosen, 1996; Zhou and Rosen, 2003). The relations he got are:

$$\beta_{mic} = In(a_1 C_{12,mic}/X_{1,mic} C_{1,mic})/(1-X_{1,mic})^2 \tag{9}$$

$$\beta_{surf} = In(a C_{12}/X_1 C_1°)/(1-X_1)^2 \tag{10}$$

Equation (9) a_1 is the mole fraction of species 1 in the fluid: The same holds for $C_{1,\,mic}$ and $X_{1,\,mic}$. C_{12} is the sum of C_1 and C_2 in solution, calculated at a mole fraction of a_1 that gives a well-defined surface tension. Other subscripts have their usual meaning. X_1 in Eqs. (9-10) indicates a (water-depleted) mole fraction of species 1 in the mixed monolayer. The two equations give the concentrations of the surfactant species in bulk and at surfaces. The energy gain associated with both processes can be better rationalized by the ratio β_{surf}/β_{mic}.

Note that:

$$\beta_{mic}/\beta_{surf} = [(1-X_1)^2/(1-X_{1,mic})^2][ln(a_1 C_{12,mic})(X_1 C_1°)/(aC_{12})(X_{1,mic} C_{1,mic})] \tag{11}$$

$$\beta_{mic}/\beta_{surf} = [(1-X_1)/(1-X_{1,mic})]^2 \, ln([(a_1 C_{12,mic})/(aC_{12})][(X_1 C_1°)/(X_{1,mic} C_{1,mic})]) \quad (12)$$

What seems to be a troublesome relation indicates a partition of species 2 between the surface phase and the solution in equilibrium with it; it is $(1-X_1)$. $C_{12} = (C_1 + C_2)$; both terms refer to bulk equilibrium between the same phases. The meaning of X_1 is obvious. From the retro-analysis of Eqs. (11-12) is possibly getting cogent results. A serious problem to face is to consider the molecular solution, or the micellar one, as a reference value. In the first case, non-ideality arises from the amount of molecular surfactant; in the second, the role of micellar aggregates is relevant. There is a major point to be considered: Note that the ratios among mole fractions in the equations are significant below, or up to, the *cmc*. Above that threshold, the amount of surfactant spread at the interface remains constant, when the concentration of the species in micellar form may vary. In cases like such, the partition remains badly defined. For the above reasons, we supposed the term $[(X_1 C_1°)/(X_{1,mic} C_{1,mic})]$ in Eq. 12 to be the independent variable. The reasons are manyfold and take into account the fact that $C_1°$ is a reference value for the bulk phase.

A plot of the ratio β_{surf}/β_{mic} versus $[(X_1 C_1°)/(X_{1,mic} C_{1,mic})]$ indicates that the links among these quantities are not easily quantified and erratic. According to Fig. 6, β_{surf} is always more negative than β_{mic}: The difference is 2 RT units with a shallow minimum centered about 30 CTAB wt%. The significant synergism of layers implies that non-ideality is higher than in aggregates. Presumably, the interactions between chains are slightly favored at the interface, as expected from their degrees of freedom. β_{surf} and β_{mic} depend on T and are larger in the cationic-rich side of the diagram, as in Fig. 6.
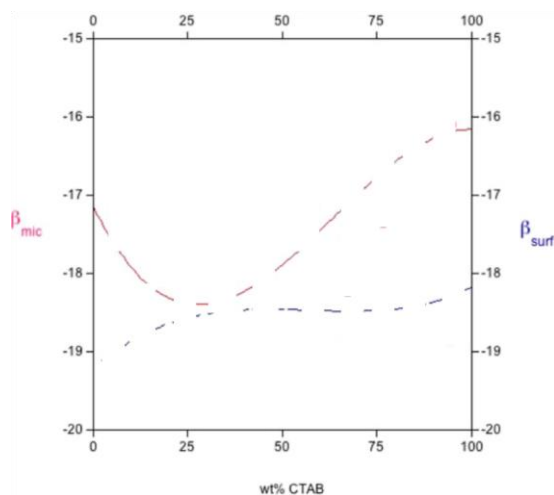

Fig. 6: The interact + on parameter in bulk, β_{mic} (cyan), and in the surface phase, β_{surf}, vs. the CTAB wt% in CTABSDS surfactant mixtures, at 25.0°C. The surface terms are systema + cally lower than bulk ones. $\beta_{surf}-\beta_{mic}$ indicates the transfer of the surfactant mixture (at a given composite + on) from the bulk to the surface

Polar head-group hydration may be the reason for that if we consider that SDS is much more heavily hydrated than CTAB. Presumably, electrostatic attraction occurring in the SDS-rich region is more significant and more sensitive to T. This is rather counterintuitive if one thinks that alkyltrimethylammonium moieties are bulky, relatively hydrophobic, and thus, presumably, much more sensitive to an increase in temperature. It is well acquainted, however, that $N(CH_3)_3$ groups are excellent loci for the binding of big and polarizable ions as Br- (Ninham and Yaminsky, 1997; Duignan *et al.*, 2013). In the CTAB-rich part of the phase diagram, therefore, such an effect could possibly occur. Maybe this is the reason why the difference $\beta_{surf}-\beta_{mic}$ is particularly high in such regimes. We are conscious that a tentative and simplified, approach does not allow us, at the moment, to get an explanation for the aforementioned behavior. This is, at the moment, an open question.

Conclusion

Some aspects relative to mixtures of oppositely charged surfactants, termed Cat-Anionic, are outlined here. The above systems find substantial interest in soft matter sciences and bio-medicine. Important, but not much investigated, is the behavior they show at air-water, or oil-water, interfaces. Attempts were made to relate the behavior at bulk phases to that occurring at the surface, using the interaction parameter, indicated here as β. The latter accounts for the non-ideality of surfactants mixing in two such phases. According to experimental evidence, non-ideality is more substantial in surface phases. The possible reasons underlying the observed behavior are briefly outlined here.

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Ethics

I address any ethical issues that may arise after the publication of this manuscript.

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