



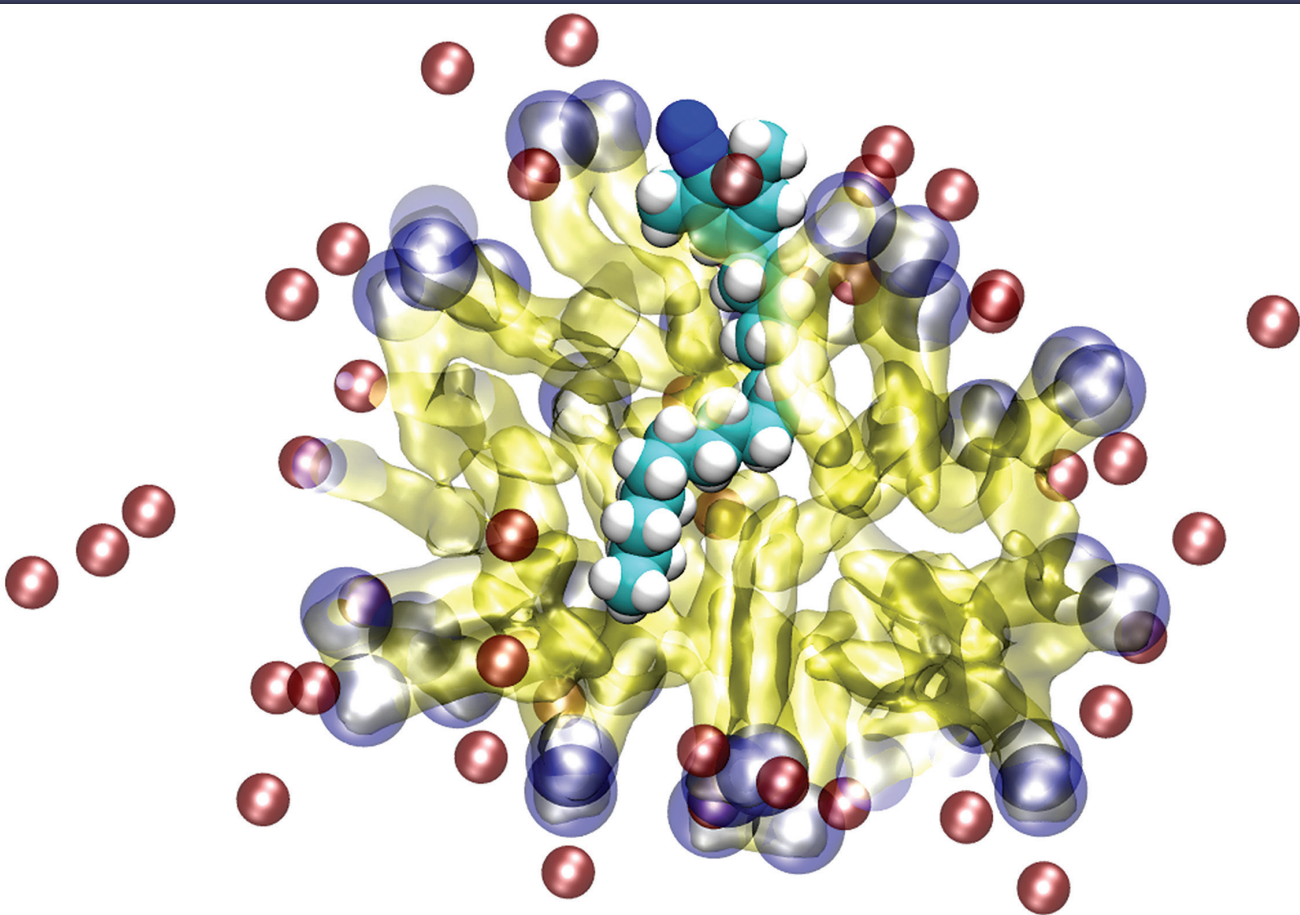
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A Festschrift in honor of
Dr. Kash Mittal

SURFACTANT SCIENCE AND TECHNOLOGY

Edited by
Laurence S. Romsted

RETROSPECTS AND PROSPECTS



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Laurence S. Romsted

Rutgers University, New Brunswick, New Jersey, USA

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Cover Image: Cross section of a gemini micelle and probe molecule courtesy of Michel Laguerre and Massimiliano Porrini, Institut Européen de Chimie et Biologie (IECB), Bordeaux, France. A molecular dynamics simulation of a chemical trapping probe, 4-hexadecyl-2,6-dimethylbenzenediazonium ion, nestled in a cross section of micelle composed of decanediyl- α,ω -bis (dodecyldimethylammonium chloride) or 10-2-10 2Cl (aggregation number = 27). Depicted are chloride ions (red), a spaghetti-like core of decyl tails (golden yellow), gemini nitrogens (steel blue), and the chemical probe with carbons (cyan), hydrogens (white), and diazonio group (dark blue). For esthetic purposes, various groups in the gemini micelle cross section are not quite to scale. (Examples of probe applications: X. Gao et al., *Langmuir* **2013**, 29, 4928; Q. Gu et al., *J. Coll. I. Sci.*, **2013**, 400, 41; and Y. Zhang et al., *Langmuir*, **2013**, 29, 534.)

