Precipitation and association in a mixture of dodecylammonium chloride and sodium dodecyl sulfate in aqueous medium

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Abstract: The precipitation boundary in aqueous mixtures of dodecylammonium chloride (DDACl) and sodium dodecyl sulfate (NaDS) was determined in the absence and in the presence of 1 mol dm\(^{-3}\) NaCl. The structure and the composition of the solid phase was characterized by x-ray and chemical analysis, respectively. Activities of Cl\(^-\) and Na\(^+\) ions in the aqueous phase were measured by ion-selective electrodes. As determined by calorimetry, precipitation is an exothermic process.

The DDA·DS precipitate was formed in the equimolar region of the precipitation components. Its crystallographic structure is described. In an excess of sodium dodecyl sulfate, the precipitate incorporated substantial amounts of NaDS, as detected by analyses of both solid and liquid phases. X-ray analysis of the dry sample showed peaks of crystalline NaDS. According to the polarization microscopy of wet samples, one may conclude that liquid crystals, containing an excess of NaDS, are incorporated in the solid DDA·DS phase. The same was found in the case of an excess of DDACl; mixed liquid crystals with an excess of DDACl were incorporated in the solid DDA·DS.

Interpretation of the solubility boundary points to the presence of DDA\(^+\)·DS\(^-\) ion pairs. Formation of these species at low ionic strengths is characterized by the equilibrium constant \(K_\ell \approx 10^6\). However, in the 1 mol dm\(^{-3}\) NaCl, the association of DDA\(^+\) and DS\(^-\) ions into pairs is inhibited \((K_\ell \approx 0)\). This finding can be explained in terms of ionic clouds around the charged surfactant heads: if these heads are not in close contact, but separated due to structural effects of the chains, the dense distribution of counterions around them at high ionic strengths may compensate for electrostatic attraction and, thus, inhibit ion-pairing.

Key words: Surfactant precipitation; surfactant association; dodecylammonium chloride; sodium dodecyl sulfate

Introduction

Characteristics of mixed anionic/cationic aqueous systems are of interest from both practical and theoretical points of view. Due to strong interactions between oppositely charged heads, these systems show a strong synergistic effect with respect to the characteristics of individual components [1-9]. Accordingly, micellization is promoted so that mixed aggregates are formed with compositions depending on the anionic/cationic surfactant ratio. These systems also show a high tendency towards precipitation [10-12]. Solubility of mixed anionic/nonionic [13] and cationic/anionic surfactant [1] systems was successfully interpreted on the basis of the ionic solubility product (equilibrium constant of dissolution) and by the regular solution theory describing the mixed micelle formation. Counterion exchange at the micellar interface may also play a significant role in precipitation phenomena [14].

Experiments [1] with dodecylpyridinium chloride (DDPCI) and sodium dodecyl sulfate (NaDS) showed a pronounced increase of solubility due to the formation of DDP/DS mixed micelles characterized by the interaction energy parameter.
$W = -8.6RT$. As expected, this value is higher than the one obtained for the interaction of non-ionic/anionic chains; $W = -6RT$ [13]. It was established [1, 3, 4, 6–9] that, at high surfactant contents, the precipitation of cationic/anionic systems occurred only near the equimolar ratio of the components.

In order to test the validity of the general approach (ionic solubility product and regular solution theory) to the solubility phenomena in mixed surfactant systems, the precipitation–solubility behavior of the dodecylammonium chloride/sodium dodecyl sulfate aqueous system was investigated. This system is similar to those previously described [1] but is characterized by different values of the equilibrium parameters. Another difference is the pairing of oppositely charged surfactant ions that takes place at low ionic strengths but not at high concentration of NaCl due to compensation of the attractive electrostatic forces. In addition, the non-stoichiometric composition of the solid phase, precipitated in an excess of either DDAC1 or NaDS, is considered.

Experimental

Dodecylammonium chloride (DDAC1) was prepared according to [15], while sodium dodecyl sulfate (especially pure) was obtained from BDH Chemical Ltd. The surfactants were purified through several recrystallizations, and their purity was tested by surface tension measurements. Their c.m.c. values were determined using conductivity and surface tension methods. The results agreed with the literature data [16]: c.m.c. (DDAC1) = $1.47 \times 10^{-2}$ mol dm$^{-3}$; c.m.c. (NaDS) = $8.1 \times 10^{-3}$ mol dm$^{-3}$.

The precipitation–solubility boundary (Fig. 1) was taken as the maximum concentration of reactants (DDAC1, NaDS) that did not result in the solid phase formation, as detected visually [17].

The activities of Na$^+$ and Cl$^-$ ions were determined with the corresponding ion-selective electrodes [6]. They were calibrated with standard NaCl solutions. The decrease in the ionic bulk concentrations, i.e., their fractions in the solid phase, were calculated using the Nernst equation. No acid or base was added to adjust the pH so that it was always between 6.5 and 7 and hydrolysis could be neglected [18].

An elemental analysis of the precipitate was made after filtering the crystals, washing them with cold water and drying under vacuum.

The crystal structure was examined by means of x-ray analysis of dry powder. The x-ray diffractometer (Phillips) with a proportional counter using CuK$\alpha$ radiation (graphite monochromator) was used. An x-ray pattern of the sample, calibrated with graphite as internal standard, was recorded and used for the evaluation of interplanar distances $d_{hkl}$.

The heat of precipitation was determined with an isoperibolic reaction calorimeter [19] as described previously [20]. All experiments were carried out at 25.0°C.

Results

Figure 1 shows precipitation–solubility boundaries for the DDAC1/NaDS system in the presence (1 mol dm$^{-3}$) and in the absence of NaCl. For comparison, total concentrations of the precipitation components corresponding to structural and elemental analyses, and to calorimetry experiments, are also given. As described later, the lines were calculated by assuming both the absence and the presence of an association of DDA$^+$ and DS$^-$ ionic chains. In a solution of 1 mol dm$^{-3}$ NaCl, the solubility of surfactant is significantly lower than that at low ionic strengths (absence of NaCl). The plot of log[DDAC1] vs. log[NaDS] is approximately linear with a slope of $-1$. Contrary to the expectation, at low ionic strengths the solubility...