Hydration of Alkylammonium Salt Micelles – Influence of Bromide and Chloride Counterions

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The micellization process of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) was studied. Nuclear magnetic resonance method was used. The ^{1}H NMR and ^{13}C NMR spectra were taken at higher and lower concentrations than the critical micelle concentrations (CMC) of the compounds studied. Chemical shifts were analysed. The studies performed were prompted by earlier calorimetric measurements which showed that there were significant qualitative and quantitative differences in the micellization process of the compounds studied. Namely, DTAB micelle dissociation was found to be an endothermic process while that of DTAC was exothermic. The differences found must be the result of differentiated influence of bromide and chloride counterions on the micellization process, including the phenomenon of micelle hydration. The objective of the work was to check whether cationic surfactant counterions can influence the micelle hydration process. Indeed, DTAB and DTAC, as monomers, exhibit similar hydrophobic hydration, but DTAB micelles are more hydrated than DTAC ones.

It seems that the differences found in micellization of both salts studied may be attributed to different physicochemical properties of bromide and chloride ions, such as their mobilities and radii of their hydrated forms. Moreover, the effect of anions on the water structure must be taken into account. It is important whether the anions can be classified as water ordering kosmotropes, that hold the first hydration shell tightly, or water disordering chaotropes, that hold water molecules in that shell loosely.