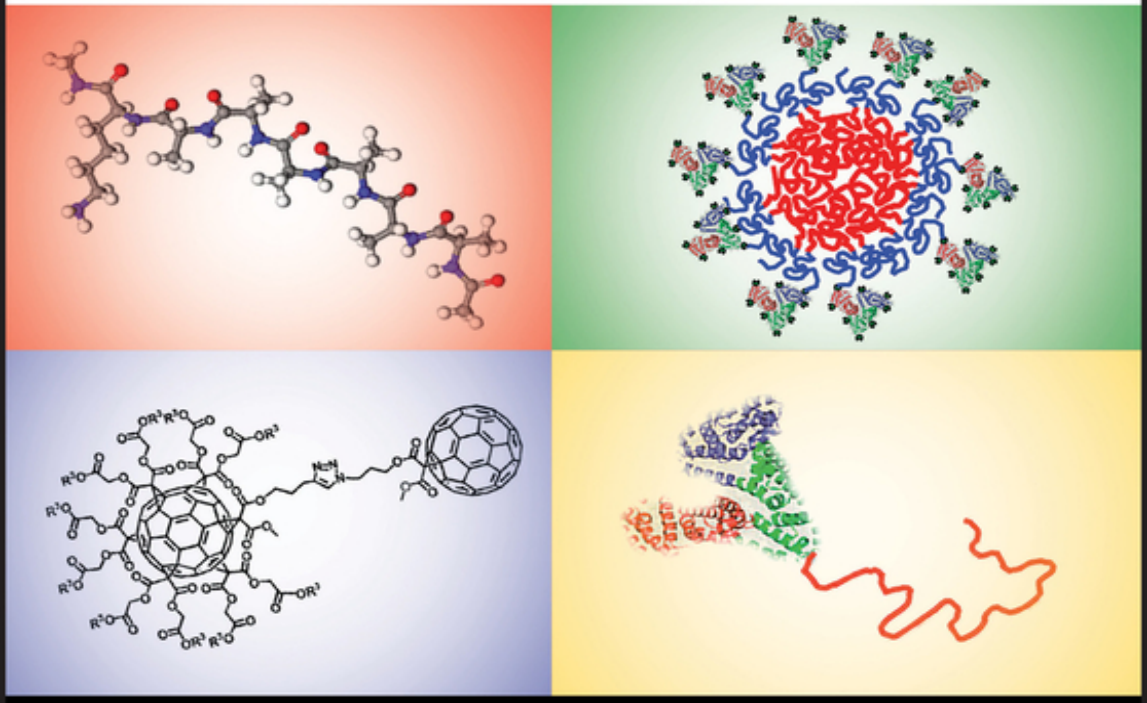
Wiley Series on Surface and Interfacial Chemistry

Ponisseril Somasundaran and Nissim Garti, Series Editors

SELF-ASSEMBLY

FROM SURFACTANTS TO NANOPARTICLES

Edited by Ramanathan Nagarajan



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Self-Assembly

From Surfactants to Nanoparticles

Edited by

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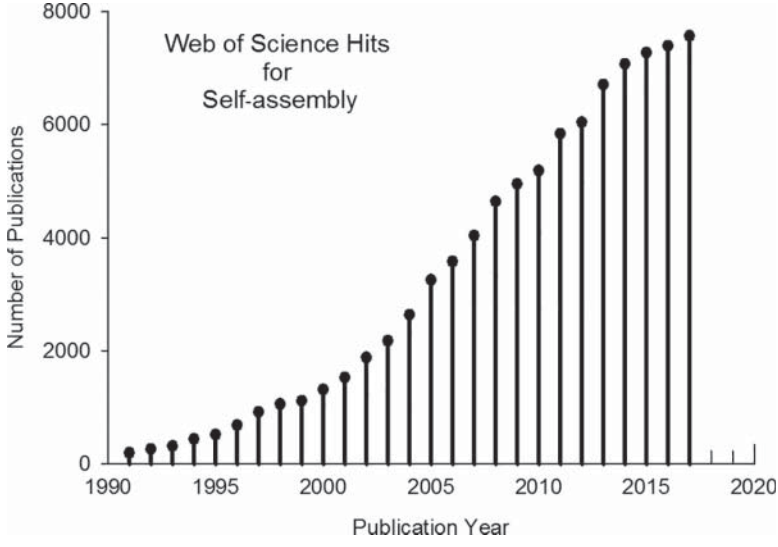
Preface

