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# Interaction between surfactants and proteins

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**Abstract.** Several approaches have been focused on the protein-surfactant interaction. Surfactant-protein interactions are very common in the fields of medicine, chemistry, biology etc. Indeed, many aspects of this interaction have been studied, such as the influence of the aggregation state of the surfactant (monomer, pre-micellar aggregate, micelle, and liposomes) on the protein structure, the properties of the surfactant-protein system, the characterization of the interaction sites on the protein surface, the identification of the intermediate protein conformations etc. The interaction of several types of proteins with the different kind of surfactant can furnish various information to the research of biochemical and biophysical systems, such as the structure-activity relationship of proteins as well as the mechanism of interaction between proteins and amphiphilic molecules. In this context, proteins with prosthetic group are very interesting ones, since the presence of the non-amino acid group can furnishes various information through different instrumental techniques of analysis, acting as a label of all polypeptide chains. The present work analyzes this topic and the potential of these studies.

**Keywords:** Protein, ionic surfactant, structure-function relationship, protein-surfactant interaction

## *Interação entre surfactantes e proteínas*

**Resumo.** Muitas abordagens têm sido focadas sobre a interação proteína-surfactante. Interações surfactantes-proteína são muito comuns nos campos da medicina, química, biologia etc. De fato, têm sido estudado diversos aspectos dessa interação, tais como a influência do estado de agregação do surfactante (monômero, agregado pré-micelar, micela e lipossoma) sobre a estrutura proteica, as propriedades do sistema surfactante-proteína, a caracterização dos sítios de interação na superfície proteica, a identificação de conformações proteicas intermediárias etc. A interação de diversos tipos de proteína com as diferentes espécies de surfactante pode fornecer várias informações para a pesquisa de sistemas bioquímicos e biofísicos, tais como a relação estrutura-atividade de proteínas assim como o mecanismo de interação entre proteínas e moléculas anfifílicas. Nesse contexto, proteínas com grupo prostético são exemplos muito interessantes, uma vez que a presença de um grupo não-aminoacídico pode fornecer várias informações através de diferentes técnicas instrumentais de análise, atuando como uma sonda de todas as cadeias polipeptídicas. O presente trabalho analisa esse tópico e o potencial desses estudos.

**Palavras-chaves:** Proteína, surfactante iônico, relação estrutura-função, interação proteína-surfactante

## *Interacción entre tensioactivos y proteínas*

**Resumen.** Muchos enfoques se han centrado en la interacción proteína-surfactante. Las interacciones surfactante-proteína son muy comunes en los campos de la medicina, la química, la biología etc. De hecho, se han estudiado varios aspectos de esta interacción, como la influencia del estado de agregación del surfactante (monómero, agregado premicroclear, micela y liposoma) sobre la estructura proteica, las propiedades del sistema

surfactante-proteína, la caracterización de los sitios de interacción en la superficie proteica, la identificación de conformaciones proteicas intermedias, etc. La interacción de varios tipos de proteínas con las diferentes especies de surfactante puede proporcionar información diversa para la investigación de sistemas bioquímicos y biofísicos, como la relación estructura-actividad de las proteínas, así como el mecanismo de interacción entre proteínas y moléculas anfifílicas. En este contexto, las proteínas con grupo protésico son ejemplos muy interesantes, ya que la presencia de un grupo no aminoácido puede proporcionar información diversa a través de diferentes técnicas de análisis instrumental, actuando como sonda de todas las cadenas polipeptídicas. El presente trabajo analiza este tema y el potencial de estos estudios.

**Palabras clave:** Proteína, surfactante iónico, relación estructura-función, interacción proteína-surfactante

## Introduction

The interaction between protein with chemical compounds of different polarity properties is one of the more relevant chemical processes in the biological medium. The called "active sites" of proteins and/or enzymes interact with different types of "substrates", being that this kind of interaction is responsible for several relevant biochemical processes. Hormone actions, neurotransmissions, pharmacological and toxicological processes are associated to interactions with proteins.

The interaction between surfactants and proteins can happen through contacts among the apolar parts of surfactants ("tails") and proteins (lateral chains of apolar amino acids); involving polar and/or ionic parts of surfactants and proteins. This kind of study is an interesting tool as model system to evaluate several biochemical interactions of great relevance, such as the interaction between drug (active principle) and pharmacological receptor (which, frequently, is a specific site in the surface of polypeptide chains, i. e., in an accessible external region of a protein).