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Dedication

IN HONOR OF KASHMIRI LAL MITTAL



A special symposium was held in honor of the publication of Kashmiri Mittal's 100th edited book as a part of the 18th Surfactants in Solution (SIS) meeting in 2010 in Melbourne, Australia. The title of the symposium, *Surfactant Science and Technology: Retrospects and Prospects*, became the title of this Festschrift. Speakers, and others unable to attend the meeting, were invited to present overviews of their research areas at the meeting and in the chapters of this book recalling the past, summarizing the present, and projecting into the future. The book title reflects the major and continuing contributions of Kashmiri, or Kash as he is known to most. For nearly four decades he has brought together seasoned and new scientists and students of surfactant chemistry at international meetings, in journals, and in books. The totality of his contributions is one of a kind.

Kash was born in the village of Kilrodh, district Rohtak, Haryana, India, in 1945. He obtained a BSc degree from Panjab University in Chandigarh, India, in 1964, and an MSc degree (First Position) in chemistry from the Indian Institute of Technology, New Delhi, in 1966 (thesis title: "Ion Exchange Capacity of Clays"). Shortly thereafter, he migrated to the United States and earned a PhD degree in colloid chemistry in 1970 at the University of Southern California, Los Angeles (thesis title: "Factors Affecting Ultracentrifugal Stability of Oil-in-Water Emulsions," advisor: Professor Robert D. Vold). Kash completed two postdoctoral positions, one at Pennsylvania State University and one at the University of Pennsylvania. He joined the IBM Corporation in 1972 as a postdoctoral fellow and investigated adhesion science until 1994. Since leaving IBM, he has been teaching and consulting worldwide in the broad area of adhesion science.

Kash's professional contributions and awards are listed at the end of this dedication. Kash's edited books and journals have reported scientific progress in colloid and adhesion sciences (see list of published edited books) and chronicle the spawning of future work from past accomplishments. The Surfactants in Solution meetings he has chaired have provided forums for scientists to meet, talk, and sometimes plan new collaborations. Equally important, the meetings enhance the education of scientists in training and provide them an opportunity to display their work. Kash has received numerous awards for his contributions. Some numbers give a feel for the extent of Kash's unique contributions to stimulating scientific research up to 2013: edited books, 112; SIS meetings, 20; journals created, 2; member of editorial boards, 13; and awards, 18. But in reality, the outcomes from this exchange of information and ideas by so many people over many decades cannot be quantified.

I am most familiar with the biennial Surfactants in Solution meetings (see list of SIS meetings), which is, as some of us say, Kash's baby. The first SIS meeting was in 1976 in Albany, New York, and the 20th will be in Coimbra, Portugal, in June 2014. The fundamental and applied research talks presented at these meetings for nearly forty years are a running record of the growth and progress in surfactant chemistry. In 1976, the emphasis of the research talks and the companion books published in 1977 was on the properties of optically transparent micellar solutions, their structures, and internal organization, i.e., hydrocarbon-like cores and polar interfaces, physical properties of the aggregates such as size and shape, adsorption of ions and molecules, and their effects on chemical reactivity. At the meeting in Coimbra in 2014, the proposed topics include many of the same areas, but with the advancement in instrumentation, new understanding is reaching new areas at a greater level of molecular detail. For example, talks on wetting, interfacial tension and rheology, monolayers and films, electrokinetic phenomena, phase behavior, self-assembly, thermodynamics and kinetics, association colloids, liposomes, and emulsions. But also on niosomes, colloidosomes, polymerizable surfactants, biosurfactants, surfactants in pharmacy, energy production, and nanotechnology. Surfactant chemistry is critical to virtually every aspect of the organization of life and of materials science. The SIS meetings have been in the forefront of these advances.

However, SIS meetings do even more because, unlike meetings organized by chemical societies in specific countries, these meetings have been held in many countries (see list of SIS meetings) routinely bringing together people from around the globe. The meetings have also intentionally involved and recognized the contributions of women and young scientists. The poster sessions also provide graduate students from many countries the opportunity to display their work in an international setting, also a unique contribution. Speaking for myself, I was a newly minted PhD just turned postdoc in 1976 when I attended the first, and also my first, SIS meeting. I found that the opportunity to listen and learn from and present to the people whose research I was reading was awesome.

In addition to all these contributions, Kash has published approximately 75 papers in the areas of surface and colloid chemistry, adhesion, polymers, and surface cleaning. He has also served on the advisory boards and committees of numerous international conferences, has given seminars and lectures on many aspects of adhesion science and technology around the globe, and is listed in numerous biographical references including *American Men and Women of Science*, *International Who's Who of Contemporary Achievement*, *Men of Achievement*, *Who's Who in Frontier Science and Technology*, *Who's Who of Intellectuals*, *Who's Who in the East (USA)*, and *Who's Who in Technology Today*.

Congratulations, Kash, for carving out a unique and productive career that is of extraordinary value to the surfactant and adhesion sciences.