Self-assembly was first recognized by James McBain in classical colloid science almost 100 years ago, with the discovery of spontaneous formation of multimolecular aggregates of soap molecules. For almost 80 years after the initial discovery, self-assembly studies were dominated by classical soap and surfactant molecules, and for the latter part of this period, studies on high-molecular-weight block copolymer systems were also prevalent. However, the term "self-assembly" did not appear in the literature until 1966, as revealed by a Web of Science search. In the following decade, the term began to appear in publications, but less than 10 times each year, and only to describe the self-assembly of protein or viral subunits. To the best of my knowledge, the first use of the term to describe amphiphilic systems was in the classic paper of Israelachvili, Mitchell, and Ninham "Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers." Since then, there has been an explosion of studies in the literature, invoking the terminology of self-assembly.



Over the last 20 years, the study of self-assembly has emerged as a distinct field, encompassing much larger and more complex molecular and nanoparticle systems. The study of self-assembly has extended far beyond surfactants and block copolymers and has been applied to peptide amphiphiles, DNA amphiphiles, protein–polymer conjugates, and nanoparticles. Self-assembly of molecules to create nanoparticles, self-assembly of nanoparticles to create new materials or devices, self-assembly in biological cell and its components contributing to essential life functions, self-assembly of proteins leading to neurodegenerative diseases, self-assembly of molecules/particles for nanomedicine applications of drug delivery, imaging, molecular diagnostics and theranostics, and self-assembly as the processing method to design materials to specification such as smart responsive materials and self-healing materials, have all made self-assembly a topic of great importance and have assured its continuing growth.

This book provides an effective entry for new researchers into this exciting field while also assessing state-of-the-art understanding of these diverse self-assembling systems. The book introduces the fundamentals and applications of self-assembled systems to academic and industrial scientists and engineers. Within its 10 chapters, the fundamental physical chemical principles that govern the formation and properties of self-assembled systems are considered. Important experimental techniques that can be used to characterize the properties of self-assembled systems, particularly the nature of molecular organization and structure at the nano-, meso-, or micro-scales, are reviewed. The synthesis and functionalization of self-assembled nanoparticles and the further self-assembly of the nanoparticles into one-, two-, or three-dimensional materials are discussed. Numerous potential applications of self-assembled structures are discussed. The book provides the first exhaustive accounting of self-assembly derived from various kinds of biomolecules including peptides, DNA, and proteins. Unifying as well as contrasting features of self-assembly, as we move from surfactant molecules to nanoparticles, are highlighted.

The first chapter discusses the essential similarity in the self-assembly behavior of low molecular weight surfactants and high molecular weight block copolymers from the point of view of the head-tail construct in amphiphilic systems. The emphasis on the head and neglect of the tail in surfactant free energy models is contrasted against the emphasis on the tail and minimal attention to the head in block copolymer free energy models. This difference, when resolved, allows for an unified treatment of self-assembly. The head–tail dependent free energy models are then suggested as a way to describe the self-assembly phenomena for a variety of non-classical amphiphilic systems involving dendrimers, DNA, peptides, proteins, and nanoparticles as critical head or tail components.

Chapter 2 is devoted to self-assembled systems of strongly growing and branching wormlike micelles that form reversible spatial networks in solutions.

Network reversibility and controllable viscosity make such systems very useful in numerous applications such as for drag reduction, paints, self-healing, and coatings. Relation of the observed viscoelasticity of a micellar solution to its structure is explained within the framework of the kinetic theories of breaking and recombining chainlike aggregates. The growth of non-ionic and ionic micelles, electrostatic rigidity, effects of branching, and scaling of the viscosity with the concentration of surfactant are all discussed in this chapter.

