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Interaction of cationic surfactant and anionic polyelectrolytes in mixed aqueous solutions

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Abstract

Surfactant–polymer interactions in aqueous solutions have been studied using dynamic surface tension, polyelectrolyte titration, nephelometric turbidity, and dynamic light scattering. For the preparation of complexes, a technical cationic surfactant was used in combination with two poly(maleic acid-co-polymers) of similar structure but different hydrophobicity. The dynamic surface tensions of mixed solutions as functions of surfactant concentration at constant polyelectrolyte content, as well as changes in the surface activity due to the influence of polyanion at constant surfactant concentration are discussed in terms of a complex or aggregate formation in the bulk phase. The interaction of the surfactant with poly(maleic acid-alt-propene) (P-MS-P) and poly(maleic acid-alt-α-methylstyrene) (P-MS-MeSty), respectively, is strong in both cases and results in the formation of nanoparticles with properties depending on the composition of the corresponding mixture.

Keywords: Dynamic surface tension; Light scattering; Polyelectrolyte–surfactant interaction; Complex formation; Complex dispersion stability

1. Introduction

Mixtures of polymers and surfactants are common in many industrial formulations. The interaction between surfactants and water-soluble polymers provides special effects, e.g. enhancing the surface activity, stabilizing foams and emulsions, etc. It is, therefore, very important to study the interaction between surfactants and water-soluble polymers, especially between components of opposite charge. The first results were already described in the literature of the 1970s, and from 1980 until now much work has been done to improve the understanding of such systems [1–4]. Very detailed investigations by using different characterization methods such as surface tensiometry [5–9], light scattering [10,11], neutron scattering [12,13] or NMR [12,14,15] or ESR [14] and also surface rheological methods [16–19] are mentioned. Usually, mixed solutions at fixed polyelectrolyte and variable surfactant concentrations are investigated and it can be shown that the association between polyelectrolytes and oppositely charged surfactant starts at very low surfactant concentration (typically 1–3 orders of magnitude below the critical micelle concentration, cmc, of the surfactant) [16]. The surface tension versus ln c plots of such systems normally display three points were the surface tension changes quite sharply.

The degree of surface tension lowering depends not only on the type of polyelectrolytes (on their hydrophobicity, charge density, molecular weight) but also on the mixing protocol (order of addition, influence of time) and salt content [20]. In most studies a fixed polyelectrolyte amount was added to solutions of an oppositely charged surfactant (the so called ‘polymer to surfactant regime’ according to ref. [20]). Because the interaction between polymer and surfactant starts at very low surfactant concentration, basic research is often carried out below the cmc, but for the application in industry the interaction with polymers at higher surfactant concentration is important too. However, despite the importance and common use of polymer–surfactant complexes there are only very few publications about application relevant properties.

In our previous work, we showed that it is possible to tailor stable, differently charged complex dispersions which were used for different applications, such as surface modification of powders [21], sorption of organic molecules from wastewater [22] or as flocculants [23,24].

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In the present work, interactions between a technical cationic surfactant Quartolan and two anionic polyelectrolytes, both co-polymers of maleic acid of similar structure but different hydrophobicity, will be investigated in two different regimes in order to answer the following questions:

A: How does the addition of polyanions at fixed concentration influence the dynamic surface tension of aqueous surfactant solutions and
B: How does the structure and concentration of polyanions influence the dynamic surface tension at constant surfactant concentration?

The results of surface tension measurement will be supported by polyelectrolyte titration, turbidity measurements and dynamic light scattering (DLS).

The used dynamic surface tensions measured by bubble pressure tensiometry will serve as a tool to qualitatively determine which of the main components, polyelectrolyte/surfactant complex or free surfactant, governs the interface.

2. Experimental

2.1. Surfactant and polymers

For preparation of complexes, a technical cationic surfactant Quartolan (benzyl(dodecylcarbamoyl)methyl) dimethyl ammonium chloride (CAS 100-95-8) as well as two maleic acid co-polymers as anionic polyelectrolytes were used. Quartolan was obtained form DHW Rodleben (Germany); polyelectrolytes were supplied by Leuna (Germany). Some characteristics of the polymers (polyanions), which are differing in their structure and hydrophobicity, are detailed in Table 1. Concentrated stock solutions of them were prepared by hydrolysis of the corresponding anhydride with overstoichiometric amounts of NaOH as described [25]. The stock concentration of each polyanion in Millipore water was about 0.01 mol/l (concentration of the anionic entities). The exact concentration of charged units was determined by polyelectrolyte titration as described in Section 2.3.

2.2. Experimental regimes

Interactions between surfactant and polyanion were studied in two regimes over respective concentration ranges of both components.

Regime A is the ‘usual way’ to investigate such systems. A fixed amount of 3×10^{-4} mol/l of each polyanion was added to diluted Quartolan solutions; the concentration of the surfactant was varied in the range 10^{-5} to 3×10^{-3} mol/l.

Regime B: Variable polyanion concentration up to 7×10^{-3} mol/l at fixed surfactant concentration of 5×10^{-3} mol/l.

In both cases, aqueous solutions containing about 0.01 mol/l anionic units was slowly added to corresponding aqueous solutions of Quartolan under stirring. After addition, the mixture was stirred for 10 min and then allowed to rest for 30 min before the turbidity was measured.

2.3. Characterization of mixtures/complex dispersions

It is well known that systems containing polymers have a very long relaxation (in the order of hours) towards equilibrium [3]. Therefore, all measurements, except charge and turbidity determination, were carried out at least 24 h after the sample preparation.

Dynamic surface tensions of aqueous solutions containing surfactant (S) and polyelectrolyte (PI, PII) as well as their mixtures were measured at room temperature using the bubble pressure tensiometer BPA-1P (SINTERFACE Technologies, Berlin) as described in detail elsewhere [26,27]. The instrument provides data for adsorption times between 10 ms and 60 s. The error in the measured surface tension data calculated as the standard deviation did not exceed 1 mN/m.

The precise charge of aqueous polymer (anionic units) and surfactant solutions as well as of their mixtures was determined by polyelectrolyte titration with a particle charge detector PCD 02 (Mütek, Germany). This system, based on the streaming potential principle, was used to detect the isoelectric point of solutions and mixtures during the titration process. An aqueous solution of the cationic polyelectrolyte poly-diallyl-dimethyl-ammoniumchloride (PDADMAC, 0.001 mol/l) was used as a titrant for anionically charged solutions and mixtures, and sodium polyethylensulfonate (0.001 mol/l) for the ones with cationic charge.

In addition, the surfactant solution was titrated with an instrument Orion 960 (Thermo Electron Corporation, Germany) to calculate the titration endpoint from the first derivative of the titration curve. In the case of Quartolan, the results of both methods are in good agreement. From the titration data, the charge ratio $n-/n+$ of the individual components in the mixture can be calculated. The charge of formed complexes (Zeta potential) was determined by Zeta-Master (Malvern, UK).

Table 1
Characteristics of polyelectrolytes used

Polyelectrolyte type	Abbreviation	D_p	Molecular weight[a] (g/mol)	Surface tension at fixed concentration[b] (mN/m)
Poly(maleic acid-alt-propene)	P-MS-P, PI	357	50,000	70.1
Poly(maleic acid-alt-α-methylstyrene)	P-MS-MeSty, PII	116	24,000	73.5

D_p: degree of polymerization.
[a] Measured by gel permeation chromatography.
[b] Fixed concentration of 3×10^{-4} mol/l.