ABSTRACT

During this thesis, several mixed surfactant systems due to the interest in considering the structural influence shown by them, and that have not been explored extensively with the mixed micelles theory.

Systems with mixed surfactants have a wide range of practical uses in several industries like cleaning, and manufacturing of pharmaceuticals, pesticides, cosmetics, food and many others. In many cases the mixture of different surfactants may have properties differing from those of the sum of the pure components.

A particular type of mixed surfactants are called catanionic, constituted by mixtures of a cationic surfactant and an anionic one, that show some rare types of structures, like giant micelles, spontaneous and stable vesicles, and sometimes, extremely low solubility if their proportion is 1:1. Also, liquid crystals may appear at very low concentration, and show very high surface activity, among other properties. The study of these mixtures is relatively recent.

Due to the anionic surfactants tendency to precipitate in mixtures with cationic surfactants, these mixtures are seldom used, regardless of the advantage of including cationic surfactants in the formulation, which have bactericide and fungicide properties. The coprecipititation interferes with the germicide activity of cationic surfactants. This points out the importance of finding the conditions with which the components of a catanionic mixture could be made compatible, which would be of a significant practical importance, in addition to the improvement of understanding of the nature of the interactions involved, which are of a significant theoretical interest.

In this thesis, I studied a **catanionic system** composed by a cationic surfactant, dodecyltrimethyammonium bromide, **DTAB**, and sodium 10-undecenoate, **SUD**, a soap of approximately the same hydrocarbon chain length, containing a double bond.

It was found that this system would not precipitate in any proportion, although a coacervate zone was observed, that is, two mutually immiscible liquid phases of different composition, in equilibrium. Micelles showed a preferential composition of $X_{SUD}=0.37$, significantly

different to what would be expected in a ideal mixture. This could be explained by considering that the double bonds will be covering the hydrocarbon surface of SUD. This behaviour, can be attributed to the formation of hydrogen bonds between the Π-electrons and water, decreasing considerably the Gibbs free energy between hydrocarbon core and water. Structural calculations showed that this proportion ($X_{SUD}=0.37$), produces complete coverage of the hydrophobic surface of the micelle with the terminal double bonds.

A non ideal behaviour of the molar partial volume was observed when the mixture is prepared, both in micellised state and below critical micelle concentration, CMC. The complex behaviour of micelle hydration showed to be non ideal, reflecting a complex structure and composition of micellar surface.

Limits for the existence of the coacervate have been found to be between $\alpha_{SUD}=0.44$ and 0.675. Different experimental techniques have shown that when approaching the biphase region from both extremes of composition diagram, micelle size is increased, together with their aggregates, Z- potential is reduced and micelles aggregate in clusters of high polydispersity whose size increases. In the limit, when the Z- potential tends to zero coacervate appears, due to the disappearance of the energy repulsive barrier.

The computational modeling performed demonstrated that the role of water is crucial to understand the composition and structure of mixed micelles with unsaturated bonds in their composition, and confirmed that the interaction between these aliphatic Π electrons is stronger than the water-water hydrogen bond. This is a known situation between aromatic Π and water, but there was still some controversy about the extrapolability to aliphatic double bonds.

To determine when how much of the observed non ideality would correspond to interactions between polar groups of opposed charges and how is attributable to the interactions of SUD's double bond with water, the **anionic mixed system** formed by **SUD** and Sodium Dodecanoate, **SDD**, where studied, both of which have the same polar group.
It was observed a non ideal behaviour and a preferential micellar composition of $X_{SUD}=0.33$-0.47. After an analysis of activity coefficients it was concluded that in mixed micelles the contact between the hydrocarbon chains of SDD and water is reduced when SUD proportion is micelles is increased, thus rendering them an increased stability. The degree of ionization of micelles showed to be almost independent of composition, implying that the electrostatic contribution to the excess intramicellar interaction energy is not significant. Aggregation numbers of mixed micelles showed a non ideal behaviour, and higher than theorically

expected values where obtained. Thus, it was verified that the cause of the non ideality of the mixture is due to the interaction between double bonds one of the components of the mixture and water, as the structure of the Stern ionization layer of micelles was not altered respect to that of the pure SUD micelles.