Chapter 3 reviews ways in which the self-assembly of redox-active and light-responsive surfactants have been used to achieve spatial and temporal control over interfacial and bulk properties of aqueous systems, including the interactions of surfactants with biomolecules. The switching of stimuli-responsive functional groups on the surfactants is shown to permit tuning of the surface tensions of aqueous systems, to induce surface tension gradient-driven flows, to change the state of aggregation of the surfactants in bulk solution, to permit temporal control over the transport of DNA across cell membranes and to achieve spatial control of surfactant-based microfluidic systems.

Chapter 4 highlights the importance of self-assembly to life processes. The knowledge about self-assembly of amphiphiles in aqueous environments is translated to the understanding of how lipids are uniquely connected to the formation of the cell, with cellular identity, with cellular functions, and also with cell death. The chapter discusses the idea that the spontaneous self-assembly of membranes may also be fundamental in the emergence of the first living cells in the context of an early Earth devoid of life. It describes how single-hydrocarbon-chain amphiphiles have been used to construct protocellular compartments in origin of life studies.

Chapter 5 shows how we can dynamically manipulate self-assembly. It develops the concept of programming the formation of synthetic assemblies using biomolecules, particularly peptides and nucleic acids. Biomolecules are utilized as recognition elements enabling the building of analytical probes or functional systems capable of performing sense-and-response processes in living systems. The focus is on the use of peptides and nucleic acids as the programming element. Examples are presented to highlight the ability of the programming element to control properties such as micelle formation, morphology, binding, reactivity, and spatial organization.

Protein analogous micelles (PAMs) resulting from the self-assembly of peptides conjugated to lipid tails or peptide amphiphiles are discussed in Chapter 6. Using the machinery of self-assembly, PAMs can be designed to include mixtures of different peptide amphiphiles leading to multifunctional, multivalent assemblies that can be stimuli responsive. This chapter discusses physicochemical aspects related to the design of PAMs including thermodynamic driving forces, the role of peptide secondary structure, micelle shape, amphiphile geometry, mixed micelles, and stimuli responsiveness. Based on

these properties of PAMs, their applications for tissue engineering, diagnostics, and therapeutics are discussed, focusing on how the PAM structure dictates function.

Chapter 7 explores the approach to controlling the self-assembly of proteins into materials by incorporating them as one block in a block copolymer, creating the protein conjugate block copolymer. The folded conformation of the protein significantly impacts the nanostructure formation in the materials. This chapter focuses on the physics of self-assembly of the protein-conjugate block copolymers based on a categorization of the bioconjugates by the shape of the protein block: rod-like proteins, crystallizable proteins, cyclic proteins, coil-like proteins, and globular proteins. The thermodynamics of self-assembly for each shape is summarized, with an emphasis on general principles that guide the development of new materials.

Chapter 8 discusses the design and creation of novel materials with unique properties where DNA-nanoparticles self-assembly plays a critical role. The ability to independently alter individual components of the system, such as nanoparticle shape, size, and composition, as well as DNA length, sequence, and coating density results in a highly customizable system. The inherent self-assembly capability of the DNA-coated nanoparticles provides a unique platform for constructing complex crystalline structures. These nanoscale building blocks hold great potential for applications in medical diagnostics, plasmonics, catalysis, and photonics. This chapter emphasizes the recent progress in the field using multiscale modeling and simulation directed towards designing and predicting novel DNA-nanoparticle assemblies.

Chapter 9 addresses the intriguing phenomenon of using self-assembled lipid vesicles to controllably transport nanoparticles. It uses dissipative particle dynamics to model the interaction between fluid-driven lipid vesicles and Janus nanoparticles in order to establish design rules for the vesicle-mediated particle transport. The transport is enabled by adaptive behavior of the vesicle, shedding lipids to cover the Janus particle and undergoing a self-healing process after the particle deposition, so that the vesicle can be used in successive particle pick-up and delivery events.

Chapter 10 describes "giant surfactants," which are analogs of classical surfactants but with one or more molecular nanoparticles as headgroups. The combination of the molecular nanoparticle heads having diverse symmetries and surface functionalities with the tails possessing variable compositions and architectures is shown to generate a large family of giant surfactants. These novel giant amphiphiles self-assemble into a great variety of ordered supramolecular structures in solution. The universal principles that govern their self-assemblies are explored in this chapter in order to provide guidance to the rational design and manipulation of new functional materials for technologically relevant applications.

