



Historical perspective

## Polymer–surfactant systems in bulk and at fluid interfaces



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### ARTICLE INFO

Available online 10 November 2015

#### Keywords:

Polymers  
Polyelectrolytes  
Surfactant  
Interfaces  
Interfacial tension  
Interfacial rheology

### ABSTRACT

The interest of polymer–surfactant systems has undergone a spectacular development in the last thirty years due to their complex behavior and their importance in different industrial sectors. The importance can be mainly associated with the rich phase behavior of these mixtures that confers a wide range of physico-chemical properties to the complexes formed by polymers and surfactants, both in bulk and at the interfaces. This latter aspect is especially relevant because of the use of their mixture for the stabilization of dispersed systems such as foams and emulsions, with an increasing interest in several fields such as cosmetic, food science or fabrication of controlled drug delivery structures. This review presents a comprehensive analysis of different aspects related to the phase behavior of these mixtures and their intriguing behavior after adsorption at the liquid/air interface. A discussion of some physical properties of the bulk is also included. The discussion clearly points out that much more work is needed for obtaining the necessary insights for designing polymer–surfactant mixtures for specific applications.

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## 1. Introduction

Supramolecular aggregation of surfactants, polymers, proteins and their mixed systems has attracted many research efforts in the last fifty years due to their interesting behavior and their multiple technological applications [1–12]. Neutral hydrophilic polymers, mixtures of surfactants and block copolymers, proteins, hydrophobically modified polymers and polyelectrolyte–surfactant (neutral, ionic or zwitterionic) mixtures are among the most studied systems [2,3,13].

Supramolecular association of polymer and surfactant leads to the formation of a broad range of structures [14,15]: micelle-like aggregates, complexes, coacervates, precipitates and gels [16]. The bulk behavior of these systems is relevant for understanding their adsorption processes at fluid/vapor and fluid/solid interfaces, as well as, the surface rheological properties at fluid interfaces. The latter has been found to be important in areas ranging from food technology to cosmetics, and from drug delivery to coating fabrication [1,3,17–21]. They are also relevant for the stabilization of dispersed systems such as emulsion, and foams, in which they form a protective layer around the liquid drops or air bubbles [22–26]. Other applications for these systems can be found in different fields such as foods, pharmaceutical, detergents or mineral processing. In most of these applications these mixed systems are added to the products for rheology control, stabilization or modification of their adsorption at surfaces [27–29].

Interfacial tension and rheology measurements have shown the existence of a competitive adsorption between the different species in solution [17,20,30–32]. Proper design of the mixtures to be used for a given technological application cannot be done unless the interactions between the different species, both in bulk and at the interface, are known. The interfacial properties of polymer/protein–surfactant mixed systems are governed by many variables, such as the conformation and rigidity of the polymers/proteins, the type of surfactant (i.e. hydrophilic–lipophilic balance, HLB, and charge), the nature of the interface (water/air or water/oil or fluid/solid), pH, ionic strength, and temperature, and the formation of supramolecular aggregates [33–35]. The polymer/protein–surfactant interaction depends mainly on three aspects: charge density of the chains, hydrophobicity and ionic character of the surfactant, and on the interactions (electrostatic, Van der Waals, hydrogen bond or other types of weak interactions) between the chains and the surfactant molecules or micelles [36]. Thus, the formation of polymer–surfactant aggregates in aqueous solution is mediated by an intricate balance between different attractive and repulsive interactions that strongly depend on the specific chemical nature of both polymer and surfactant [37–39]. Some of the reported factors to be considered in the appearance of complexes are:

- 1) Electrostatic interactions between the polar or ionic head groups of the surfactant molecules and the polymer backbone.
- 2) Hydrophobic contributions associated with the interaction between surfactant tails or between them, and the hydrophobic backbone of the polymer.
- 3) The release of counterions strongly changes the entropy of the assembling process.
- 4) The interaction between polymer and micellar-like aggregates of the surfactant can drive the reduction of the repulsion between the polar head groups in the micelles.
- 5) The interaction of the polymer and surfactant aggregates can reduce the interaction of the hydrophobic region of the micelles with water.

It must be remarked that non-covalent binding mechanisms involved in the formation of the complexes suggest the interaction of

polymer and micelle-like surfactant aggregates that involves steric factors, and the release of hydration water and counterions from the binding sites. Therefore, it is expected that favorable interactions occur only when specific regions or groups are present in the polymer and surfactant molecules, e.g. the behavior of polyvinylpyrrolidone (PVP) mixed with two surfactants that differ only on their head groups, namely sodium dodecylsulfate (SDS) and sodium dodecylsulfonate, is different [40,41]. In the case of SDS there is a high affinity between the surfactant and PVP, whereas for sodium dodecylsulfonate the affinity it is small. These specific effects are even more dramatic when non-ionic surfactants interact with polymers [42,43].

## 2. Polymer–surfactant phase behavior

The phase behavior and the interfacial properties are linked to the bulk properties of polymer–surfactant mixtures because the chemical potential in each coexisting phase, including the bulk and the interface must be identical. Furthermore, parameters such as the cac and the aggregation number of the surfactant ( $N_{ag}$ ) are strongly dependent on physicochemical properties such as polymer concentration, polymer charge density, flexibility and hydrophobicity of the polymer chain [44,45]. Several physicochemical properties have been used in literature to obtain information about the bulk behavior of polymer–surfactant mixed systems [3,16,37]. In the following sections, we will review the most relevant aspects associated with polymer–surfactant association and their phase behavior. The bulk characterization of polymer–surfactant mixtures can be carried out by many physico-chemical properties for this purpose and several techniques can be used (further details are provided as Appendix A), including:  $\zeta$ -potential/electrophoretic mobility measurements, dynamic and static light scattering, neutron scattering and X-ray diffraction, turbidimetry, bulk rheology, calorimetry, and conductimetry.

### 2.1. Surfactant binding to polymer chains

The interactions between polymer and surfactants determine the phase behavior of the polymer–surfactant mixtures, making difficult the prediction of the regions of the phase diagram [1,14,46,47]. The phase behavior depends on the properties of both polymer and surfactant. In the case of the polymer chains the hydrophilicity/hydrophobicity of the molecules and their charge density, molecular weight, chain flexibility and degree of branching are the most important parameters. For the surfactants, the nature of the hydrophilic head, the hydrophobic chain length, and the concentration can be considered as the most relevant aspects controlling the formation of complexes. Furthermore, the solution conditions, i.e. pH, ionic strength and temperature play an important role in the aggregation mechanism of polymer chains and surfactant molecules. Monte Carlo calculations by Wallin and Linse [44,45] have shown qualitatively the changes induced by the aforementioned variables in the phase behavior of the mixtures. The binding of surfactant molecules to polymer chains modifies the conformation of the chains, but the effect found is not the expected one from the screening provoked by the addition of inert salts to polymer solutions [48,49].

Strong interactions make the chains to act as aggregation nuclei, thus leading to the formation of surfactant micelles along the polymer chains for surfactant concentrations well below the corresponding critical micellar concentration, cmc [43]. In this case the cac is almost independent of the concentration and molecular weight of the polymer [43]. Above the cac, the surfactant molecules aggregate along the polymer chains as bound micelle-like structures, forming a pearl-necklace-like structure [43,50–53]. In general, the cac is between one

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