Polyelectrolyte/surfactant mixtures in the bulk and at water/oil interfaces

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ABSTRACT

Stabilization of emulsions by mixed polyelectrolyte/surfactant systems is a prominent example for the application in modern technologies. The formation of complexes between the polymers and the surfactants depends on the type of surfactant (ionic, non-ionic) and the mixing ratio. The surface activity (hydrophilic–lipophilic balance) of the resulting complexes is an important quantity for its efficiency in stabilizing emulsions. The interfacial adsorption properties observed at liquid/oil interfaces are more or less equivalent to those observed at the aqueous solution/air interface, however, the corresponding interfacial dilational and shear rheology parameters differ quite significantly. The interfacial properties are directly linked to bulk properties, which support the picture for the complex formation of polyelectrolyte/surfactant mixtures, which is the result of electrostatic and hydrophobic interactions. For long alkyl chain surfactants the interfacial behavior is strongly influenced by hydrophobic interactions while the complex formation with short chain surfactants is mainly governed by electrostatic interactions.

Contents

1. Introduction

Polymer/surfactant mixtures have a wide range of industrial and technological applications due to their specific behavior at different interfaces. Surfactants reduce the surface and interfacial tensions strongly, effectively and quickly, while polymers provide a rather important mechanical behavior to surface and interfacial layers which cannot be provided by surfactants alone. Among the polymers used in such systems, polyelectrolytes are quite interesting because they exhibit the properties of polybases, polyacids and polyampholytes due to their functional groups. Due to the electrostatic interaction with oppositely charged ionic surfactants polyelectrolytes can create associates and/or polycomplexes, which modify the interfacial properties respectively [1].

A lot of data were published showing their ambiguous effects on the properties of mixed interfacial layers at liquid/gas [1–12,14–16,28,32,41], liquid/liquid [22–30,33] and liquid/solid interfaces [42,43,44]. In particular, this is clearly seen in metastable micrometer and sub-micrometer heterogenous disperse systems, such as foams [18,20,21,41], emulsions [19,21,22,29,30] and dispersions [52,53,54].

It can be assumed that in the transition to the micro- and nanosize area the picture becomes more complex and unpredictable. In this regard, it is interesting to conduct a systematic experimental study of the behavior of polyelectrolytes and surfactants at liquid/liquid interfaces (water/organic solvent), as well as a comparative analysis of the results with those reported in the literature for the water/air interface, for which a large number of publications are devoted [1–12,14–17].

Polyelectrolyte/surfactant mixtures are studied in the bulk and at the solution surface, for which their properties are mainly discussed. There are many comprehensive reviews made for example by Taylor, Penfold, Langevin, Lindman and others [1,8–16,23], where the interaction of polyelectrolyte/surfactant mixtures was discussed in terms of complex formation, competitive adsorption between surface active polyelectrolyte/surfactant complexes and polymer/surfactant aggregates in solution. Several works focused on the effect of surfactant hydrophobicity on the surface properties of polyelectrolyte/surfactant complexes where their adsorption was explained by the competition between the formation of surface active polymer/surfactant complexes and polymer/surfactant aggregates in the solution bulk. It was found that the addition of electrolyte leads to variations in the critical micelle concentration and critical aggregation concentration associated with surfactants of different alkyl chain lengths [31].

Due to the lack of experimental techniques the polyelectrolyte/surfactant mixtures were studied less at water/oil interfaces, however, now higher attention is paid to studies of such systems [19,21–30,33]. In the present paper we will review the recent state of the art of the properties of polyelectrolyte/surfactant mixtures in the bulk and at water/oil interfaces by means of interfacial tensiometry, dilational and shear rheology, and by hydrodynamic and electrokinetic measurements. This approach can help in explaining many features of polyelectrolytes, in particular the influence of surfactants on surface phenomena at liquid interfaces.

2. Interfacial tension of oppositely charged polyelectrolyte/surfactant mixtures at the water/oil interface

Different techniques are used to describe the interfacial behavior of polyelectrolytes, surfactants and their mixed solutions. Although the interfacial tension cannot fully explain the observed interfacial behavior, it is now the classical method without which no investigation of polyelectrolyte/surfactant mixtures at the water/oil interfaces can be done.

As it is known amphiphilic molecules in the solution accumulate at interfaces and reduce the excess of free energy. This spontaneous process (adsorption) proceeds until the saturation of the interface by adsorbed surfactants is reached. Excessive amounts of surfactant molecules in the solution form aggregates (micelles) with different morphologies. A similar phenomenon occurs in aqueous solutions of natural and synthetic amphiphilic polymers [36,37].

