Salt-tolerance of ethoxy or propoxylated anionic surfactants: Rationalization of the enhancing effect of non-ionic groups

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Anionic and non-ionic surfactants are widely used in end-use products, but their functional properties are generally weakened and eventually lost in hard water or high salinity media. Actually, most of the aqueous solutions of anionic surfactants are not salt-tolerant and precipitate in the presence of high concentration monoor di- valent cations. However, many applications areas such as detergency, personal care or petroleum extraction require surfactants that are salt-tolerant in a wide temperature range¹. A synergistic effect has been pointed out by mixing anionic surfactants with ethoxylated non-ionic surfactants, increasing the resistance to the salt addition. These results have guided the design of non-ionic/anionic hybrids surfactants in the hope of cumulating the strong hydrophilicity of anionic polar head and the salt resistance of ethylene oxide groups. The salt resistance to NaCl and CaCl₂ of several surfactants is evaluated at 5% wt. as shown in figure $1.^2$



Figure 1. Influence of NaCl (●) and CaCl₂ (●) on the cloud point of ethoxylated and propoxylated sulfates at 5 wt.%. a) C₁₂-E₇-SO₄Na, (b) C₁₂-PO₇-SO₄Na. Blue area indicates the zone in which the surfactant is completely soluble into the aqueous solution of CaCl₂.

Comparing three C_{12} -sulfates group *i.e* SDS, C_{12} -EO₇-SO₄Na and C_{12} -PO₇-SO₄Na we observed that the salt tolerance is higher with the hydrophilic ethoxy groups than with the propoxy ones, however in both cases the Krafft temperature is vanished. This result is not intuitive since it is known that propoxy groups are slightly hydrophobic. However, the propoxy groups increases the entropy in the micelles and do not promote the precipitation phenomena. In the case of ethoxylated sulfates, the more the EO groups content in the hybrid surfactant, the higher the amount of salt needed to make the phase separation appearing, whereas the reverse trend is observed when increasing the PO groups. Alkyl ethoxy carboxylates hybrid surfactants are more salt resistant than alkyl ethoxy sulfates.

- (1) K.L. Stellner, J.F. Scamehorn, Surfactant precipitation in aqueous solutions containing mixtures of anionic and nonionic surfactants, J. Am. Oil Chem. Soc. 63 (1986) 566–574.
- (2) E. Illous. Propriétés amphiphiles d'hydrotropes et de tensioactifs salino-résistants et biosourcés (Doctoral dissertation, Lille 1). (2017).