Laurence S. Romsted

*Department of Chemistry and Chemical Biology (CCB) Rutgers
The State University of New Jersey
New Brunswick, New Jersey
romsted@rutchem.rutgers.edu
http://chem.rutgers.edu/romsted_laurence_s*

PROFESSIONAL CONTRIBUTIONS OF KASHMIRI LAL MITTAL

PUBLISHED BOOKS, HONORS, RECOGNITION AND AWARDS, JOURNAL EDITORIAL BOARD MEMBERSHIPS, JOURNALS INITIATED, AND SIS MEETINGS

A. Edited Books

Title	Year
1. <i>Adsorption at Interfaces</i>	1975
2. <i>Colloidal Dispersions and Micellar Behavior</i>	1975
3. <i>Micellization, Solubilization, and Microemulsions, Vol. 1</i>	1977
4. <i>Micellization, Solubilization, and Microemulsions, Vol. 2</i>	1977
5. <i>Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings</i>	1978
6. <i>Surface Contamination: Genesis, Detection and Control, Vol. 1</i>	1979
7. <i>Surface Contamination: Genesis, Detection and Control, Vol. 2</i>	1979
8. <i>Solution Chemistry of Surfactants, Vol. 1</i>	1979
9. <i>Solution Chemistry of Surfactants, Vol. 2</i>	1979
10. <i>Solution Behavior of Surfactants: Theoretical and Applied Aspects, Vol. 1</i>	1982
11. <i>Solution Behavior of Surfactants: Theoretical and Applied Aspects, Vol. 2</i>	1982
12. <i>Physicochemical Aspects of Polymer Surfaces, Vol. 1</i>	1983
13. <i>Physicochemical Aspects of Polymer Surfaces, Vol. 2</i>	1983
14. <i>Adhesion Aspects of Polymeric Coatings</i>	1983
15. <i>Surfactants in Solution, Vol. 1</i>	1984
16. <i>Surfactants in Solution, Vol. 2</i>	1984
17. <i>Surfactants in Solution, Vol. 3</i>	1984
18. <i>Adhesive Joints: Formation, Characteristics and Testing</i>	1984
19. <i>Polyimides: Synthesis, Characterization and Applications, Vol. 1</i>	1984
20. <i>Polyimides: Synthesis, Characterization and Applications, Vol. 2</i>	1984
21. <i>Surfactants in Solution, Vol. 4</i>	1986
22. <i>Surfactants in Solution, Vol. 5</i>	1986
23. <i>Surfactants in Solution, Vol. 6</i>	1986
24. <i>Treatise on Clean Surface Technology, Vol. 1</i>	1987
25. <i>Surface and Colloid Science in Computer Technology</i>	1987
26. <i>Particles on Surfaces 1: Detection, Adhesion and Removal</i>	1988
27. <i>Opportunities and Research Needs in Adhesion Science and Technology</i>	1988
28. <i>Particles in Gases and Liquids 1: Detection, Characterization and Control</i>	1989
29. <i>Surfactants in Solution, Vol. 7</i>	1989
30. <i>Surfactants in Solution, Vol. 8</i>	1989
31. <i>Surfactants in Solution, Vol. 9</i>	1989
32. <i>Surfactants in Solution, Vol. 10</i>	1989
33. <i>Particles on Surfaces 2: Detection, Adhesion and Removal</i>	1989
34. <i>Metallized Plastics 1: Fundamental and Applied Aspects</i>	1989
35. <i>Polymers in Information Storage Technology</i>	1989
36. <i>Particles in Gases and Liquids 2: Detection, Characterization and Control</i>	1990
37. <i>Acid-Base Interactions: Relevance to Adhesion Science and Technology</i>	1991
38. <i>Particles on Surfaces 3: Detection, Adhesion and Removal</i>	1991
39. <i>Metallized Plastics 2: Fundamental and Applied Aspects</i>	1991
40. <i>Surfactants in Solution, Vol. 11</i>	1991

41.	<i>Silanes and Other Coupling Agents</i>	1992
42.	<i>Metallized Plastics 3: Fundamental and Applied Aspects</i>	1993
43.	<i>Particles in Gases and Liquids 3: Detection, Characterization and Control</i>	1993
44.	<i>Contact Angle, Wettability and Adhesion</i>	1993
45.	<i>Handbook of Adhesive Technology</i>	1994
46.	<i>Plasma Surface Modification of Polymers: Relevance to Adhesion</i>	1994
47.	<i>Particles on Surfaces: Detection, Adhesion and Removal</i>	1995
48.	<i>Fundamentals of Adhesion and Interfaces</i>	1995
49.	<i>Adhesion Measurement of Films and Coatings</i>	1995
50.	<i>Polymer Surface Modification: Relevance to Adhesion</i>	1996
51.	<i>Polyimides: Fundamentals and Applications</i>	1996
52.	<i>Surfactants in Solution</i>	1996
53.	<i>Polymer Surfaces and Interfaces: Characterization, Modification and Application</i>	1997
54.	<i>Metallized Plastics: Fundamentals and Applications</i>	1998
55.	<i>Metallized Plastics 5&6: Fundamental and Applied Aspects</i>	1999
56.	<i>Adhesion Promotion Techniques: Technological Applications</i>	1999
57.	<i>Handbook of Microemulsion Science and Technology</i>	1999
58.	<i>Particles on Surfaces 5&6: Detection, Adhesion and Removal</i>	1999
59.	<i>Emulsions, Foams and Thin Films</i>	2000
60.	<i>Apparent and Microscopic Contact Angles</i>	2000
61.	<i>Acid–Base Interactions: Relevance to Adhesion Science and Technology, Vol. 2</i>	2000
62.	<i>Silanes and Other Coupling Agents, Vol. 2</i>	2000
63.	<i>Polymer Surface Modification: Relevance to Adhesion, Vol. 2</i>	2000
64.	<i>Adhesion Measurement of Films and Coatings, Vol. 2</i>	2000
65.	<i>Adhesion Aspects of Thin Films, Vol. 1</i>	2001
66.	<i>Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol. 1</i>	2001
67.	<i>Metallized Plastics 7: Fundamental and Applied Aspects</i>	2001
68.	<i>Adhesive Joints: Formation, Characteristics and Testing, Vol. 2</i>	2002
69.	<i>Particles on Surfaces 7: Detection, Adhesion and Removal</i>	2002
70.	<i>Contact Angle, Wettability and Adhesion, Vol. 2</i>	2002
71.	<i>Adsorption and Aggregation of Surfactants in Solution</i>	2003
72.	<i>Adhesion Aspects of Polymeric Coatings, Vol. 2</i>	2003
73.	<i>Handbook of Adhesive Technology, 2nd edition</i>	2003
74.	<i>Surface Contamination and Cleaning, Vol. 1</i>	2003
75.	<i>Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol. 2</i>	2003
76.	<i>Particles on Surfaces 8: Detection, Adhesion and Removal</i>	2003
77.	<i>Contact Angle, Wettability and Adhesion, Vol. 3</i>	2004
78.	<i>Polymer Surface Modification: Relevance to Adhesion, Vol. 3</i>	2004
79.	<i>Silanes and Other Coupling Agents, Vol. 3</i>	2004
80.	<i>Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol. 3</i>	2005
81.	<i>Adhesion, Aspects of Thin Films, Vol. 2</i>	2005
82.	<i>Atomic Force Microscopy in Adhesion Studies</i>	2005
83.	<i>Contact Angle, Wettability and Adhesion, Vol. 4</i>	2006
84.	<i>Particles on Surfaces 9: Detection, Adhesion and Removal</i>	2006

