Calorimetric Investigations of the Interaction Between Non-Ionic Polymers and Ionic Surfactants

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Techniques such as isothermal titration and differential scanning calorimetry, ITC and DSC, have recently shown an increasing use in the investigation of the association between surfactants and polymers. This communication will present a few examples on how these techniques provide important insights on the association of ionic surfactants with non-ionic polymers. Polymers studied comprise mostly hydrophilic polymers such as poly(alkylene oxides), and their copolymers, and poly(N-isopropylacrylamide), PNIPAM. Their interaction with different surfactants was investigated by determining a series of parameters such as: their critical aggregation concentration, which allows a direct comparison of the intensity of interaction; the shape of the ITC curves and the number of surfactant molecules bound per monomeric unit. In general, anionic surfactants interact more strongly with these polymers, while cationic alkyltrimethylammonium surfactants display a rather weak interaction. Interaction of these polymers with cationic surfactants may become more intense for more hydrophobic surfactants (longer alkyl chains), or by decreasing the volume of their headgroups, for instance, by using dodecylammonium chloride.

Since all of these polymers display an LCST behavior (reduced aqueous solubility with increase in temperature), a temperature raise leads to an increased interaction, as a result a less intense polymer hydration and consequent reduced competition between surfactant and water for the polymer interaction. These effects, however, are only significant rather close to the polymer LCST. DSC curves for the phase separation in these polymers solutions confirm this hypothesis. Although not changing significantly the cac values, temperature increase may lead to changes in the process of association, as observed for the interaction of SDS with PEO. Addition of surfactants to polymer solutions above the LCST leads to polymer redissolution, which is associated with an exothermic effect due to its re-hydration. The same process can be assessed by DSC measurements and this redissolution process follows a trend similar to that displayed by cac values.