Interactions between surfaces coated with cationic hydrophobically modified polyelectrolyte in the presence and the absence of oppositely charged surfactant

Abstract The association between a cationic hydrophobically modified polyelectrolyte and an anionic surfactant was investigated in bulk solution and at a negatively charged solid surface. The bulk association was followed by measurements of turbidity and electrophoretic mobility. The maximum turbidity of the solution was found to closely coincide with the point of zero electrophoretic mobility of the aggregates. The forces acting between negatively charged mica surfaces across a dilute aqueous solution of the hydrophobically modified polyelectrolyte were monitored using surface force measurements. The presence of hydrophobic side chains on the polyelectrolyte leads to adsorption in an inner rather compact layer and an outer extended layer. After dilution only the inner layer remains adsorbed to the surface. In the next step, sodium dodecyl sulphate (SDS) was added. It was found that the anionic surfactant is incorporated in the adsorbed layer even at very low bulk concentrations. As the surfactant concentration is increased stepwise the layer first swells and relaxes very slowly during compression. At higher SDS concentrations, desorption occurs. The interfacial properties of the hydrophobically modified polyelectrolyte alone and in mixtures with SDS are in many ways strikingly different to those of non-hydrophobically modified polyelectrolytes having a similar linear charge density. This is due to the importance of hydrophobic interactions between the hydrophobic side chains of the polyelectrolyte and between these groups and the non-polar part of the surfactant.

Key words Surface forces · Polyelectrolyte · Surfactant · Sodium dodecyl sulphate · Polyelectrolyte–surfactant association

Introduction

The association behaviour of polyelectrolytes and oppositely charged surfactants has been extensively studied and there are many recent reviews and books covering different aspects of this fascinating topic [1–6]. The overwhelming majority of the studies on the subject are concerned with association in bulk solution. One rationale for this is the importance of polyelectrolyte–surfactant systems as rheology modifiers [5, 7], gelation agents [8], and solubilizers for sparingly soluble substances such as dyes [9, 10], perfumes, or pollutants [11, 12]. However, in many applications these mixtures, or the hydrophobically modified polyelectrolytes alone, are active at interfaces where they may control emulsion [13], dispersion [14] and foam stability [12, 15, 16], the wetting behaviour [17], and particle deposition [18]. It is fair to say that the body of knowledge about the properties of polyelectrolyte–surfactant mixtures at interfaces is too limited considering the technological
importance of these systems. Among the experimental techniques that have been used in the study of interfacial properties of polyelectrolyte–surfactant mixtures and hydrophobically modified polyelectrolytes one can mention ellipsometry and reflectometry [19–23], specular neutron reflectivity [24], variable angle of incidence evanescent wave spectroscopy [25], and surface force instruments [19, 26]. Our research group has mainly used the latter technique to investigate interactions between polyelectrolytes and surfactants at solid–liquid interfaces [27–33]. One complication is the fact that the properties of the adsorbed layer in many cases depend not only on the surface and the bulk composition but also on the experimental path [20, 33, 34]. Hence, the approach towards true equilibrium is extremely slow. In particular, we have shown that the properties of the adsorbed layer depend crucially on whether it is formed by adsorption of preformed polyelectrolyte–surfactant aggregates or by allowing the surfactant to associate with preadsorbed polyelectrolyte layers [33]. In the latter case, it has been established that hardly any incorporation of surfactant in the adsorbed layer occurs until a critical surfactant concentration has been reached. This critical association concentration at the surface (c_{ac}) is different from the critical association concentration in bulk solution (c_{ac}), and it is expected to depend not only on the nature of the polyelectrolyte and the surfactant but also on the nature of the solid surface [29]. The study presented here is also concerned with interactions between preadsorbed polyelectrolyte layers and oppositely charged surfactants. It differs from our previous studies in that the polyelectrolyte used is highly hydrophobic, having 40% of the segments carrying a grafted dodecyl chain. This study is a continuation of our effort in establishing the relation between the chemical structure of polyelectrolytes and the properties of adsorbed polyelectrolyte layers in the absence and presence of oppositely charged surfactants. As will be seen in the following, the presence of the hydrophobic side chains has a significant impact on the structure of the polyelectrolyte layer before addition of the surfactant, on the incorporation of surfactant in the adsorbed layer, and on the interactions between surfaces coated with polyelectrolyte–surfactant aggregates.

### Materials and methods

The amphiphilic polyelectrolyte used in this investigation is shown in Fig. 1. It was obtained by quaternisation of a precursor, poly(vinylbenzyl chloride) (PVBC), as described in Ref. [35]. In brief, the precursor PVBC was quaternised in two steps in CHCl₃. In the first step 40% of the VBC units were reacted with dimethyldecylamine, while in the second one the remaining VBC units were quaternised with triethylamine. The final copolymer was purified by precipitation in dimethyl ether, followed by dissolution in water and freeze-drying. The composition of the copolymer was confirmed by NMR and elemental analysis. Owing to the synthesis route followed we expect a random distribution of the dodecyl side chains. The degree of polymerisation and the polydispersity of the precursor PVBC were estimated by size-exclusion chromatography in tetrahydrofuran. We found DPₐ ≈ 100 (molecular weight ≈ 3 × 10⁴ g/mol) and DPₐ/DPₙ ≈ 2. This polyelectrolyte will be referred to as 40 DT. Some data are also presented for another cationic polyelectrolyte, poly[2-(propionyloxy)ethyl]trimethylammonium chloride (PCMA). This polymer also carries one charge per segment but it has no grafted hydrophobic side chains. We note, however, that each cationic group is located at the end of a short side chain with partly hydrophobic character (Fig. 1). The molecular weight of the PCMA used is 1.6 × 10⁶ g/mol (DP ≈ 8000); therefore it differs significantly from the hydrophobically modified polyelectrolyte. The surfactant, sodium dodecyl sulphate (SDS), especially pure grade for biochemical work (above 99% pure) obtained from BDH was used as received. The water was first pretreated with a MilliRO 10 Plus system and was further purified with a Milli-Q Plus 185 system. KBr of pro analysis grade from Merck was roasted prior to use. Muscovite mica (Reliance, New York) was chosen as a substrate. It is a layered aluminosilicate mineral. Each layer is strongly negatively charged, about 2.1 × 10¹⁴ lattice charges/cm². The negative charge of the mica lattice stems from the fact that a quarter of the tetravalent Si atoms are substituted by trivalent Al atoms. In the crystal these charges are compensated mainly by K⁺ ions located between the aluminosilicate sheets. Mica acquires a net negative charge when immersed in water or electrolyte solution. This is due to desorption of the K⁺ ions located on the surface, which are only partly replaced by other positive ions present in solution.

![Fig. 1](image-url) The molecular structures of the monomers of the copolyelectrolyte 40 DT (see text) are shown together with that of poly[2-(propionyloxy)ethyl]trimethylammonium chloride (PCMA). In 40 DT, 40% of the segments have a grafted hydrophobic side chain.