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Association and structure formation in oppositely charged polyelectrolyte–surfactant mixtures

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ABSTRACT

Investigations dealing with association behaviour and structure formation in oppositely charged polyelectrolyte–surfactant mixtures in aqueous solutions are reviewed. Discussion is limited to a selection of vinyl based anionic polyelectrolytes that, when completely ionized, posses the same structural value of the linear charge density parameter. Particular emphasis is placed on the role of polymer chain properties in aggregates with surfactants. Chain characteristics are varied by changing the nature of the charged group, its ionization degree — when possible, the spatial distribution of these groups along the chain, *i.e.* the tacticity, and the hydrophobic character of other substituents attached to the chain. Quantitative information on the degree of binding in the form of binding isotherms is obtained using surfactant-sensitive membrane electrodes and microstructures of polyelectrolyte–surfactant complexes are determined by synchrotron small angle X-ray scattering. Considerable differences in the degree of binding (including the critical association concentration, CAC, values) and in structures are found. It is concluded that strong interactions in these systems arise from the electrostatic attraction, but this only forms the basis for initial extensive accumulation (anchoring) of surfactant ions in the vicinity of the polyion chain. When this is accomplished, additional specific interactions and effects may come into play. The most powerful of these interactions, the hydrophobic association between the chain and the micelle core, were found in polystyrenesulfonate, PSS, solutions. Other properties are less influential but still lead to CAC values that differ by more than one order of magnitude. These differences are explained by taking into account the chain conformation, flexibility, and hydrophobic character. Specific interactions between PSS and cetylpyridinium, CP, cations result in a soluble non-stoichiometric PSS–CP complex that could be characterized by measuring various solution properties as a function of polymer concentration and degree of complexation. The review is supplemented by including studies of complexation between the spherical fullerene hexamalonate anion and cationic surfactants, which demonstrate a high association tendency with characteristics similar to those found in binding of surfactants by linear polyelectrolytes.

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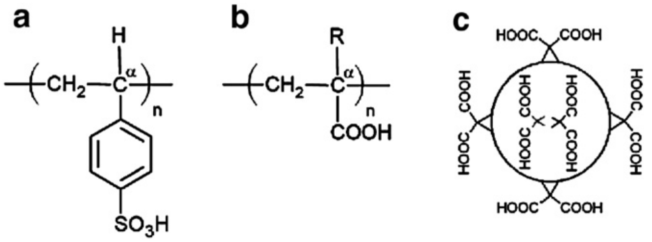
1. Introduction

Aqueous mixtures of oppositely charged polyelectrolytes and surfactants have been studied extensively for the last decades due to numerous applications of these systems in pharmaceutical formulations, personal care and food products, and in other industrial areas. Besides, motivation for these studies definitely comes from the fundamental interest in inter-molecular interactions and (self-) association phenomena. Initially, the priority was the determination of binding isotherms [1–4] in relation to structural features of individual components and other easily variable experimental parameters. Later, the nature of the aggregates, in particular their structural organization, was put forward [5–14].

Taking into account the wide scope of published reviews on polyelectrolyte–surfactant systems, this review will focus primarily on the association between vinyl-based anionic polyelectrolytes and cationic surfactants in aqueous solutions, which were and still are our main research interest. It is well established that interactions in these systems are strong and lead to the formation of a polyelectrolyte–surfactant complex, PSC, in which surfactant monomers are self-assembled (or co-assembled [15]) into aggregates of different geometries. Surfactant aggregates in PSCs may be further packed in a disordered fashion or they can be organized into structures that display long range liquid-crystalline order. The precise structure of the PSC will of course depend on the structure of the interacting molecules, on their concentration, and on the nature and concentration of other species (in particular simple salts) present in the solution.