It is my hope that this book will most efficiently introduce the reader to the field of self-assembly, providing from basic to advanced information, on each of the multiple topics covered. There are no textbooks or courses (or even professional short courses) covering all of these topics in any one place. The contributors are pioneers in their respective topical areas of research. I hope the book stimulates both entrant and experienced researchers to become active participants in this field of research.

Ramanathan Nagarajan

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This book project was initiated in March 2014. The first chapter was delivered in December 2014, but it has taken this long to bring it to a conclusion. I first want to thank all the chaper authors for their contributions and infinite patience. The active interest from Mr. Jonathan Rose, Wiley senior editor, and Ms. Aruna Pragasam, content editor, was critical in the final stages of this book project to get it completed. My work on this book would not have been possible without the support from the Natick Soldier Research, Development and Engineering Center, my colleagues there, and its director, Mr. Douglas Tamilio. I very much appreciate their understanding that while Soldiers have many immediate capability needs that researchers should work on addressing, it is very important to also take a long-term view and explore new scientific ideas that can qualitatively transform the technological capabilities that can be made available to them. Finally, the support from my family always remains the foundation for my work.

1

Self-Assembly from Surfactants to Nanoparticles – Head vs. Tail

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1.1 Introduction

Surfactant molecules are amphiphilic, composed of a polar headgroup that likes water and a nonpolar tail that dislikes water, thus contributing to an intrinsic duality in their molecular characteristics. Despite their mutual antipathy, the headgroup and tail of the surfactant cannot leave one another because they are covalently connected. The dilemma of mutual antipathy and forced coexistence faced by these molecules is resolved in nature by the intriguing phenomenon of molecular self-assembly, wherein the surfactant molecules self-assemble into three-dimensional structures with distinct and separate regions composed of the nonpolar parts and the polar parts, having minimal contact with one another. Block copolymers are an important class of high molecular weight polymer molecules that share great molecular similarity with the surfactants. A diblock copolymer is made up of repeating units A and B, with the repeating units occurring as blocks, covalently connected to one another. If one block (B) is hydrophilic or solvophilic (head) while the other block (A) is hydrophobic or solvophobic (tail), the block copolymer becomes a high molecular weight analog of the low molecular weight surfactant. Surfactants and block copolymers display characteristic molecular self-assembly behavior in solutions, at interfaces as well as in bulk, generating nanoscale structures of different shapes. These nanoscale features determine many macroscopic properties of these amphiphile systems, relevant for their practical applications.

The ability to generate desired nanoscale morphologies by synthesizing novel amphiphiles so that the amphiphilic systems can be tailored for specific applications as well as the ability to manipulate the morphologies using chemical and physical stimuli remain active goals of research in this field. Critical to

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achieving these goals is an understanding of the link between the molecular structure of the amphiphiles and their self-assembly behavior. Studies on surfactants have a long history, starting with the pioneering recognition of the existence of aggregates of soap molecules by McBain [1], over 100 years ago. He coined the term micelles to describe these aggregates and visualized a lamellar morphology for these aggregates. The proposal of a spherical micelle structure was made by Hartley [2] who suggested that the "aggregates are essentially liquid and since they will tend to present the minimum surface to the water, they will presumably be roughly spherical and of the largest radius consistent with none of the heads being submerged in the paraffin interior." Theoretical developments relating to surfactants have a rich history of 70 years starting with a pioneering model proposed by Debye [3]. The historical developments in the evolution of theories applied to surfactants leading up to current state of the art have recently been summarized [4].

The first synthesis of block copolymers was reported by Dunn and Melville [5] who synthesized and characterized a diblock copolymer of poly(methyl methacrylate)-b-poly(styrene). The observation that solvents can cause segregation of polymer blocks was first made by Merrett [6] based on studies of graft copolymers with rubber as backbone and grafted blocks of poly(methyl methacrylate) interacting with solvent mixtures involving benzene and methanol, benzene being a good solvent for rubber and methanol a good solvent for poly(methyl methacrylate). Merrett also used the term micelle to describe the graft copolymer aggregates. The first report of block copolymer aggregates in solution was from Climie and White [7] who studied poly(methyl methacrylate)-b-poly (acrylonitrile) in a mixed solvent of dimethyl formamide, which is a good solvent for both blocks and benzene, which is a nonsolvent for the poly(acrylonitrile) block. The clear demonstration of block copolymer micelles formed in dilute solutions was reported by Krause [8]. In this study using poly(styrene)-b-poly(methyl methacrylate) block copolymer, micelles were obtained in acetone, a non-solvent for poly(styrene), and in triethylbenzene, a nonsolvent for poly(methyl methacrylate). Block copolymer aggregates thus have a rich history of nearly 60 years and these early developments along with a comprehensive discussion of the synthesis and solution properties of block copolymers have been reviewed some years ago by Riess [9].

