Calcium-tolerant anionic surfactants
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Summary

One of the problems of applying anionic surfactants in, for example, laundry detergents is the precipitation of calcium salts. Much effort has been directed towards avoiding precipitation. There are at least three ways for tackling the problem. The first involves the use of a large quantity of surfactant to solubilize the calcium salt of the surfactant. A second approach uses additives (builders) in order to enhance tolerance towards calcium ions. Phosphates, zeolites and silicates possess a larger affinity for calcium ions and prevent, by binding calcium ions, the decrease in detergency. The third option is the development of anionic surfactants which do not precipitate in the presence of calcium ions. This thesis deals mainly with the third option.

Chapter 1 contains a general introduction. The relation is described between the geometrical structure of surfactants and the morphology of the aggregate. The relation between the physico-chemical properties of the aqueous solutions of anionic surfactants and their tolerance towards calcium is discussed. The current solutions for the problem of calcium intolerance of surfactants in, for example, laundry detergents are briefly described. A survey of this thesis is given at the end of chapter 1.

Chapter 2 reports a study of the role of the headgroup and counterions of surfactants as well as the role of additives to surfactant solutions on the precipitation in the presence of calcium ions. The addition of a polymer (polyethylene oxide) to an aqueous solution of an anionic surfactant enhances the tolerance towards calcium. Both the effects of counterions (Na\(^+\), K\(^+\), Cs\(^+\) and Me\(_4\)N\(^+\)) on the precipitation of carboxylates and the effect of a water-soluble polymer on the precipitation of an alkylsulfate are discussed. The effect of counterions is still not well understood. The effect, however, is small and presumably determined by the efficiency of the exchange of the counterion for the calcium ion. The effect of the headgroup is a major factor for calcium tolerance of surfactants. The precipitation is discussed of alkylcarboxylates, sulfonates, sulfates and phosphates in the presence of calcium ions. The surfactants possessing a sulfonate or sulfate headgroup exhibit the most calcium-tolerant behavior; they do not precipitate below a critical Ca\(^{2+}\) concentration. Anionic surfactants having a carboxylate, malonate or phosphate headgroup precipitate almost immediately upon
addition of only a small amount of calcium ions. However, the precipitation of the alkylphosphates depends on the degree of ionization of the headgroup. Mono-protonated alkylphosphate is more calcium-tolerant than disodium alkylphosphate.

In chapter 3 the effect of introducing a second polar group into surfactant molecules is described. The synthesis and the physico-chemical properties, including the precipitation of a series of disodium 2-n-alkyl-1,3-propanediyl bisulfates in the presence of calcium ions, are reported. Titration conductometry is discussed as a method to determine the critical micelle concentration and the counterion binding. The Krafft temperatures and the aggregation numbers of the bisulfate surfactants are reported. The main result of this chapter is, that, in comparison with standard surfactants such as sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (LAS), the disodium 2-n-alkyl-1,3-propanediyl bisulfates exhibit highly calcium-tolerant behavior.

In chapter 4 this system is described in more detail. Emphasis is placed on the structure of the surfactant molecule near the headgroup and of its hydrophobic moiety. The synthesis of two classes of surfactants, namely the branched disodium 2,2-dialkyl-1,3-propanediyl bisulfates and the alkali metal 2-(hydroxymethyl)-1-alkylsulfates is described along with their physicochemical properties. The crystal structures are compared of the potassium and the calcium salts of the monosulfate surfactants. The relation is discussed of the crystal structures and the calcium-tolerance of anionic surfactants. The lyotropic and thermotropic liquid crystalline behavior are reported for the potassium 2-(hydroxymethyl)-1-alkylsulfates.

Chapter 5 deals with the thermodynamics of micellization of the disodium bisulfate surfactants (linear and branched). The thermodynamic nonideality of solutions and problems in processing the data are discussed. The thermodynamics of micellization of 2-alkyl-1,3-propanediyl bisulfate (chapter 3) and that of disodium 2,2-dialkyl-1,3-propanediyl bisulfate with a total chain length of 16 carbon atoms (chapter 4) are described. It is concluded that the effect of branching of the alkyl chain on the thermodynamics is modest.

In chapter 6, the first reported example of complex formation of an alkylglycoside with a calcium ion is described. Titration microcalorimetry is
used to show that calcium ions form a weak complex with 1-O-n-octyl-β-D-
mannofuranoside.

The results of detergency tests are discussed in chapter 7. In the
standard tests, the detergency of disodium 2-n-hexadecyl-1,3-propanediyl
bissulfate is compared to that of standard surfactants such as SDS, LAS and
an alkylethersulfate, a commercial calcium-tolerant surfactant. The
performance of the bissulfate surfactant is similar to that of the commercial
calcium-tolerant surfactant, with and without builder, indicating that detergent
formulation without builders is feasible. This is important from a commercial
and an environmental point of view. Finally, a qualitative model for the design
of calcium-tolerant anionic surfactants is presented.