INTERACTION OF A THERMOSENSITIVE POLYMER WITH SURFACTANT AT THE AIR-WATER INTERFACE

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The ability to trigger a strong response with a low-level stimulus is one of the remarkable features in soft condensed matter. In colloidal systems, these responses may be expansion or collapse of a macromolecule, dispersion or self-assembly of small molecules and specific binding or unbinding between two components. The common external parameters that can generate these transitions in behavior are temperature, solvent quality, pH, specific ions and the action of a force field. For instance, there is a family of polymers which is soluble in water at low temperatures but phase-separates out of water when heated above a critical temperature, T_c. A particularly interesting example of this family of thermosensitive polymers is poly(N-isopropylacrylamide) (PNIPAM), that has an expansion-collapse "switching" temperature at 33 °C, near the body temperature. This makes it biologically important, with potential applications[1] which include immunoassay technology and enzyme isolation where a two-phase partitioning technique is used to separate antigens and enzymes. Another important application which involves the coil-globule collapse is rate-controlled drug release. As a general viscosity modifier, its thermosensitivity provides an additional controlling parameter compared to other polymers.

Our interests lie in the applications of PNIPAM to systems that contain interfaces, such as emulsions, foams and dispersions, where the interfaces are frequently stabilized by adsorbed polymer layers. In such systems, surfactants are usually present. Therefore a relevant question is how the adsorbed polymer may be modified by other surface-active molecules. In this case, changes may occur directly at the interface where the polymer and surfactant may compete for adsorption sites or, they may mutually enhance their adsorption. Alternatively, changes may arise from interactions of the two species in the bulk phase, modifying the chemical potential of the adsorbing species and the equilibrium between the bulk and the surface. Indeed, it has been shown that PNIPAM interacts very strongly with an anionic surfactant, sodium dodecyl sulfate (SDS) in solution, resulting in a shift in the T_c to higher temperatures[2].

In this work, we investigate the effects of such interactions at the air-water interface. There are two main points of interest: firstly, how will PNIPAM adsorption be affected by the presence of SDS? Secondly, are their interactions and their resulting structural properties in solution reflected by those at the interface? To address these questions, we have used neutron reflectivity to determine the properties of the adsorbed polymer layers. Neutron reflectivity, coupled with isotopic substitution where the index of refraction of a component can be adjusted to match that of the solvent, is the only technique which allows the study of individual components in a mixed surface layer.

Figure 1 shows the sensitivity of neutron reflectivity to the presence of adsorbed PNIPAM at the air-water interface. The figure shows the normalized reflectivity, R/R_f, versus the momentum transfer, Q. R_f is the Fresnel reflectivity of the pure solvent. In this representation, any deviation from $R/R_f =1$ is due only to the adsorbed polymer layer: the larger the deviation, the higher the amount of polymer adsorbed. These reflectivity curves also show the sensitivity of PNIPAM adsorption to temperature - an increase in temperature increases adsorption, a result due to a decrease in solvent quality. The continuous lines are the best-fits to the data using the concentration profiles shown in the inset. The profile consists of a thin monomer-rich zone near the surface followed by a central diffuse zone. As temperature increases, the monomer-rich zone becomes thicker and the central zone increases in density. Only a small increase in the overall thickness of the adsorbed layer is obtained.

The effect of surfactant on the adsorption of PNIPAM was investigated using SDS whose refractive index is matched to that of the solvent, allowing only the signal from the polymer to be registered. In Figure 2, the adsorption density of PNIPAM, Γ_p, obtained by integration of the concentration profile, is shown as a function of SDS concentration, C_s. At low C_s, PNIPAM adsorption is unaffected; at high C_s, it decreases progressively until very little polymer is left at the surface. Interestingly, the surfactant concentration at which Γ_p starts to

decrease corresponds to the critical aggregation fluorescence technique (2), where the surfactant interacts with the polymer in the bulk phase. This loss of polymer from the surface is observed even at high temperatures where the steep rise in adsorption is attenuated and pushed to higher temperatures (Figure 3).
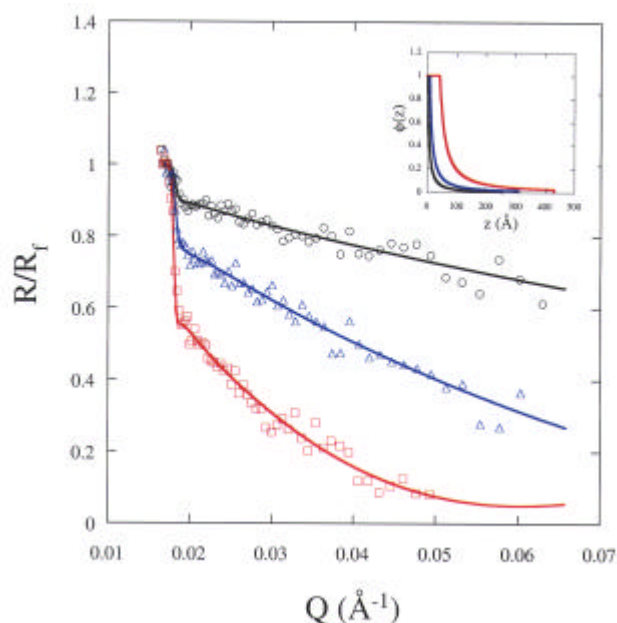