In this chapter, we focus mainly on the theoretical ideas based on which quantitative models to describe the self-assembly of surfactants and block copolymers have been developed. Tanford [10] and Israelachvili et al. [11] pioneered two of the most important models that currently dominate our understanding of surfactant self-assembly. Tanford proposed the concept of opposing forces to formulate a quantitative expression for the standard free energy change when a singly dispersed surfactant molecule in solution becomes part of a multimolecular surfactant aggregate, also in the solution. In his model, the formation of the equilibrium aggregate resulted from balancing the interfacial free energy

at the micelle-water interface against the repulsions between the surfactant headgroups also located at the interface. Using this free energy expression, with the controlling role played by the headgroup, he was able to explain why surfactant aggregates form in aqueous solutions, why they grow, and why they do not keep growing but remain finite in size. Israelachvili, Mitchell, and Ninham proposed the concept of a molecular packing parameter P defined as $P = v_o/a_e\ell_o$, where v_o and ℓ_o are the volume and length of the surfactant tail and a_e is the equilibrium area per molecule of the surfactant aggregate at the hydrophobic core-water interface. They demonstrated how the size and the shape of the aggregate at equilibrium can be predicted from the magnitude of P in accordance with simple geometry driven molecular packing considerations. In the context of the Tanford model, P is mainly dependent on the headgroup interactions and therefore the aggregate size and shape predicted by the packing parameter are clearly dominated by only the headgroup interactions. Remarkably, in this model, the surfactant tail has no explicit role in influencing the aggregate shapes.

Theoretical studies of self-assembly of block copolymers evolved without any obvious contact with the surfactant self-assembly literature. Theoretical understanding of how pure block copolymers organize into microdomains was advanced through the work of Meier [12, 13] and Helfand [14, 15]. Theoretical treatments of block copolymer micelles in selective solvents or in homopolymers have been pioneered by de Gennes [16], Leibler et al. [17], Noolandi and Hong [18], and Whitmore and Noolandi [19]. de Gennes [16] analyzed the formation of a diblock copolymer micelle in selective solvents by minimizing the free energy per molecule of an isolated micelle with respect to the aggregation number or core radius. The micelle core was assumed fully segregated and devoid of any solvent. In this model framework, the free energy of formation of the core-corona interface and the elastic free energy of stretching of the core blocks compete to control the micellization behavior. Leibler et al. [17] treated the problem of micelle formation of a symmetric diblock copolymer in a homopolymer solvent. In their study, as in de Gennes' work, the interface was taken to be sharp. Noolandi and Hong [18] and Whitmore and Noolandi [19] formulated mean field models taking into account the possibility of a diffuse interface between the core and corona regions. In all treatments of block copolymer self-assembly, the elastic deformation of the core forming block (the tail) played the central role. Notably, in these models, the solvophilic block (the analog of surfactant headgroup) had no explicit role. In Section 1.2 we outline the models for surfactants and block copolymers and then show how the mutually exclusive emphasis on headgroup or tail has now given place to consideration of both head and tail, thereby improving their quantitative predictive abilities. In Section 1.3 we show that the headgroup vs. tail-based free energy concepts can rationalize self-assembly behavior

observed in many non-classical amphiphile systems involving dendrimers, DNA, peptides, proteins, and nanoparticles as head or tail components.

1.2 Classical Surfactants and Block Copolymers

1.2.1 Tanford Model for Surfactant Micelles

Surfactant molecules self-assemble into spherical, globular or cylindrical micelles, or spherical bilayers, also known as vesicles (Figure 1.1). In these aggregates, the hydrophobic domain is made up of the surfactant tails and the hydrophilic headgroups are crowded at the aggregate core-water interface.

