Statistical Thermodynamics of Amphiphile Self-Assembly: Structure and Phase Transitions in Micellar Solutions

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1.1 Introduction

The main purpose of this chapter is to present a comprehensive, statistical-thermodynamic framework for treating the sizes and shapes of micellar aggregates in aqueous surfactant solutions. In this first section, after a brief historical perspective on experimental studies and theoretical pictures of micellar structure, surface roughness and other fluctuation effects are discussed in the context of both phenomenological and computer simulation studies. In Sec. 1.2 we present the basic self-assembly theory for dilute systems; the aim is to proceed systematically from a formulation of overall partition functions for the aqueous surfactant solution to a phenomenological discussion of effective chemical potentials. By deriving this latter language, we make contact with the highly useful "law of mass action" approach which has been pursued by most workers in their analyses of micellization and size/shape effects in dilute solution. We also feature there the role of "dimensionality of growth", i.e., the basic differences between the concentration dependence of equilibrium sizes in the case of sphere ("zero-dimensional" = 0D)-, rod (1D)-, and disk (2D)-like aggregates. Following a brief discussion of the structures and relative stabilities of vesicles and mixed micelles, we close Sec. 1.2 with some remarks on the much-neglected

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and highly problematic question of "rotation/translation" contributions to micellar partition functions (and hence to the effective surfactant chemical potentials).

Section 1.3 treats the problem of separating the effects of amphiphilic "heads" and "tails" in statistical thermodynamic descriptions of micellar aggregates. The prevailing ideas concerning predictions of preferred shapes are discussed critically. We also outline there the nature of chain packing in micelles and the contribution of chain degrees of freedom to the free energies of surfactant molecules in aggregates of different curvature; in this context, a microscopic basis is provided for the bending elasticities of amphiphilic mono- and bi-layers. In Sec. 1.4 we introduce the reader to recently developed ideas concerning the way in which interactions between micelles can lead first to the enhancement of size in isotropic solutions and then to the onset of orientational and positional long-range order in nematic, hexagonal and lamellar states of concentrated surfactant-water systems.

The concept of a micelle as an aggregate of surfactant molecules arose in the early part of this century when McBain [1] in 1913 first sought to understand the anomalous concentration dependence of many physical properties of aqueous soap solutions. In the words of Debye [2]: "Soap solutions exhibit even lower osmotic activity than would be predicted if one assumed that soap existed in solution as simple undissociated molecules. They also conduct the electric current far better than would be expected from the observed osmotic effects." Figure 1.1 represents these effects and correlates their breaks in slope with sudden rise of turbidity and with leveling off in surface tension reduction, i.e., with onset of micelle formation in bulk solution. To continue in the words of Debye, writing in 1949: "Since 1913, investigators have shown considerable interest in the determination of the size and shape of the micelle." As an introduction to the subject of this chapter, in fact, it is useful to proceed further with a look at the work of Debye.

The experiments which Debye reported in his 1949 paper [2] involved light scattering studies of a series of $n$-alkyl trimethyl ammonium bromides $[C_nH_{2n+1}N(CH_3)_3Br^-]$. From the plots of turbidity ($\tau$) vs. surfactant concentration ($c$) it was concluded that, above a critical micelle concentration (CMC) aggregates appear as the dominant species: "The curves resemble typical $\tau$ vs. $c$ plots for polymer solutions." For these latter systems Debye had already shown that a plot of turbidity vs. concentration would yield the molecular weight $M$ as its slope at the origin ($c \to 0$). Hence the "Debye equation" for molecular weights of micellar aggregates [3]

$$\frac{K(c - CMC)}{\tau} = \frac{1}{M} + 2A_2(c - CMC) \quad (1.1)$$

where $K$ is the "optical" constant (determined by the incident wavelength