The emphasis in our studies is on the effect of polyion properties on interactions with surfactants, the so-called "polymer-centred" approach [1]. The strength of the interaction and the structure of resulting complexes depend primarily on the charge density of the polyion, on its flexibility, on eventual presence of hydrophobic substituents, and on the nature and distribution of ionizable groups. We have used polyions with either sulfonate or carboxylate groups (Scheme 1). Poly(styrenesulfonic acid), HPSS (Scheme 1a), with a strong acidic sulfonate group, is a representative of the first group [13,16] and poly(acrylic acid), PAA, poly(methacrylic acid), PMA, and poly(ethacrylic acid), PEA, (Scheme 1b) with a weak acidic carboxyl group belong to the second group [13,17]. In addition to these typical linear polyelectrolytes, we have employed also the spherical fullerene hexamalonate anion, FHM$^-$, (shown in the H$^+$ form in Scheme 1c) containing 12 symmetrically positioned carboxylate groups on the fullerene (Bucky ball) skeleton [18]. FHM$^-$ is clearly not a polymeric ion in the conventional sense, but it interacts in a highly cooperative manner with cationic surfactants, reminiscent to the case of linear polyelectrolytes. It turned out that mutual association of cationic surfactants with FHM$^-$ leads to the formation of densely packed aggregates with structures similar to those of PSCs. In these complexes FHM$^-$ spheres are aligned in a linear manner, in some way 'physically polymerized'.



Scheme 1. Monomer units of a) poly(styrenesulfonic acid), HPSS; b) poly(carboxylic acids): R = H (poly(acrylic acid), PAA), R = CH_3 (poly(methacrylic acid), PMA), R = C_2H_5 (poly(ethacrylic acid), PEA); and c) a schematic representation of the fullerene hexamalonic acid, FHMA, with 12 symmetrically positioned carboxyl groups (the fullerene skeleton is reduced to a circle).

Chain hydrophobicity and flexibility of vinyl based polycarboxylic acids, PCAs, are determined by the nature of substituent *R* bound next to the charged group and by the distribution of charged groups along the polyion. The above mentioned PAA, PMA, and PEA are very appropriate samples to study these effects systematically with very little change in chemical structure. By changing *R* from hydrogen, H (in PAA), to methyl, CH_3 (in PMA), and to ethyl, C_2H_5 (in PEA), the affinity of PCAs for water is varied. Thus, PAA is considered as a hydrophilic and flexible chain, whereas PMA and PEA exhibit a considerable hydrophobic character and are stiffer than PAA, owing to the presence of bulky CH_3 and C_2H_5 groups. The most obvious demonstration of polymer hydrophobicity is the conformational transition of the PMA and PEA chains in aqueous solutions upon ionization of carboxyl groups [19,20]. Besides, PMA was employed in various isomer forms differing in spatial distribution of carboxyl groups (the so-called tacticity): as an atactic polymer, aPMA, with a completely random distribution of carboxyl groups along the chain or as a syndiotactic or isotactic PMA, sPMA or iPMA, respectively, where carboxyl groups either regularly alternate (sPMA) or are positioned always on the same side (iPMA) of the plane of the polymer backbone. aPMA and sPMA on one hand and iPMA on the other, although they are chemically identical, exhibit distinctively different properties in aqueous solution, which can be related to their dissimilar hydrophobic character. iPMA and PEA (even its conventional or atactic form) are the most hydrophobic of the listed PCAs as demonstrated by the fact that they do not dissolve in water at low pH (*i.e.* at low degrees of ionization, α, of carboxyl groups) [20–23]. Concurrently, they are subjected to significant intermolecular association in aqueous solutions, possibly leading to gelation [21–23]. The strong polyelectrolyte HPSS also has some hydrophobic character due to the presence of benzene ring in the molecule. In this case, however, this group is simultaneously a part of the ionizable group, different from the spatially separated COO$^-$ and CH_3 (or C_2H_5) groups in PMA or PEA. Thus, solubility of HPSS in water is generally not limited.

A convenient measure of chain flexibility is the persistence length, l_p. Available literate data on these polyelectrolytes indicate that the polystyrenesulfonate chain is the stiffest with l_p around 1.2 nm [24a], whereas reported l_p values for, *e.g.*, atactic poly(acrylate) ($\alpha = 0.80$) or isotactic polymethacrylate ($\alpha = 0.15$) are lower than that: values in the range from around 0.5 nm to around 1.4 nm are found in 0.01 M NaCl [24b,c]. No data on l_p values are available for PEA. The stiffness of chains can be deduced also by employing molecular modelling, which was recently done for iPMA and for sPMA and separately for iPEA and for sPEA [17,23]. These results point that iPMA readily forms a helical

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