In this context, the amphiphilic compounds are very relevant ones, since their interaction with the protein surface allow to understand the mechanisms that control this type of chemical contact. Furthermore, the more drastic surfactant action upon proteins, which is usually observed in high concentrations of surfactant, can help to understand structure, dynamics, and function of distinct "active sites" of proteins as well as the mechanisms of protein denaturation.

## Membrane protein-surfactant interactions

The formation of complexes between proteins and surfactants involves a wide range of interactions, depending on the nature of both components (Feis et al., 2007). Surfactants interact with proteins in various ways which depend on surfactant concentration and tructure, being that there are several possibilities of conformational changes that proteins can undergo in the presence of molecules with self-assembling properties (Andersen et al., 2008). Membrane proteins (MPs) are usually stabilized by surfactant micelles, mainly through hydrophobic interactions like those naturally occurring in cell membranes. Soluble proteins can also give rise to protein-surfactant complex formation, which is often accompanied by protein unfolding processes ranging from moderate conformation changes to pronounced alterations of the secondary and tertiary structure (Feis et al., 2007).

The main difficulty of structural and thermodynamic studies with MPs is related to their hydrophobic character, which causes aggregation and precipitation of these MPs when they are outside of their native membrane environment (Rodnin et al., 2008). Detergent solubilization, which is a general way of handling MPs *in vitro*, very often makes them unstable. Several approaches have been suggested to avoid these limitations, like, for example, the employment of new milder nondetergent surfactants, such as amphipols or fluorinated nonionic surfactants. In fact, the fluorinated nonionic surfactants can act as chemical chaperones that maintain the MP in solution, decreases the perturbation of MP structure and dissociate from the MP during membrane insertion and avoids partition into the lipid bilayer (Rodnin et al., 2008).

## Models of protein-surfactant interaction

The mechanisms of interaction involving surfactants and proteins has been studied for several research groups. These evaluations are deeply dependent of the arrangement of the units of surfactant

molecules. In fact, each surfactant molecule can interact differently, depending on the respective specific sites on the protein surface, which would be in contact with the surfactant, as well as the spatial organization of the surfactant molecules. In this context, it is fundamental to know if the units of surfactant molecules are isolated in the solvent bulk or are organized in a more complex arrangement, such as a micelle. Indeed, the mechanisms of protein-surfactant interaction are quite different with the surfactant in the micelle form, when compared with the isolated monomer unit. Therefore, the knowledge of the surfactant concentration is a fundamental pre-requisite to infer the kind of interaction between these amphiphilic molecules and the respective protein. It occurs as function of the called "critical micelle concentration (cmc)", which dependents strongly of the ionic strength of the medium. For this reason, the cmc in the presence of buffers is completely distinct of that in the absence of any buffer. This fact occurs as function of the stabilization of the charges of same signal, which is generated by the presence of buffer molecules around the micelle. Therefore, a kind of double layer occurs around the micelle, stabilizing the localized micellar charges, especially in ionic surfactants, decreasing the reciprocal electrostatic repulsion between the surfactant units. In this way, the buffer molecules act as counter-ion (ionic par) of the units that are forming the micelle. This process explains the fact of the cmc of several surfactants to be quite different in the presence of buffer when compared with the same surfactant in "pure" aqueous solvent, without any buffer.

**Proteins interacting with different concentrations of surfactant**

Surfactants are widely employed in biochemistry and biotechnology for the purpose of protein solubilization, purification, characterization, and protein structure determination (Mikšovská et al., 2006). Surfactant-protein interactions are very common in the fields of medicine, chemistry, biology and various inter- and multidisciplinary areas (Liu et al., 2007; Orioni et al., 2006; Stenstam et al., 2003; van der Veen et al., 2004; Vasilescu et al., 1999). Several approaches have been performed in order to understand the physico-chemical properties of surfactant-protein systems, such as the type of protein-surfactant interaction (in terms of cooperativity), the influence of the aggregation state of the surfactant (monomer, pre-micellar aggregate, and micelle) on the protein structure, the characterization of the interaction sites on the protein surface, the identification of the intermediate protein conformations, between others (Ajloo et al., 2002; Liu et al., 2005, 2007). Research involving interaction of cationic and anionic surfactants with macromolecules, especially proteins, have been developed (Maulik et al., 1998; Tofani et al., 2004), being the interaction of charged headgroups the focus of these works. Furthermore, depending on the concentration, surfactants can act as unfolding and denaturant agents, which can be used to evaluate the structural properties of the different proteins and their active sites.

