

高分子学会九州支部講演会

講演題目：**Polymer-surfactant interactions: bulk and interfaces**

Manipulation of DNA by surfactant.

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日 時：6月4日(月) 13:00-15:00

Ionic surfactants generally associate with all classes of polymers-ionic and nonionic, hydrophilic and hydrophobic- but the association behaviour and the effect on macroscopic properties, like rheology, are very different. On the basis of a review of polymer-surfactant association in bulk, the behaviour of these mixed systems on solid surfaces are discussed. In particular, we consider the adsorption of mixtures of polyelectrolytes and oppositely charged surfactants on polar and nonpolar surfaces. It is found that, depending on concentration, an ionic surfactant can either induce additional polyion adsorption or induce desorption. Kinetic control of adsorption and, in particular, desorption is typical. Important consequences of this include increased adsorption on rinsing and path dependent adsorbed layers.

The interaction between DNA and cationic surfactant is strong and leads in bulk solution to cooperative binding and to condensation of DNA from an extended to a compact conformation. It also leads to an associative phase separation with a concentrated DNA-surfactant phase in equilibrium with a dilute solution. Phase diagrams are found to depend strongly on surfactant and also on DNA conformation. The difference in phase diagrams between single- and double-stranded DNA show the role of hydrophobic interactions in surfactant binding. Particles formed from DNA-surfactant solutions have different sizes and shapes depending on the stoichiometry. The particles, as well as the macroscopic phases formed, have a regular internal structure as demonstrated by small angle X-ray diffraction and cryogenic transmission electron microscopy. There is typically a 5-10 nm periodicity and the

major structures formed are lamellar and reversed or normal hexagonal, structure formed mainly determined by the surfactant chemical structure. By controlled mixing of solutions of DNA and surfactant, globular transparent gel-like particles can be formed. By chemical cross-linking of DNA, macroscopic gels can be prepared. These gels are very useful in studying DNA-cosolute interactions from simple volumetric measurements. Thus, on addition of a simple electrolytes, polycations or cationic surfactants, the gels shrink; this effect is reversible as reswelling occurs as the DNA-cosolute association is eliminated. Regarding the covalent gels, denaturation of cross-linked DNA gels has been induced by changes in temperature. This process, studied by fluorescence using ethidium bromide, appears to be reversible when a heating/cooling cycle was performed. The swelling behaviour on addition of different cosolutes, such as metal ions, polyamines, charged proteins and surfactants was investigated for different DNA gel samples, which include long and short ds-DNA and long and short ss-DNA. The DNA molecular weight has only a slight effect on the deswelling curves, while conformation shows a more pronounced one. In general, single stranded DNA gels exhibits a larger collapse, in the presence of cations, than double stranded does. This has been attributed to differences in linear charge density, chain flexibility and hydrophobicity. In the presence of surfactants with different chain lengths, the swelling behaviour displayed by ss-DNA can be interpreted in terms of an interplay between hydrophobic and electrostatic interactions, the latter being related with polymer flexibility. Increasing hydrophobicity of the network leads to a decreased critical aggregation concentration (cac) for the surfactant/gel complex, due to the strengthened hydrophobic attractive force between the surfactant ions and the gel chain. The swelling of DNA gels appears to be reversible and this process does not depend on the DNA conformation. No macroscopic separation of collapsed and swollen region is observed at intermediate degrees of binding for ds-DNA gels, whereas a dense surfactant-rich surface phase (skin) is found to co-exist with a swollen core network for ss-DNA gels with $\phi > 0.5$. One explanation to this difference is the large deformation energy required for the compression of the very stiff ds-DNA chains.

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