FROM MICELLIZATION TO MICROEMULSION FORMATION

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INTRODUCTION

Surfactant molecules aggregate in dilute aqueous solutions if their concentration is sufficiently large, generating a variety of microstructures which minimize the contact between their hydrophobic tails and water [1-5]. The hydrophobic interactions constitute the main driving force of this process. They arise mainly because the strong interactions between the water molecules are impeded by the presence of the hydrocarbon tails of the surfactant molecules. The resulting microstructures can be either in the form of compact aggregates (micelles) or as spherical bilayers (vesicles). The micellar core as well as the spherical shell of the vesicles constitute nonpolar micro-environments which can accommodate nonpolar or slightly polar solutes. The low solubility of the latter molecules in water is thus enhanced by the presence of these microstructures in solution. The dissolution of solubilizates in the micellar aggregates can occur in two different ways. The solubilize molecules can either be located among the hydrocarbon tails of the surfactant molecules or form, in addition, a core inside the aggregate. The first case is usually referred to as solubilization and the second as microemulsification. Whereas the nonionic surfactants as well as the double chain surfactants can lead by themselves to the formation of microemulsions, the ionic surfactants need the cooperation of a medium length alcohol - a cosurfactant. A simple molecular thermodynamic approach of micellization was suggested earlier[6]. That treatment was found to predict satisfactorily the observed critical micelle concentration and average aggregation numbers for a variety of nonionic, ionic and zwitterionic surfactants. The formation of vesicles and of mixtures of micelles and vesicles have also been predicted. The treatment was later extended to the case of solubilization[7,8]. The scope of the present paper is to demonstrate again that the above procedure has predictive power and can be applied to all the types of aggregation behavior from micelles to microemulsions. Various contributions to the free energy of formation of an aggregate are identified and simple expressions are proposed for their calculation. While the number of examples treated by us is large, the procedure will be illustrated here by considering the effect of alcohols on the surfactant aggregation as well as their effect on solubilization and microemulsion formation, particularly on the transition from solubilization to microemulsions. A schematic representation of various types of aggregates is given in Fig. 1.
THE SIZE SPECTRUM AND THE FREE ENERGY OF SURFACTANT AGGREGATION

To better emphasize the main physical features involved in the present calculations, let us first discuss the more "simple" case of dilute surfactant solutions. By considering the aggregates of different sizes as distinct species and neglecting the interactions between them (because the system is dilute), the following expression is obtained for the size spectrum of aggregates[4,5]:

$$ X_n = X_m^n \exp\left(-\frac{\mu_n^0 - \mu_l^0}{kT}\right), $$

(1)

where $X_m$ is the mole fraction of the micelles which contain $n$ surfactant molecules, $X_l$ is the molar fraction of the singly dispersed surfactant molecules, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $\mu_n^0$ and $\mu_l^0$ are the standard chemical potentials of an aggregate containing $n$