Studies upon the interaction of globular proteins with surfactants, with sodium dodecyl sulphate (SDS), have been carried on with the aim to understand details of the structure and function of proteins (Chattopadhyay & Mazumdar, 2003; Gębicka & Gębicki, 1999; Tanford, 1973; Yang et al., 2003). Three ranges of surfactant concentrations associated to different effects on the protein should be mentioned. The first one, at stoichiometric surfactant concentration, is related to the findings that can be correlated to specific sites on the protein, due to, mainly, electrostatic interactions (Decker et al., 2001; Moosavi-Movahedi et al., 2003; Reza et al., 2002).

At higher surfactant concentrations, near to the surfactant critical micellar concentration (cmc), pre-micellar aggregates can be originated in the different media. Above the cmc, at millimolar surfactant concentrations, the protein-surfactant interaction is an extremely complicated phenomenon. Indeed, surfactant aggregates above so-called critical micelle concentration (cmc), can originate spherical or cylindrical micelles, bilayers, vesicles, and other aggregates, depending on surfactant structure and conditions. These aggregates pressent a hydrophobic interior or core made from surfactant hydrocarbon tails covered by a hydrophilic, usually ionic, surface layer elaborated from surfactant head groups, which is like the structural organizations of globular proteins and biological membranes. For this reason, the reactivity in such aggregates based on the supramolecular imitation of enzyme catalysis is of great relevance in several research areas (Moosavi-Movahedi et al., 2008).

Generally, surfactants induce a decrease of the α-helix content, and this effect is smaller for cationic than for anionic ones (Tofani et al., 2004). However, in the case of the giant extracellular hemoglobins, which are also called erytrocruorins, such as *Glossoscolex paulistus* hemoglobin, this is not true

(Santiago et al., 2007). Probably, this is associated to the decisive influence of the value of isoelectric point (pI) in the control of the interaction with ionic surfactants, since the erytrocruorins are proteins with very acid pI, which is a very peculiar property.

Otzen & Oliveberg (2002) studying a small protein S6 in the presence of SDS, argue that monomeric SDS binds to the native state, but global unfolding would occur only above the critical micelle concentration (cmc). Indeed, this verification is corroborated by various works about interaction between surfactants and hemoproteins (Das & Medhi, 1998; Oellerich et al., 2003; Tofani et al., 2004). Oellerich et al. (2003) analyzing the interaction between SDS and cytochrome *c*, explain that the differences observed below and above the cmc are due to the different modes of binding of SDS monomers and micelles. In agreement with these authors, these alterations of the heme structure are common to both modes of interaction, implying that the sites of electrostatic and hydrophobic contacts should be in the vicinity of the cytochrome c heme pocket. Tofani et al. (2004) observed for Horse myoglobin (MbH), that only in a SDS/MbH ratio higher than 400, would occur a more significant protein unfolding and, for consequence, a more exposed and accessible heme pocket would be generated in this case. Studies focused on the SDS-cytochrome *c* interaction at neutral pH have demonstrated that the unfolded state is stabilized when occur the bis-histidine (hemichrome) species formation, being that subsequent modifications of the secondary structure are rate-limited by the histidine dissociation rate (Das & Medhi, 1998). Therefore, the hemichrome (i.e., a bis-histidine complex) formation anchors the E helix into the ferric center, and, with the E and F helices maintained connected to the metallic center, the new polypeptide chains arrangement is stabilized, at least, partially. This observation illustrates the correlation between the oligomeric assembly changes with the modifications that occur in the first coordination sphere of the metal in hemoproteins.