To determine if the presence of the double bonds in both components of the mixture would produce any effect, another **anionic mixed system**, composed of surfactants, both with double bonds in their hydrocarbon chains was studied; Sodium olate **NaOL**, a surfactant with a double bond in the middle of the hydrocarbon chain, and Sodium Linoleate NaLin, **NaLin**, as soap with two double bonds in its hydrocarbon chain.

The aggregation of NaOL and NaLin mixtures ocurred in a gradual way, first a type of premicellar aggregates appeared, followed by the formation of true micelles, which, in turn started to change their structure until they formed micelles with higher solubilizing strength, probably cylinders or discs. As expected, micelles are richer in the more hydrophobic component NaOL, but the interaction is repulsive. This repulsion is relatively low in micelles richer in NaLin, but growths faster NaOL is predominant in the micelles.
It was observed that micellization behaviour was not ideal, although the commonly accepted theory predicts an ideal behaviour (it's length differs only in a methylene group). Non ideality is again owed to the interaction through hydrogen bonds between water and $\prod$-electrons of the double bonds.

When the interphase solution-air was studied, it was found that, contrary to micellas pseudophase, below the CMC the absorbed layer has a preferential composition of $X^S_{OL}=0.7$. The interaction is still non ideal, but here it is attractive, with parameters of interaction in surface (βs) monotonically negative, showing a minimum in $X^S_{OL} \approx 0.72$, which is coherent with preferential composition. The surface is also systematically richer in sodium oleate than linoleate, compared to system's total composition, reflecting the higher hydrophobicity of the first component.

This study showed that the complex relationship between micelle components and mixed surfaces are affected by the presence of double bonds in the hydrocarbon chains and its interactions with water.

During the development of the research, question aroused if the length difference in the hydrocarbon chain of both mixture components, Δn_C, could be the cause of observed non ideality, because when the interactions in mixed micelles where studied, all possible sources of non ideality have to be considered. For that reason, several different **mixtures of**

homologous surfactants, some of them already explored in literature, like mixtures of anionic and non ionic surfactants, and experimental studies were performed with mixed cationic surfactants, of which information in literature was scarce or incomplete. The micellar interaction parameter βM was calculated, in order to see if these values differed statistically from zero, a characteristic value of an ideal mixture, and several different types of surfactants, to ensure that the effect is due to the hydrocarbon chains, and not to the modifications in the Stern micellar layer.

When calculating βM, it was found that an attractive interaction exists, and that the interaction parameter depends linearly with the chain length difference among the components of the mixture. The dependence found resulted to be independent of the nature of the polar group. A value of βM of zero was obtained (ideal behaviour), and a Δn_C value of 0.76±0.06.

The interaction among homologous surfactants in mixed micelles was found to be non ideal, contrary to what is supposed by the theory of regular solutions for mixed micelles. This phenomenon can be understood as an effect of reduction of the hydrocarbon-water micellar interphase by the inclusion of an analogous surfactant of a shorter chain, which produces an improved compaction of the chains in micelles, caused by a reduction of the folding of the hydrocarbon chain.

In order to study in detail the non ideality of homologous mixtures, a system composed by a **cationic mixture** of two homologous surfactant like; decyltrimethylammonium bromide, **$C_{10}TAB$**, y hexadecyltrimethilammonium bromide, **$C_{16}TAB$**, for these mixtures $\Delta nC=6$. This mixture was chosen in order to have the highest differences in chain length with easily available surfactants.

The studied mixture was shown to be non ideal, and it was concluded that the component of longer chain length acts as solvent of the shorter chained one. The formation of the mixed monolayer in the interphase air/solution was also not ideal, here the $C_{16}TAB$ again acted as a solvent of the shorter chained one. This was interpreted as being caused by the inclusion of the chain of the short-chain component in the spaces left by the larger one, a space produced by the folding of the hydrocarbon chains of more than 8 carbon atoms.

It was verified that the conclusion found the study of mixed homologous surfactant systems, in that these are not ideal, and that the nonideality increases with the difference in

chain length between both components, and that the cause fro this is a reduction of the hydrocarbon-water contact in micelle surface.

To conclude, it was found that two structural factors not accounted in the usually employed theories for the treatment of micelles and mixed monolayers, the presence of double bonds in hydrocarbon chains, and the difference in the lengths of chains of the mixture components, are the cause of a strong non ideality, and should be accounted for when planning mixtures of surfactants.