

STRUCTURE—PERFORMANCE RELATIONSHIPS IN SURFACTANTS

edited by

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Preface

Surfactant molecules can self-assemble in water, oil, oil–water, or solid–liquid mixtures to give a large variety of colloidal structures. Structure–performance relationships in surfactants are of great importance in nearly all fundamental studies and practical applications of surfactants. To understand the properties and performance of surfactants at various interfaces, such as air–liquid, liquid–liquid, and solid–liquid, considerable theoretical and experimental work has been carried out. Thirteen years ago, volume 253 in the American Chemical Society Symposium Series, *Structure–Performance Relationships in Surfactants* (M. Rosen, ed.), was the first to discuss this topic. Now, greatly expanded interest and additional important work in this field lead us to revisit this topic.

The volume has 13 chapters. R. Nagarajan deals with the theories of micellization of surfactants, surfactant–polymer mixtures, and surfactant molecular structure in Chapter 1. In Chapter 2, M. Aratono and N. Ikeda outline the adsorption characteristics of various surfactants at the air–liquid interface and discuss the relationship between surface properties and structures of surfactants. M. Ueno and H. Asano focus on the mixed properties of bile salts and some nonionic surfactants and give examples for applications of these systems in Chapter 3. The molecular design and organized assemblies of biosurfactants are discussed along with applications of multifunctional structure of biosurfactants in Chapter 4 by Y. Ishigami. Chapter 5, by Y. Koide, deals with the physicochemical properties of ring structured surfactants including those of crown ether type, polyamine type, cyclodextrin, and calix[n]arene. R. Zana discusses the physicochemical properties of dimeric surfactants, such as micelle formation, solubilization, micelle size and shape, rheology, and phase behavior in Chapter 6. In Chapter 7, by H. Hoffmann and W. Ulbricht, various types of viscoelas-

tic surfactant systems are discussed and compared. Their rheological properties are described, and some models are presented for the understanding of the different flow behaviors on the basis of the different microstructures. T. Kato presents the micelle structure of nonionic surfactants in dilute, semidilute, and concentrated solutions and discusses the thermodynamic models for micellar solutions and the phase transitions in liquid crystal phases in Chapter 8. In Chapter 9, by H. Kunieda, A. C. John, R. Pons, and C. Solans, the high internal phase ratio emulsions are described, and the mechanism of formation, rheology, phase behavior, stability, and structure of these systems are discussed.

In Chapter 10, L. K. Koopal outlines the modeling of micellization and that of adsorption and discusses the self-consistent field (SCF) lattice model developed for the association and adsorption of surfactants. Chapter 11, by K. Esumi, focuses on the dispersion of particles by surfactants as well as the properties of surfactant adsorbed layers. In Chapter 12, H. Otsuka and K. Esumi deal with the interaction between polymers and surfactants on solid particles in aqueous solution. The conformation of polymers adsorbed from particles is also discussed by electron spin resonance (ESR) measurements. K. Kon-No reviews the states of water droplets in various reversed micelles, synthesis methods, and factors affecting the size and shape of various particles in Chapter 13.

We would like to thank Dr. Martin J. Schick for his advice and help. We would also like to thank the authors who participated in this effort.

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1

Theory of Micelle Formation: Quantitative Approach to Predicting Micellar Properties from Surfactant Molecular Structure

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I. INTRODUCTION

The widespread applications of surfactants originate from the intrinsic duality in their molecular characteristics—namely, they are composed of a polar head group that likes water and a nonpolar tail group that dislikes water. Numerous variations are possible in the types of the head groups and tail groups of surfactants. For example, the head group can be anionic, cationic, zwitterionic, or non-ionic. It can be small and compact in size, or a polymeric chain. The tail group can be a hydrocarbon, a fluorocarbon, or a siloxane. It can contain straight chains, branched or ring structures, multiple chains, and so forth. The tail group can also be polymeric in character. Further, surfactant molecules with two head groups (bola surfactants) are also available. This variety in the molecular structure of surfactants allows for extensive variation in their solution and interfacial properties. One would naturally like to discover the link between the molecular structure of the surfactant and its physicochemical action so that surfactants can be synthesized or selected specifically for a given practical application.

Pioneering contributions to our understanding of the general principles of surfactant self-assembly in solutions have come from the work of Tanford [1–3], Shinoda [4], and Mukerjee [5–9]. Utilizing their results, we have focused our efforts in the last 20 years on developing quantitative molecular thermodynamic models to predict the aggregation behavior of surfactants in solutions starting from the surfactant molecular structure and the solution conditions. In our approach, the physicochemical factors controlling self-assembly are first identified by examining all the changes experienced by a singly dispersed surfactant molecule when it becomes part of an aggregate [10–13]. Relatively simple, explicit equations are then formulated to calculate the contribution to the free energy of aggregation associated with each of these factors. Since the chemical structure of the surfactant and the solution conditions are sufficient for estimating the molecular constants appearing in these equations, the free energy expressions can be used to make *a priori* predictions.

