In this work, three anionic hydrophobically modified polyelectrolytes (HMPEs) poly(sodium *N*-acrylamidomethylpropanesulfonate-*co*-*N*-dodecylacrylamide), poly(sodium N-acrylamido-glycinate-co-N-dodecylacrylamide), and poly(sodium Nacrylamido-L-valinate-co-N-dodecylacrylamide) and one cationic HMPE, poly(3acrylamidopropyltrimethylammonium chloride-co-dodecylacrylate) were synthesized and characterized. The HMPEs were found to be surface active. The viscosity of aqueous solution was observed to decrease with the increase of polymer concentration. Fluorescence probe, dynamic light scattering, and transmission electron microscopic studies suggested formation of nanometer size aggregates (micelles) by these HMPEs in water at a very low polymer concentration. Solution behavior of their aqueous mixtures with eight ionic surfactants of similar or opposite charge was investigated. The effect of changing the ionic headgroup of the HMPE and surfactant and thus to reveal the complex patterns of interaction displayed by these polymer-surfactant (P-S) systems has been studied. The effects of length and structure of the surfactant hydrophobic tail on the P-S interactions have also been investigated.

In the low concentration regime of the surfactant, both anionic and cationic HMPEs were found to form nanosize complexes (i.e., surfactant-bound polymer micelles) through hydrophobic association. The presence of larger concentration of anionic surfactant (sodium dodecylsulfate or sodium laurylsarcosinate), however, disrupts these complexes, producing polymer-bound surfactant micelles (or vesicles). With oppositely charged surfactants (DTAB and CTAB), first, an insoluble complex was formed which subsequently get dissolved in the presence of excess surfactant. In contrast, polyethyleneglycol monomethylether (mPEG) derived cationic as well as anionic surfactants upon interaction with the polymeric micelles produced completely watersoluble polymer-decorated vesicles at all concentrations. The micro-environment of the P-S complexes was observed to be more hydrophobic than polymeric micelles. The stability of the P-S complexes against increasing salt concentration and temperature was investigated and were found to be stable under physiological condition. The polymer-surfactant complexes were found to have good encapsulation efficiency for hydrophobic drugs, such as griseofulvin, camptothecin, naringenin, and tetracycline.

Keywords: Polyelectrolytes, surfactants, micelles, vesicles, interactions