85.	<i>Silanes and Other Coupling Agents, Vol. 4</i>	2007
86.	<i>Polymer Surface Modification: Relevance to Adhesion, Vol. 4</i>	2007
87.	<i>Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol. 4</i>	2007
88.	<i>Adhesion Aspects of Thin Films, Vol. 3</i>	2007
89.	<i>Developments in Surface Contamination and Cleaning: Fundamentals and Applied Aspects</i>	2008
90.	<i>Surfactants in Tribology</i>	2008
91.	<i>Contact Angle, Wettability and Adhesion, Vol. 5</i>	2008
92.	<i>Electrically Conductive Adhesives</i>	2008
93.	<i>Polymer Surface Modification: Relevance to Adhesion, Vol. 5</i>	2009
94.	<i>Silanes and Other Coupling Agents, Vol. 5</i>	2009
95.	<i>Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Vol. 5</i>	2009
96.	<i>Superhydrophobic Surfaces</i>	2009
97.	<i>Contact Angle, Wettability and Adhesion, Vol. 6</i>	2009
98.	<i>Adhesion Aspects in Dentistry</i>	2009
99.	<i>Handbook of Sealant Technology</i>	2009
100.	<i>Developments in Surface Contamination and Cleaning: Vol. 2</i>	2010
101.	<i>Surfactants in Tribology, Vol. 2</i>	2011
102.	<i>Developments in Surface Contamination and Cleaning, Vol. 3</i>	2011
103.	<i>Wood Adhesives</i>	2011
104.	<i>Surface and Interfacial Aspects of Cell Adhesion</i>	2011
105.	<i>Adhesion Aspects in MEMS/NEMS</i>	2011
106.	<i>Developments in Surface Contamination and Cleaning, Vol. 4</i>	2012
107.	<i>Surfactants in Tribology, Vol. 3</i>	2013
108.	<i>Developments in Surface Contamination and Cleaning, Vol. 5</i>	2013
109.	<i>Advances in Contact Angle, Wettability and Adhesion, Vol. 1</i>	2013
110.	<i>Atmospheric Pressure Plasma Treatment of Polymers: Relevance to Adhesion</i>	2013
111.	<i>Developments in Surface Contamination and Cleaning, Vol. 6</i>	2013
112.	<i>Advances in Modeling and Design of Adhesively Bonded Systems</i>	2013

B. General Chair, Biennial Surfactants in Solution (SIS) Meetings

1976	Albany, USA	1996	Jerusalem, Israel
1978	Knoxville, USA	1998	Stockholm, Sweden
1980	Potsdam, USA	2000	Gainesville, USA
1982	Lund, Sweden	2002	Barcelona, Spain
1984	Bordeaux, France	2004	Fortaleza, Brazil
1986	New Delhi, India	2006	Seoul, South Korea
1988	Ottawa, Canada	2008	Berlin, Germany
1990	Gainesville, USA	2010	Melbourne, Australia
1992	Varna, Bulgaria	2012	Edmonton, Canada
1994	Caracas, Venezuela	2014	Coimbra, Portugal