In this chapter, we describe in detail our quantitative approach to predicting the micellization properties of surfactants from their molecular structures. First, we summarize the geometrical relations for various shapes of aggregates including spherical, globular, and rodlike micelles and spherical bilayer vesicles, and we present the general thermodynamic equations that govern the aggregation properties of surfactants in solutions. We then provide explicit equations to calculate the free energy of formation of different types of aggregates, suggest how the molecular constants appearing in these equations can be estimated, and describe the computational approach suitable for making predictive calculations. Finally, we demonstrate the predictive power of the molecular theory developed in our studies via illustrative calculations performed on a number of

surfactant molecules having a variety of head and tail groups, numerous binary mixtures of surfactants, and surfactants in the presence of nonionic polymers.

II. MICELLIZATION OF SURFACTANTS

A. Geometrical Properties of Aggregates

1. Packing Constraint

The hydrophobic domain of a surfactant aggregate contains the surfactant tails. If the density in this domain is equal to that in similar hydrocarbon liquids, the surfactant tails must entirely fill the space in this domain. This implies that, irrespective of the shape of the aggregate, no point within the aggregate can be farther than the distance ℓ_s from the aggregate-water interface, where ℓ_s is the extended length of the surfactant tail. Therefore, at least one dimension of the surfactant aggregate should be smaller than or at most equal to $2\ell_s$ [1-3,14]. The volume of the hydrophobic domain is determined from the number of surfactant molecules g in the aggregate and the volume v_s of the surfactant tail.

2. Aggregate Shapes

Figure 1 illustrates the shapes of surfactant aggregates formed in dilute solutions. The small micelles are spherical in shape. When large rodlike micelles form, they are visualized as having a cylindrical middle portion and parts of spheres as endcaps. The cylindrical middle and the spherical endcaps are allowed to have different diameters. When surfactants cannot pack into spheres (this happens for aggregation numbers for which a spherical aggregate will have a radius larger than ℓ_s), and if at the same time the rodlike micelles are not yet favored by equilibrium considerations, then small nonspherical globular aggregates form. Israelachvili et al. [15] have suggested globular shapes generated via ellipses of revolution for the aggregates in the sphere-to-rod transition region, after examining the local molecular packing requirements for various nonspherical shapes. The average surface area per surfactant molecule of the ellipses of revolution suggested by Israelachvili et al. [15] is practically the same as that of prolate ellipsoids, for aggregation numbers up to three times larger than that of the largest spherical micelles. Therefore, the average geometrical properties of globular aggregates in the sphere-to-rod transition region can be computed as for prolate ellipsoids. Some surfactants pack into a spherical bilayer structure, called a vesicle, that encloses an aqueous cavity. In the outer and the inner layers of the vesicle, the surface area (in contact with water) per surfactant molecule and the number of surfactant molecules need not be equal to one another, and the thicknesses of the two layers can also be different.

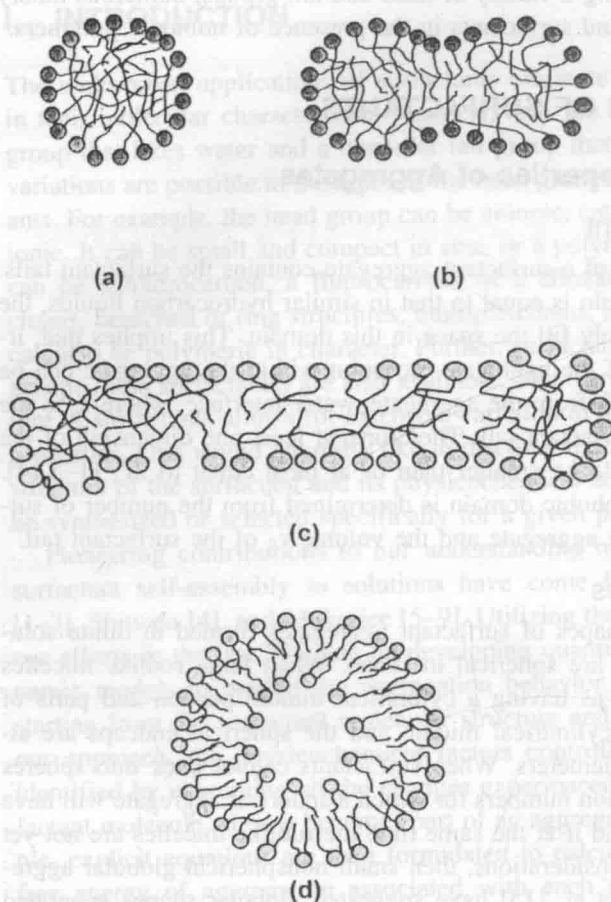


FIG. 1 Schematic representation of surfactant aggregates in dilute aqueous solutions. The structures formed include spherical micelles (a), globular micelles (b), spherocylindrical micelles (c), and spherical bilayer vesicles (d).

3. Geometrical Relations for Aggregates

For aggregates of various shapes containing g surfactant molecules, the volume of the hydrophobic domain of the aggregate, V_g , the surface area of contact between the aggregate and water, A_g , and the surface area at a distance δ from the aggregate-water interface, $A_{g\delta}$, are listed in Table 1. Also given in the table is a packing parameter P , defined in terms of the geometrical variables characterizing the aggregate. The area $A_{g\delta}$ is employed in the computation of the free energy of electrostatic interactions between surfactant head groups, whereas the packing parameter P is used in the computation of the free energy of tail deformation; both are discussed in Sec. II.D. From the geometrical relations pro-