Figure 1. Normalized reflectivity of PNIPAM (M_w = 165 K) adsorbed at the air-water interface at T=20.2 °C (black circles), T=28.2 °C (blue triangles) and T=31.2 °C (red squares). The solid lines are best-fit curves using the concentration profiles shown in the inset.
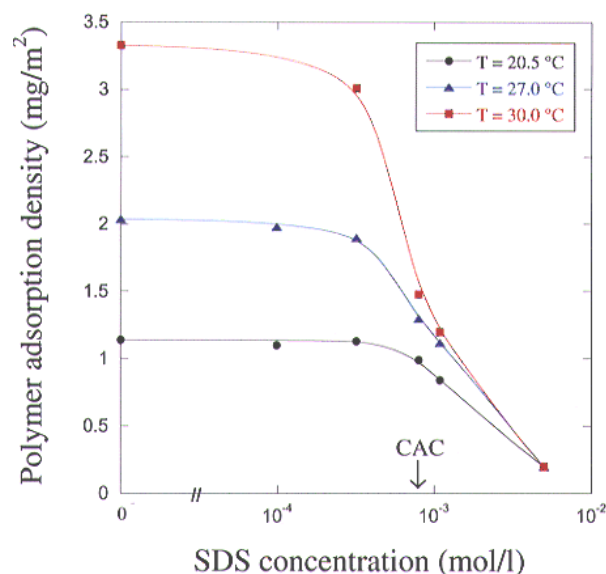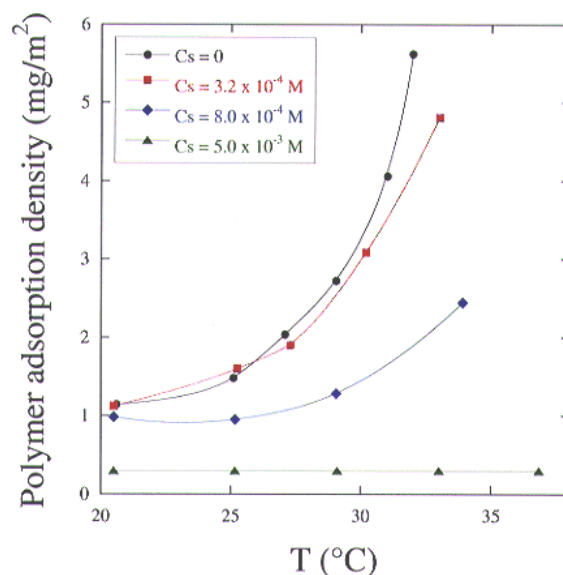

Figure 2. Effect of SDS on the adsorption density of PNIPAM.

Two possible reasons can account for the loss of polymer from the surface: it is displaced by an increasing surfactant pressure, or, it is depleted

concentration (CAC), as measured by

from the surface due to complexation with surfactants in the bulk solution. However, surface tension results show that in the range of C_s where the polymer is displaced, the surface pressure of the polymer layer is greater than that of the SDS. This fact strongly suggests that the loss of polymer from the surface is related to polymer-surfactant complexation in the bulk. Such complexes have been studied using small angle neutron scattering[3]. It is found that above the CAC, the mixed aggregate has a "necklace" structure consisting of several micellar aggregates adsorbed on a polymer chain (Figure 4). Above T_c, the phase-separated PNIPAM is resolubilized by SDS in two steps: at low C_s, the precipitated polymer is dispersed into colloidal particles, and at high C_s, these particles are solubilized

into charged "necklaces".

Figure 3. Effect of temperature on the adsorption density of PNIPAM in the presence of SDS.

At the surface, the loss of polymer above the CAC can therefore be attributed to the formation of charged polymer-surfactant "necklaces" in the bulk phase. In this case, what is the structure of the polymer that is left at the surface? Is the charged "necklace" structure observed in the bulk conserved at the surface? The concentration profiles in Figure 5 show that in the absence of surfactant, an increase in temperature produces a dense adsorbed layer due to reduced excluded-volume interactions between monomers. At the same temperature in the presence of SDS, a diffuse layer is obtained. This result suggests strongly the presence of micellar aggregates, the repulsions of which decrease the monomer