C. Honors, Awards and Special Recognitions in Surfactant and Adhesion Sciences (reverse chronological order):

- Special Issue of *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (Volume 391, Issues 1–3, 2011) dedicated to him to honor the publication of his 100th edited book.
- Special Symposium on “Surfactant Science and Technology: Retrospects and Prospects” in Melbourne, Australia (November 2010), organized in his honor to commemorate the publication of his 100th edited book. The current volume represents the Festschrift from this event dedicated to him.
- Special Symposium on “Recent Advances in Adhesion Science and Technology” organized in honor of publication of his 100th edited book at the American Chemical Society (ACS) meeting in Boston, August 2010, documented in a Festschrift from this event dedicated to him.
- Special Issue of *Particulate Science and Technology—An International Journal*, Vol. 25, No. 1 (Jan./Feb. 2007), dedicated to him on his 60th birthday.
- *Advances in Colloid and Interface Science* (Vols. 123–126, 2006), dedicated to him in his honor on his 60th birthday.
- Title of Doctor *honoris causa* awarded by the Maria Curie–Sklodowska University, Lublin/Poland (2003).
- Establishment of the biennial *Kash Mittal Award* by the worldwide surface and colloid science community (awarded to peer-assessed scientists active in this field) in recognition of his large contributions to the field of colloid and interface chemistry (2002).
- *Adhesives Age Award* (1997).
- *Adhesives Award* of ASTM International Committee D-14 (1997).
- *John A. Wagnon Technical Achievement Award* of the International Microelectronics and Packaging Society (IMAPS) (1977).
- *Thomas D. Callinan Award* of the Dielectric Science and Technology Division of the Electrochemical Society (1995).
- The 1st International Congress on Adhesion Science & Technology held in his honor on his 50th birthday in Amsterdam, the Netherlands, October 1995 (235 papers from 38 countries were presented).
- Special issue (Vol. 13, Nos. 3 and 4, July–December 1995) of *Particulate Science and Technology—An International Journal* dedicated to him on the occasion of his 50th birthday.
- *Adhesives Age* (September 1995)—An interview with him recognizing his contributions marked by the Amsterdam *1st International Congress on Adhesion Science & Technology*.
- *Robert L. Patrick Fellow* title of the Adhesion Society (1990).
- *Charles B. Dudley Award* of ASTM International (1990).
- “Recognition Plaque for Continued Leadership and Distinguished Professional Service” presented by the international surface and colloid science community comprising prominent scientists from 51 countries at the 6th International Symposium on Surfactants in Solution (SIS), New Delhi (1986).
- Invitation by the International Advisory Panel and Chinese Review Commission (under the auspices of the World Bank) as a Project Specialist to visit Shanghai Jiao Tong University, China (1985).

D. Journal Editor

In 1986, he founded the *Journal of Adhesion Science and Technology* (JAST) and was its Editor-in-Chief until April 2012. In February 2013, he started a new journal, *Reviews of Adhesion and Adhesives* and also a new book series entitled *Adhesion and Adhesives: Fundamental and Applied Aspects*.

E. Member of Editorial Boards of Journals and Encyclopedia:

1. *Adhesives Age*
2. *Advances in Colloid and Interface Science*
3. *Journal of Adhesion*
4. *Journal of Coatings Technology*
5. *Journal of Polymer Materials*
6. *Journal of Surface Science and Technology*
7. *Particulate Science and Technology: An International Journal*
8. *Precision Cleaning*
9. *Progress in Organic Coatings*
10. *Solid State Technology*
11. *Southern Brazilian Journal of Chemistry*
12. *Surface Innovations*
13. *Encyclopedia of Surface and Colloid Science*

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Preface

A celebration was held at the 18th Surfactants in Solution (SIS) meeting in November 2010 in Melbourne in honor of Kashmiri Mittal's 100th edited book.

Those who participated in the symposium are leaders in the fields of surfactant-based, physical, organic, and materials chemistries, and many agreed to contribute a chapter to this book. Some chapters are contributed by others who wanted to participate in the meeting, but were unable to attend. The authors were asked to give an overview of their research areas and to include sections on past, present, and future directions. The authors updated and revised their manuscripts as needed in 2012. The cumulative result in this volume is a broad perspective on the current developments in and future of surfactant science and technology.

The next SIS will be held in Coimbra, Portugal, in June 2014, the 20th biennial meeting over about two score years. During this time, the field of surfactant chemistry has expanded dramatically and has evolved considerably, aided by the development of modern instrumentation and new experimental techniques that permit exploration of surfactant properties in both the bulk and at molecular levels and by simulation.

The physical properties of surface-active agents, commonly known as surfactants, amphiphiles, detergents, or soaps, are governed by covalently joining two opposite chemical properties in one molecule: a water-insoluble hydrophobic tail, typically composed of linear hydrocarbon chemically bonded to polar or ionic headgroup and counterion. These surfactant monomers or unimers self-assemble into a plethora of aggregate structures such as micelles, microemulsions, vesicles, and emulsions depending on solution composition, but they also form surfactant monolayers at the air, liquid, and solid interfaces. A large variety of aggregate mesophases may be formed including aqueous and reverse micelles, flexible rod-like and hexagonal structures, cubic and lamellar phases and bicontinuous regions, and vesicles. The equilibrium sizes and shapes of surfactant aggregates are governed by a delicate balance of forces such as coulombic, dispersion, hydrogen bonding, hydration, and dipole–dipole and dipole–charge, whose strengths are typically ≤ 20 kJ/mol. Biological systems, e.g., protein coiling and stability, and the formation of biological membranes, depend on the same basic forces, and basic research in surfactant assemblies is motivated by the realization that they are “simple” models of the more complex biological ones.

Applied surfactant research is focused on tuning the properties of surfactant assemblies by identifying the optimal combination of surfactants and additives for particular applications. The number and type of applications are almost limitless and include some of the most important industrial, medical, and personal applications: washing and cleaning, microelectronics, viscosity control, speeding reactions, stabilizing drugs, drug delivery, compartmentalization, cosmetics, enhanced oil recovery, and foods.

This book is divided into six parts. An asterisk (*) indicates the corresponding author.