However, the formation of adsorption layers by polymer is a long lasting process [23,35]. The duration of this process, reflected by the slow decrease of surface tension was associated with a variety of factors. In particular, it is explained by the slow unfolding of the macromolecules in the adsorption layers, increasing penetration layers and the formation of multilayers [35].

2.1. Dynamic interfacial tensions

According to [36,38], the slow kinetics of the surface tension reduction of polymer solutions is associated with a slow differentiation

at the interface according to the polarity difference of groups in the macromolecular chains. In fact, the amphiphilic macromolecular coils diffuse to the interface and initially are adsorbed by random segments. Then the adsorbed macromolecules, due to the differentiation of their segments in polarity, undergo re-conformation at the interface. This process corresponds to Rebinder's rule of phase polarity equalization [39] and goes spontaneously.

Significant effects on the adsorption kinetics of macromolecules can be caused by their association with surfactants or other substances leading to a change in their hydrophilic–lipophilic balance. This can be seen in the kinetics of interfacial tension reduction of polyelectrolyte/surfactant mixtures in comparison with pure surfactants.

The adsorption equilibrium of the mixed polyallylamine hydrochloride (PAH)/sodium dodecyl sulphate (SDS) solutions is reached slowly at low surfactant concentrations ($1 * 10^{-4}$ M) in comparison with pure surfactant solutions (Fig. 1). But with increasing surfactant concentration the equilibrium interfacial tensions are reached faster. The observed features of the kinetics of interfacial tension reduction of PAH/SDS solutions can be explained by the association of oppositely charged polyelectrolyte macromolecules and surfactant in the solutions, based on electrostatic interactions which leads to a significant hydrophobicity of the polycomplexes and consequently to the reduction of electrostatic free energy of polyions [23]. This can be the reason, in addition to the faster diffusion process in higher concentrated solutions, for the accelerated interfacial tension reduction in the initial part of the curves because increase of the compaction in accordance to the Stokes–Einstein equation leads to increased diffusion rates.

The interaction between polyelectrolytes and surfactants is accompanied by significant conformational transformations of the polyelectrolyte statistical coils and chains. The electrostatic binding of ionic surfactants to a polyelectrolyte chain is typically accompanied by an increased macromolecular compaction and density. In contrast, the binding of surfactants to polyelectrolytes via hydrophobic interactions leads to a loosening of the macromolecular coil and to an increase in the complex solubility [40].

It is interesting that with the increase of the surfactant alkyl chain length the kinetics of interfacial tension reduction changes too (Fig. 2). For shorter surfactant alkyl chains the interfacial tension curves as a function of time have the same shape. However, for longer alkyl chains the kinetics of interfacial tension of PAH–sodium hexadecyl sulfate (SHS) reaches final value slower. This is due to the slower diffusion of the surfactant molecules to the surface because of the larger size. For PAH–sodium tetradecyl sulfate (STS) complexes the slow establishment of the equilibrium adsorption state (equilibrium interfacial tension
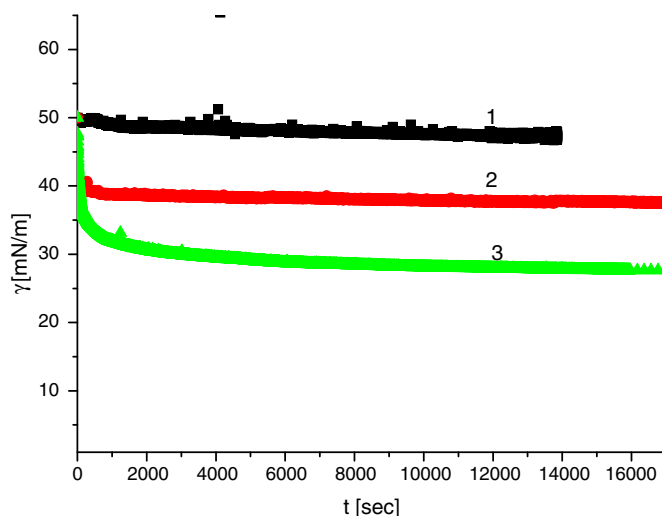

Fig. 1. Effect of surfactant on the interfacial tension kinetic reduction of PAH (curve 1), SDS (curve 2) and their mixtures (curve 3) at the water/hexane interface; according to [23].