If the density in the hydrophobic domain is considered equal to that in similar liquid hydrocarbons, the surfactant tails must entirely fill the space in these domains. As a result, irrespective of the shape of the aggregate, no point within the aggregate can be farther than ℓ_o from the aggregate-water interface, where ℓ_o is the extended length of the surfactant tail. Therefore, at least one dimension of the surfactant aggregates should be smaller than or at most equal to $2\ell_o$. This is purely a geometrical or packing constraint that the surfactant aggregate will have to satisfy [10, 11]. The geometrical relations governing these different aggregate shapes are summarized in Table 1.1.

The size and shape of the aggregates are dependent on the surfactant molecular structure as well as the solution conditions. The Gibbs equilibrium condition

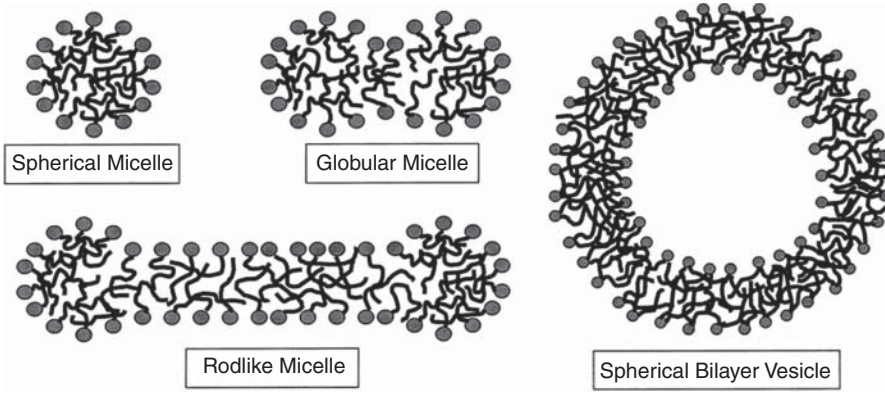

Figure 1.1 Schematic representation of surfactant aggregates in dilute aqueous solutions. The structures include spherical micelles, globular micelles not much larger than the spherical micelles, large cylindrical micelles with globular endcaps, and spherical bilayer vesicles. The length of the surfactant tail constrains one characteristic dimension in each of these aggregates (radius for the micelles and half-bilayer thickness for the vesicles). More complex aggregates involving branching of cylindrical micelles and network formation among them are discussed in detail by Victorov in Chapter 2 of this book.

Table 1.1 Geometrical relations for spherical and cylindrical micelles and bilayers.[a)]

Variable	Sphere	Cylinder	Planar bilayer
Volume of core $V = g\, v_o$	$4\pi\, R^3/3$	$\pi\, R^2$	$2R$
Surface area of core $A = g\, a$	$4\pi\, R^2$	$2\pi\, R$	2
Area per molecule a	$3v_o/R$	$2v_o/R$	v_o/R
Aggregation number g	$36\pi v_o^2/a^3$	$4\pi v_o/a^2$	$2/a$

a) R is the core radius in case of spherical, globular or cylindrical micelles and in the case of bilayer, it represents the half-bilayer thickness. g denotes the number of surfactant molecules in the aggregate. v_o is the volume and ℓ_o is the extended length of the surfactant tail. The variables V, A, and g refer to the entire aggregate in the case of a sphere, unit length in the case of a cylinder or unit area in the case of a bilayer.

stipulates the equality of chemical potential of a surfactant molecule present in the singly dispersed state and that incorporated within a multimolecular aggregate of any given size and shape [10]. This chemical potential equality allows one to relate the concentration X_g of surfactant aggregates of size g and any shape to the concentration X_1 of the singly dispersed surfactant through the equation

$$X_g = X_1^g \exp(-\mathrm{g}\, \Delta\mu_g^o/kT), \quad \Delta\mu_g^o = \frac{\mu_g^o}{g} - \mu_1^o \tag{1.1}$$