The dependence of the kind of protein-surfactant interaction with the surfactant concentration is also found to other types of protein. Bovine Serum Albumin (BSA), for example, presents initial high affinity binding sites for surfactants, which correspond to an intense electrostatic binding, which is characteristic for. anionic compounds and BSA. The higher surfactant concentrations reveal nucleation sites for binding of "micelle-like" aggregates (Gelamo et al., 2004). Despite the great predominance of the electrostatic contribution in the interaction of SDS with hemoproteins, the hydrophobic contacts present a significant importance to the total interaction. Gębicka & Gębicki (1999) argue that the hydrocarbon part geometry from the surfactant in the SDS-cytochrome *c* interaction is responsible for great influence on the spatial configuration of the heme pocket.

Polar lipids of biological membranes are predominantly zwitterionic phophatidylcholine and phophatidyllethanolamine. Therefore, micelles of the zwitterionic surfactant N-hexadecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (HPS) may be considered as a convenient model of lipid aggregates (Yushmanov et al., 1994). Despite this significant biological relevance, the number of works in the literature focusing on the interaction of zwitterionic surfactants, such as HPS, with hemeproteins is significantly lower as compared to the studies regarding the interactions of hemeproteins and cationic and anionic surfactants.

## Technological applications of protein-surfactant systems

Many technological applications require the adsorption of amphiphilic molecules, such as protein or surfactant, to modify properties of compounds, such as nanoparticles, for specific applications. For example, protein-coated nanoparticles have enhanced biocompatibility and have been used in diverse potential applications in drug delivery and biosensors. Indeed, the adsorption of surfactant to nanoparticles gives enhanced colloid stability, which is useful in detergent and cosmetic industry, being that the properties of such complexes can be varied by several parameters, which include charge on individual component, pH, ionic strength etc (Mehan et al., 2014).

## Technological applications of hemoproteins

The understanding of interactions between proteins and surfaces is critically important in many fields of biochemical science, from biosensors to biocompatible materials. The development of biosensors, for instance, presents a critical step, which is the immobilization of proteins with intact functions onto the surface of a transducer. Although many proteins spontaneously adsorb onto solid surfaces, the adsorbed

proteins often denature or adapt undesirable orientation on the surfaces. To avoid these problems, various methods have been developed, each one of them with its own advantages and disadvantages (Boussaad & Tao, 1999).

In recent years, a novel technique of layer-by-layer self-assembly has provoked more interests among researchers and it has been developed into a general approach for fabricating ultrathin films on solid surfaces. This molecular architecture method is fundamentally based on the alternate adsorption of oppositely charged species from their solutions with precise thickness control on the nanometer scale. The layer-by-layer assembly has been extended to building up protein or other biomacromolecules films and has been successfully employed for the design and construction of biodevices (Shen & Hu, 2005).

It is important to notice, for example, the development of a novel method for fabricating hydrogen peroxide ($H_2O_2$) sensor, which has been presented based on the self-assembly of $ZrO_2$ nanoparticles with heme proteins on functional glassy carbon electrode (Zhao et al., 2005). The immobilized proteins realized their direct electrochemistry with the formal potential of -0.032 V for hemoglobin and -0.026 V for myoglobin in pH 6.0, respectively. In fact, the resultant heme-protein electrode exhibited fast amperometric response (within 10 seconds) to $H_2O_2$, excellent stability, long-term life (more than one month) and good reproducibility (Zhao et al., 2005). Another interesting study was elaborated by Yao and co-workers (Yao et al., 2007), which made an electrochemical and electrocatalytic system of hemoglobin immobilized on glass carbon electrode containing gelatin films, which is associated to a fast amperometric response to the reduction of $H_2O_2$ and nitrite (Yao et al., 2007).

**Technological applications of surfactant-hemoprotein systems**

Several applications have been developed employing the interactions between proteins and surfactants (Hu et al., 2007; Shan et al., 2008). In fact, the design of heme proteins is an active field of biochemical objectives focused on to delineate the structure-activity relationships of natural protein catalysis. These studies have provided insight into natural heme protein sequence design, the effects of cofactors incorporation on protein folding, stability, and structure as well as the modulation of heme electrochemistry by the protein matrix (Moosavi-Movahedi et al., 2008).