PART I. THEORY OF SELF-ASSEMBLY AND ION-SPECIFIC EFFECTS (TWO CHAPTERS)

R. Nagarajan provides an extensive overview of the development of the theory of micellization, and R. I. Slavchov,* S. I. Karakashev, and I. B. Ivanov introduce a model for interpreting ion-specific effects on aggregate properties including adsorption, micellization, and thin liquid films.

PART II. SURFACTANTS AT SOLID–LIQUID INTERFACES (FIVE CHAPTERS)

The focus is on interactions of surfactant solutions with solid supports. E. Chibowski,* M. Jurak, and L. Holysz used different methods to deposit lipid layers and measured contact angles to understand the hydrophobic/hydrophilic changes in the lipid layer. R. Miller,* V. B. Fainerman, V. Pradines, V. I. Kovalchuk, N. M. Kovalchuk, E. V. Aksenenko, L. Liggieri, F. Ravera, G. Loglio, A. Sharipova, Y. Vysotsky, D. Vollhardt, N. Mucic, R. Wüstneck, J. Krägel, and A. Javadi evaluated equilibrium and dynamic surface tensions and other methods to obtain information on the arrangement of molecules at interfaces. N. Ivanova and V. M. Starov* provide an overview of surfactant effects on dynamic and spreading phenomena. V. I. Kovalchuk, E. K. Zholkovskiy, M. P. Bondarenko, and D. Vollhardt* have studied the mechanism of pattern formation on solid surfaces with high contrast resolution at the nanometer scale. M. Ferrari,* F. Ravera, L. Liggieri, and L. Navarini show that tensiometry provides new information on the contributions of beverage components to *espresso* flavor.

PART III. POLYMERIC SURFACTANTS AND POLYMER/SURFACTANT MIXTURES (THREE CHAPTERS)

M. C. Morán,* D. Costa, M. da Graça Miguel, and B. Lindman used their general understanding of the interactions of DNA and oppositely charged molecules, e.g., cationic surfactants, to create novel DNA-based materials. C. W. Park, H.-M. Yang, S. R. Yoon, and J.-D. Kim* prepared multi-functional poly(amino acid) graft polymers for improved drug delivery and diagnosis and report on the morphological transitions of the aggregates. Th. Tadros discusses the classification of polymeric surfactants and illustrates their adsorption isotherms and the effects on emulsification in terms of a combination of intermolecular interactions and steric stabilization.

PART IV. BIOSURFACTANTS (TWO CHAPTERS)

G. Biresaw describes the preparation, properties, and applications of farm-based biosurfactants synthesized from natural products, and their surface and interfacial properties are discussed. P. Somasundaran,* P. Patra, J. D. Albino, and I. M. Nambi describe the preparation, structures, and properties of “greener” biosurfactants obtained from bacteria.

PART V. FORMULATION AND APPLICATION OF SURFACTANT AGGREGATES (FIVE CHAPTERS)

D. Libster, A. Aserin, and N. Garti* describe the structural features of lyotropic liquid crystals, their application for solubilization and drug and biomacromolecule release, and the use of cell-penetrating peptides to enhance drug penetration of the skin. M. Win, P. Lang, M. Vashishtha,* and D. O. Shah review the properties of microemulsions, their efficacy in drug delivery, and controlled release by tailoring the microemulsion properties. K. Holmberg characterizes the structure/function relationships for hydrotropes, their ability to improve the solubility of poorly soluble organic compounds, and their use in formulations by destabilizing surfactant liquid crystals and changing interfacial curvature. P. Brown, C. Butts, and J. Eastoe* discuss the possibility that ionic liquids can be combined to generate tunable and selective reaction media and provide a focus on new directions. J. Texter provides a detailed overview of the origin, properties, and future developments of stimuli-responsive surfactants including topics such as surfimers and inisurfs, biosurfactants, photochromic and pH-sensitive surfactants, and their diverse applications for dispersion stabilization, electrode coating, and shape memory of polymers.

VI. FORMULATION AND APPLICATION OF EMULSIONS (THREE CHAPTERS)

J.-L. Salager,* A. Forgiarini, and J. Bullón review the development in designing emulsion properties for particular applications for foods, agrochemicals, water treatment, asphalts, and paints. P. M. Mwangi and D. N. Rao* describe the role of surfactants in the oil and gas industries such as enhanced oil recovery, drilling, spill remediation, oil flotation, and emulsion breaking. C. A. Miller discusses the surfactant mechanisms for soil removal, considering the conversion of soils into microemulsions and the possibility of spontaneous emulsification.

This book reflects the cumulative wisdom of a number of major contributors to the broad field of surfactant chemistry. The chapters should be useful to both neophytes (as a general introduction) and veteran researchers (as a commentary on current status). Those engaged in surfactant chemistry in a variety of industries and academic disciplines including surface and colloid science, chemical engineering, cosmetics, pharmaceuticals, biomedical, and nanotechnology will find this book of immense interest.

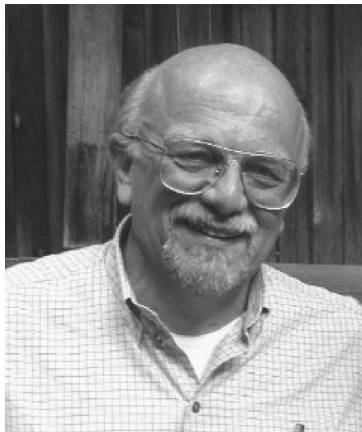
Laurence S. Romsted

*Department of Chemistry and Chemical Biology (CCB) Rutgers
The State University of New Jersey
New Brunswick, New Jersey*

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Editor



Laurence (Larry) S. Romsted was born in Chicago, Illinois, USA, in 1941. He is the grandchild of immigrants, and at the end of World War II, his parents moved to one of the suburbs, where he learned much in school but little about the world. He entered DePauw University, Greencastle, Indiana, in 1959 with a taste for doing chemistry fostered first by an excellent high school science teacher. Second, by an introduction to colloids and food emulsions in a summer job at Kraft Foods Research Labs in his hometown that was amplified by stories about scientists making cool discoveries that helped people and Sputnik. And third, the quixotic hope that a science career meant a minimal amount of writing work.