where, μ_g^o is the standard state chemical potential of an isolated micelle of aggregation number g while μ_1^o is the standard state chemical potential of a singly dispersed surfactant, both in bulk solvent. k is the Boltzmann constant and T is the temperature. Based on Eq. (1.1), the fundamental quantity of interest that will allow one to determine all aggregation properties is the standard state chemical potential difference $\Delta\mu_g^o$, also referred to as the standard free energy change on aggregation. Tanford [10, 20] formulated a quantitative expression for $\Delta\mu_g^o$ on phenomenological grounds, invoking the concept of opposing forces. The standard free energy change is composed of three contributions:

$$\left(\frac{\Delta\mu_g^o}{kT}\right) = \left(\frac{\Delta\mu_g^o}{kT}\right)_{Tail} + \left(\frac{\Delta\mu_g^o}{kT}\right)_{Int} + \left(\frac{\Delta\mu_g^o}{kT}\right)_{Head} \tag{1.2}$$

The first term $(\Delta\mu_g^o/kT)_{Tail}$ is a negative free energy contribution arising from the transfer of the surfactant tail from its unfavorable contact with water to the favorable hydrocarbon-like environment of the aggregate core. This transfer free energy contribution depends on the surfactant tail but not on the aggregate shape or size. The second term $(\Delta\mu_g^o/kT)_{Int}$ is a positive free energy contribution that accounts for the residual contact between the surfactant tails and water at the aggregate core-water interface. This is represented as the product of a contact free energy per unit area σ (or an interfacial free energy per unit area,

or interfacial tension) and the surface area per molecule of the aggregate core, a. The third term $(\Delta\mu_g^o/kT)_{Head}$ is another positive free energy contribution that accounts for the repulsive interactions between the headgroups because they crowd at the aggregate surface. The repulsions may be due to steric interactions (for any type of headgroup) and also electrostatic interactions (dipole–dipole interactions for zwitterionic headgroups and ion–ion repulsions for ionic headgroups). Since the repulsions would increase if the headgroups come close to one another, Tanford proposed an expression for this free energy contribution with an inverse dependence on a. Thus, the standard free energy change per molecule on aggregation proposed by Tanford has the form:

$$\left(\frac{\Delta\mu_g^o}{kT}\right) = \left(\frac{\Delta\mu_g^o}{kT}\right)_{Tail} + \left(\frac{\sigma}{kT}\right)a + \left(\frac{\alpha}{kT}\right)\frac{1}{a} \tag{1.3}$$

where α represents the headgroup repulsion parameter. One may note that this phenomenological parameter α has to be connected to the surfactant headgroup features and solution conditions if one wants to carry out any predictive computations of aggregation.

From the free energy model of Tanford, the equilibrium aggregation behavior can be examined either by treating the surfactant solution as consisting of aggregates with a distribution of sizes (as represented by Eq. (1.1)) or by treating the aggregate as constituting a pseudophase. If the aggregate is viewed as a pseudophase, in the sense of small systems thermodynamics, the equilibrium condition corresponds to a minimum in the standard free energy change per molecule, $\Delta\mu_g^o/kT$. The minimization can be done with respect to either the aggregation number g or the core surface area per molecule a, since they are dependent on one another through the geometrical relations given in Table 1.1. One obtains, in this manner, the equilibrium core surface area a_e per molecule characterizing the aggregate:

$$\frac{\partial}{\partial a}\left(\frac{\Delta\mu_g^o}{kT}\right) = \left(\frac{\sigma}{kT}\right) - \left(\frac{\alpha}{kT}\right)\frac{1}{a^2} = 0, at\ a = a_e \quad \Rightarrow \quad a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2} \tag{1.4}$$

The critical micelle concentration (cmc, denoted as X_C in mole fraction units), in the pseudophase approximation, is obtained from the relation,

$$ln\, X_C = \left(\frac{\Delta\mu_g^o}{kT}\right)_{Tail} + \left(\frac{\sigma}{kT}\right)a_e + \left(\frac{\alpha}{kT}\right)\frac{1}{a_e} = \left(\frac{\Delta\mu_g^o}{kT}\right)_{Tail} + \left(\frac{2\sigma^{1/2}\alpha^{1/2}}{kT}\right) \tag{1.5}$$

The principal outcomes from the free energy model are the equilibrium area per molecule and the cmc. From the equilibrium area per molecule, one can