packing density in the adsorbed layer even at raised temperature (Figure 6).
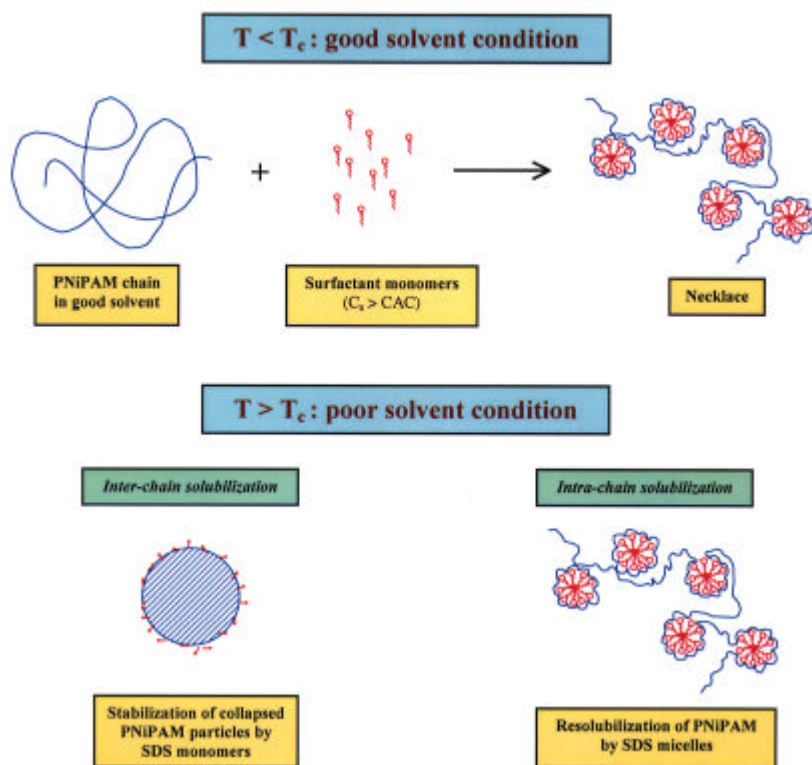

Figure 4. Interaction of PNIPAM with SDS in solution below and above the critical temperature T_c.
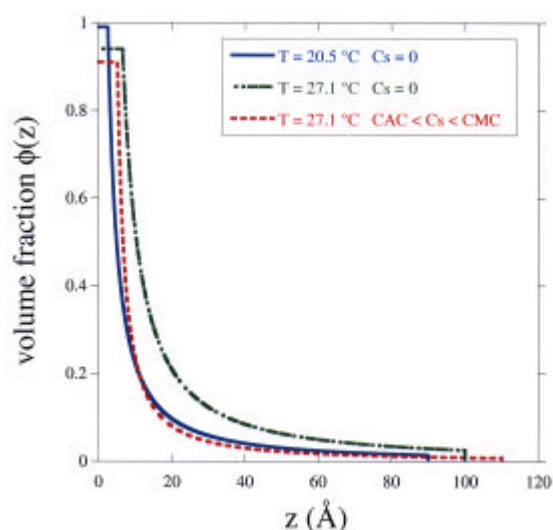

Figure 5. Concentration profiles of adsorbed PNIPAM: effects of temperature and surfactant (CMC = Critical Micelle Concentration).

In summary, PNIPAM adsorption at the air-water interface is very sensitive to small variations in temperature. In the presence of SDS, the polymer is progressively displaced from the surface due to formation of charged polymer-micelle "necklaces" in solution. Furthermore, the sensitivity of the polymer adsorption to temperature is attenuated and pushed to higher temperatures. This behavior parallels the solubilization of PNIPAM by SDS in the bulk phase and the resulting elevation in T_c. Therefore, PNIPAM-SDS interaction at the surface reflects that in the bulk solution. The concentration profiles of the adsorbed polymer show that diffuse or dense layers can be obtained, depending on the temperature and surfactant concentrations. Therefore, it is possible to modulate the T_c of PNIPAM by addition of SDS, and to control the molecular structures of the polymer both in solution and at the surface: swollen coil or collapsed globule in solution, and diffuse or dense adsorbed layers at the interface. This permits a great flexibility in tailoring the transition of the molecular structures of the thermosensitive polymer to specific uses both in solution and at interfaces.
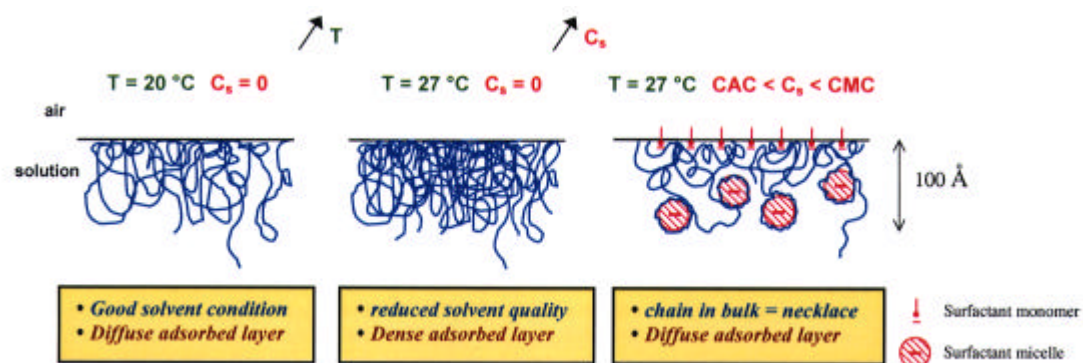
Figure 6. Structure of adsorbed layer of PNIPAM at the air-water interface: effects of temperature and surfactant.

References
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