Abstract

Micellization process of alkali carboxylates and quaternary ammonium chlorides, as one of the most common classical ionic surfactants, was studied in water with isothermal titration calorimetry (ITC). Density, electrical conductivity and zeta potential measurements of aqueous solutions were also performed. Hydration of the free surfactant monomers and micelles for quaternary ammonium surfactants in water solutions was studied using dielectric relaxation spectroscopy (DRS).

Models used to interpret the experimental ITC data were improved by eliminating the usually used assumptions which were either wrong or made application of the model difficult in a wide temperature range. However, even the improved models assume micellization can be presented as equilibrium between monomers and micelles of one size *i.e.* as one-step models with a constant aggregation number which turned out to be insufficient for surfactants with low aggregation numbers when applied in a wide temperature range. Therefore, a two-step micellization model was derived, where each step has its own equilibrium constant, aggregation number and thermodynamic parameters.

For the studied classical ionic surfactants it was confirmed that the process of micellization is entropy driven, thus the hydrophobic effect is the driving force behind the formation of micelles in aqueous solutions. Furthermore, the average aggregation number turned out to be significantly temperature and concentration depended for surfactants with less than 12 carbon atoms in the alkyl chain. Nevertheless, for catanionic surfactants with comparable lengths of the alkyl chains to classical surfactants, the aggregation number was higher and could be interpreted with one equilibrium. However, the two-step model, in which for one of the steps formation of neutral micelles was assumed and for the other step formation of charged micelles, yielded better fits of the experimental data. In the first step neutral smaller micelles are formed with the alkyl chains still partly hydrated while in the second step bigger charged micelles are formed with fully dehydrated alkyl chains. The assumption of almost neutral micelles was confirmed by zeta potential values and the concentration dependence of the electrical conductivity.