In 1964, he joined Eugene Cordes' group, at Indiana University, Bloomington, and began graduate research on micellar catalysis as a simple model for enzymatic catalysis—that proved complex, but solvable—eventually. Uncertain about a career in chemistry and totally opposed to the Vietnam War, he joined the Peace Corps and went to the Philippines to reflect on his life, do useful service, and avoid being drafted. He returned to graduate school, but still ambivalent about his future, he dropped out again, married, and taught chemistry part-time in a community college in Ohio. Faced with a forever part-time position and vexed by a research problem he had left unfinished, he again returned to Indiana University, where Cordes said in essence, "Here's a desk, good luck." Eighteen months later, in December 1975, he defended his PhD thesis entitled, "Rate Enhancements in Micellar Systems." To his own (and Cordes') amazement, he had developed a new pseudophase model for ionic micelle effects on the rates of chemical reactions in which the micellar surface is treated as a specific ion exchanger. Pseudophase models remain the primary basis for interpreting reactivity in ionic association colloids. In 1976, Romsted joined C. A. Bunton's group at UC Santa Barbara where he had an extraordinarily fruitful postdoc, developed an appreciation for collaboration from his ornery but caring advisor who became his scientific father, and experienced the deep pleasure of formulating, testing, and carrying ideas to fruition. Doing chemistry, he later realized, had become his art.

In the fall of 1980, he took an assistant professor position at Rutgers, The State University of New Jersey, and, except for the first 3 years, occupied the same office to this day, a personal record for staying in one place. Here he developed the chemical trapping method for estimating changes in interfacial molarities of anionic and neutral nucleophiles with changes in micellar properties. His publication record is modest, 92 to date, but replete with long, data-rich, papers. He has also given about 90 invited talks at international meetings and another 90 or so university seminars. In 1991, he published a singularly important paper in *Accounts of Chemical Research*, "Ion Binding and Reactivity at Charged Aqueous Interfaces," that spread the catalysis model to the world (559 citations and counting). The Account was coauthored with C. A. Bunton (UCSB), F. Nome (UFSC), and F. Quina (USP), each of whom has made major contributions to the current understanding of micellar catalysis.

His current research is in three areas: (a) continued development of the chemical trapping method to better understand the relationships between interfacial compositions and association colloid properties; (b) creating a new method with Carlos Bravo-Díaz (University of Vigo, Spain) for determining the distributions of antioxidants in intact, opaque emulsions from measured rate constants that provide new insight into the polar paradox; and (c) a novel project applying the chemical trapping method to determine protein topologies at biomimetic interfaces. To do one's art and work with bright, engaged students is not such a bad life—most days.

Contributors

Eugene V. Aksenenko

Institute of Colloid Chemistry and Chemistry
of Water
Kiev, Ukraine

John D. Albino

Earth and Environmental Engineering
Columbia University
New York, New York

Abraham Aserin

The Institute of Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel

Girma Biresaw

Bio-Oils Research Unit
NCAUR-ARS
United States Department of Agriculture
Peoria, Illinois

Mykola P. Bondarenko

Institute of Bio-Colloid Chemistry
Kiev, Ukraine

Paul Brown

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Johnny Bullón

Laboratorio de Formulación
Universidad de Los Andes
Mérida, Venezuela

Craig Butts

School of Chemistry
University of Bristol
Bristol, United Kingdom

Emil Chibowski

Department of Physical Chemistry—Interfacial
Phenomena
Faculty of Chemistry
Maria-Curie Skłodowska University
Lublin, Poland

Diana Costa

CICS—Centro de Investigação em Ciências da
Saúde
Universidade da Beira Interior
Covilhã, Portugal

Julian Eastoe

School of Chemistry
University of Bristol
Bristol, United Kingdom

Valentin B. Fainerman

Donetsk Medical University
Donetsk, Ukraine

Michele Ferrari

Istituto per l'Energetica e le Interfasi—CNR
Genoa, Italy

Ana Forgiarini

Laboratorio de Formulación
Universidad de Los Andes
Mérida, Venezuela

Nissim Garti

Casali Institute of Applied Chemistry,
The Institute of Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel

Krister Holmberg

Chalmers University of Technology
Chemical and Biological Engineering
Göteborg, Sweden

Lucyna Holysz

Department of Physical Chemistry—Interfacial
Phenomena
Faculty of Chemistry
Maria-Curie Skłodowska University
Lublin, Poland

Ivan B. Ivanov

Laboratory of Chemical Physics and
Engineering
Sofia University
Sofia, Bulgaria

Natalia Ivanova

Department of Physics
Tyumen State University
Tyumen, Russia

Aliyar Javadi

Max Planck Institute of Colloids and
Interfaces
Potsdam/Golm, Germany

Malgorzata Jurak

Department of Physical Chemistry—Interfacial
Phenomena
Faculty of Chemistry
Maria-Curie Skłodowska University
Lublin, Poland