Since 1993, Rusling & Nassar (1993) reported The direct electron methodology (electroanalytical technique) and the iron heme protein myoglobin, which was incorporated in DDAB. The direct electrochemistry of protein has received the attention of great number of research groups (Lu et al., 2005). Rusling & Nassar (1993) reported the direct electrochemistry of proteins, such as hemoglobin, myoglobin, and horseradish peroxidase, by incorporating them into the surfactant film, the polymer film and the composite film of surfactant and clay on pyrolytic graphite electrodes. Liu et al. (2007) improved the electron transfer characteristics of proteins by embedding them into agarose hydrogel film on pyrolytic graphite electrodes. Wang and co-workers obtained the direct electron transfer of horseradish peroxidase immobilized in DMPC and DDAB films on glassy carbon electrodes immobilized in DMPC and DDAB films on glassy carbon electrodes, respectively. Wang and co-workers also reported the direct electrochemistry of hemoglobin at pyrolytic graphite electrodes modified with egg-phosphatidylcholine film and glassy carbon electrodes coated with lipid-protected gold nanoparticles separately (Lu et al., 2005).

An interesting work was developed by Shan and co-workers (Shan et al., 2008), which elaborated a self-assembled electroactive layer-by-layer film of heme proteins with anionic surfactant dihexadecyl phosphate. This film grown on pyrolytic graphite (PG) electrodes, showing a pair of well-defined and nearly reversible cyclic voltammetry peaks at around -0.35 V vs SCE at pH 7.0, which is characteristic of the heme protein Fe(III)/Fe(II) redox couples. Hu and co-workers (Hu et al. 2007) developed similar film using the cationic surfactant didodecyldimethylammonium bromide (DDAB) on PG electrodes and demonstrated two pairs of nearly reversible redox peaks at approximately -0.22 and -1.14 V vs SCE at pH 7.0, which are typical of the hemoglobin Fe(III)/Fe(II) and Fe(II)/Fe(I) redox couples, respectively. Based on the direct electrochemistry of heme proteins, the films could also be applied to electrochemically catalyze reduction of oxygen, hydrogen peroxide and nitrite with significant lowering of reduction overpotentials.

Indeed, the rapid and accurate determination of hydrogen peroxide ($H_2O_2$), for example, is of great importance because it is not only the product of the reactions catalyzed by highly selective oxidases but

also an essential compound in food, pharmaceutical and environmental analyses. Among these techniques employed for hydrogen peroxide ($H_2O_2$) analysis, such as titrimetry, photometry, chemiluminescence, high performance liquid chromatography (HPLC) and electrochemistry, amperometry with enzyme-based biosensors have received considerable interest, because this class of technique is characterized by sensitivity, convenience, and high selectivity. Amperometric enzyme-based $H_2O_2$ biosensors could be divided into two categories, namely mediated biosensors, and mediated-free biosensors (Chen et al., 2007).

It is important to notice that mediated-free biosensors, third-generation biosensors, which are based on the direct electron transfer between redox proteins and electrode, re receiving a significant attention because they could overcome the disadvantages mentioned above of mediated biosensors and make the design of biosensors simple without requirements for chemical mediators (Chen et al., 2007). Electrochemical biosensors, such as a simple biomolecule or a biological macromolecule immobilized on some types of surface, have received more attention with respect to their constructions and applications due to high sensitivity, reproducibility, good biocompatibility and long stability (Liu et al., 2013).

Biomimetic chemistry attempts to improve the performance of biocatalysts by imitating enzymatic processes. Enzyme mimics catalysts are based on the principles of enzyme action, such as an initial binding interaction between the substrate and the biocatalyst, polyfunctional activation of the bound substrate by properly positioned organic catalytic groups of metallic ions (or metallic complexes, i. e., coordination compounds that present a metallic cation as coordination center), transition-state stabilization, and others. Enzyme mimics are designed mainly for practical applications as artificial enzymes and for understanding enzymatic mechanisms. Generally, simple organic molecules, metallic complexes and more sophisticated supramolecular systems can work as enzyme mimics (Moosavi-Movahedi et al., 2003, 2008).

## Conclusions

It is important to notice that the interaction between biological macromolecules and surfactant compounds consists in a very informative scientific approach, since this kind of interaction represents a model of several biological phenomena as well as a prototype of several applications in advanced areas like, for example, nanoscience, surface modifications, biosensors, electrocatalysis, evaluations of blood substitutes, between others.

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