Molecular-Level Association Behavior of Cationic Linear and Dicephalic Surfactants with Polyelectrolytes at the Air/Solution Interface

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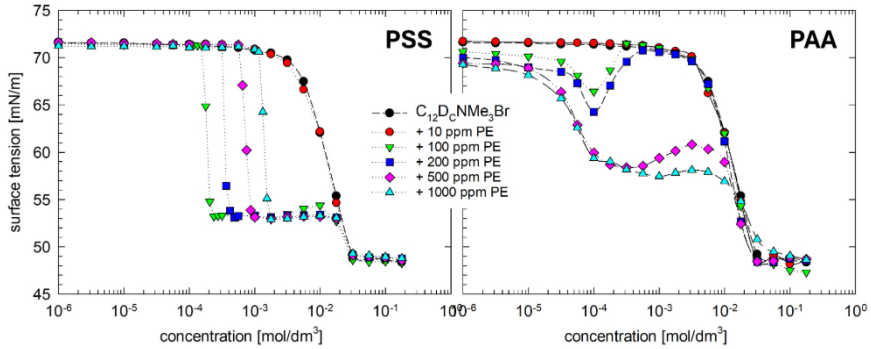
We examined the interfacial properties of polyelectrolyte-surfactant complexes (PESCs) with linear and dicephalic cationic surfactants and anionic polymers PAA (Mw=100,000) and PSS (Mw=70,000). We compared complexes formed with 2-alkyl-N,N,N,N',N',N'-hexamethyl-propan-1,3-ammonium dibromides of varying alkyl chain lengths (Cn-DcNMe3Br; n=10, 12, 14). Additionally, the interfacial behavior of PECSs made with dicephalic C12-DcNMe3Br was compared with that of the classical linear surfactant, DTAB. According to [1], two types of surface tension dependence on surfactant concentration for PESCs can be observed. Type I shows a decrease in surface tension until the critical aggregation concentration (CAC), then a plateau until the critical micellization concentration (CMC). Type II shows an increase in surface tension, usually below CMC, reaching the surfactant solution's surface tension.
For both linear and dicephalic surfactants, similar behavior can is observed. For PECS with PSS, type I behavior, characterized by a very abrupt decrease in surface tension at CAC, is observed at polyelectrolyte concentrations above 50 ppm. Despite the lower surface activity of the dicephalic surfactant, CAC values are lower than those for DTAB, which may reflect stronger electrostatic binding. For PECS with PAA, type I dependence on surfactant concentration was observed at polyelectrolyte concentrations above 500 ppm. At lower concentrations, the type II shape of the surface tension dependence was observed. However, the onset of the surface tension increase was observed for much lower dicephalic surfactant concentrations than for linear surfactant. That seems counterintuitive, as interactions between double-charged surfactant and polyanion are stronger. On the other hand, examining the pH dependence of the surface tension as a function of surfactant concentration, we observed a transition from type II to type I behavior as we increased pH from 3 to 11, i.e., from weakly charged to fully charged PAA.
We used molecular dynamics simulations for various surfactant-to-polymer ratios to correlate the interfacial behavior of PECS with the observed degree of surfactant binding and their morphology.

Keywords:
polyelectrolyte complexes, multicharged cationic surfactants, adsorption isotherm, MD simulations



The dependence of the surface tension on the C12-DcNMe3Br concentration upon the addition of PSS and PAA and formation of PECs.

References:

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