Stoyan I. Karakashev

Department of Physical Chemistry
Sofia University
Sofia, Bulgaria

Jong-Duk Kim

Department of Chemical and Biomolecular
Engineering
Korea Advanced Institute of Science and
Technology
Daejeon, Republic of Korea

Nina M. Kovalchuk

Institute of Bio-Colloid Chemistry
Kiev, Ukraine

Volodymyr I. Kovalchuk

Institute of Bio-Colloid Chemistry
Kiev, Ukraine

Jürgen Krägel

Max Planck Institute of Colloids and
Interfaces
Potsdam/Golm, Germany

Paul Lang

Rehrig Pacific Company
Vernon, California

Dima Libster

Casali Institute of Applied Chemistry,
The Institute of Chemistry
The Hebrew University of Jerusalem
Edmond J. Safra Campus, Givat Ram
Jerusalem, Israel

Libero Liggieri

Istituto per l'Energetica e le Interfasi—CNR
Genoa, Italy

Björn Lindman

Physical Chemistry 1
University of Lund
Lund, Sweden

Giuseppe Loglio

University of Florence
Sesto Fiorentino
Firenze, Italy

Maria da Graça Miguel

Departamento de Química
Universidade de Coimbra
Coimbra, Portugal

Clarence A. Miller

Department of Chemical and Biomolecular
Engineering
Rice University
Houston, Texas

Reinhard Miller

Max Planck Institute of Colloids and
Interfaces
Potsdam/Golm, Germany

M. Carmen Morán

Departament de Fisiologia
Facultat de Farmàcia
Universitat de Barcelona
Barcelona, Spain

Nenad Mucic

Max Planck Institute of Colloids and Interfaces
Potsdam/Golm, Germany

Paulina M. Mwangi

Craft & Hawkins Department of Petroleum
Engineering
Louisiana State University
Baton Rouge, Louisiana

Ramanathan Nagarajan

Molecular Sciences and Engineering Team
Natick Soldier Research, Development and
Engineering Center (NSRDEC)
Natick, Massachusetts

Indumathi M. Nambi

Department of Civil Engineering
Indian Institute of Technology Madras
Chennai, Tamil Nadu, India

Luciano Navarini

Illycaffè SpA, R&D
Trieste, Italy

Chan Woo Park

Department of Chemical and Biomolecular
Engineering
Korea Advanced Institute of Science and
Technology
Daejeon, Republic of Korea

Partha Patra

Earth and Environmental Engineering
Columbia University
New York, New York

Vincent Pradines

Laboratoire de Chimie de Coordination
Toulouse, France

Dandina N. Rao

Craft & Hawkins Department of Petroleum
Engineering
Louisiana State University
Baton Rouge, Louisiana

Francesca Ravera

Istituto per l'Energetica e le Interfasi—CNR
Genoa, Italy

Jean-Louis Salager

Laboratorio de Formulación
Universidad de Los Andes
Mérida, Venezuela

Dinesh O. Shah

Shah-Schulman Center for Surface Science and
Nanotechnology
Dharmsinh Desai University
Nadiad, Gujarat, India

and

Department of Chemical Engineering and
Department of Anesthesiology
University of Florida
Gainesville, Florida

Altynay Sharipova

Kazakh National Technical University
Almaty, Kazakhstan

Radomir I. Slavchov

Department of Physical Chemistry
Sofia University
Sofia, Bulgaria

Ponisseril Somasundaran

Earth and Environmental Engineering
Columbia University
New York, New York

Victor M. Starov

Department of Chemical Engineering
Loughborough University
Loughborough, United Kingdom

Tharwat Tadros

Consultant
Wokingham, Berkshire, United Kingdom

John Texter

Polymers and Coatings
Eastern Michigan University
Ypsilanti, Michigan

Manu Vashishtha

Shah-Schulman Center for Surface Science and
Nanotechnology
Dharmsinh Desai University
Nadiad, Gujarat, India

Dieter Vollhardt

Max Planck Institute of Colloids and Interfaces
Potsdam/Golm, Germany

Yuri Vysotsky

Donetsk National Technical University
Donetsk, Ukraine

Maung Win

Department of Biomedical Engineering
University of Minnesota
Minneapolis, Minnesota

Rainer Wüstneck

Max Planck Institute of Colloids and
Interfaces
Potsdam/Golm, Germany

Hee-Man Yang

Korea Atomic Energy Research Institute
Daedeok-daero
Daejeon, Republic of Korea

Se Rim Yoon

Amore-Pacific Corporation
R&D Center
Daejeon, Republic of Korea

Emiliy K. Zholkovskiy

Institute of Bio-Colloid Chemistry
Kiev, Ukraine

Part I

Theory of Self-Assembly and Ion-Specific Effects

1 One Hundred Years of Micelles

Evolution of the Theory of Micellization

Ramanathan Nagarajan

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1.1 INTRODUCTION

Surfactant molecules are composed of a polar head group that likes water and a nonpolar tail group that dislikes water, thus contributing to an intrinsic duality in their molecular characteristics. Despite their mutual antipathy, the head and tail groups of the surfactant cannot leave one another because they are covalently connected. The dilemma faced by these molecules is resolved in nature by the intriguing phenomenon of molecular self-assembly, wherein the amphiphiles 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.

Numerous variations are possible in the types of the head group and tail group of surfactants. For example, the head group can be anionic, cationic, zwitterionic, or nonionic. It can be small and compact in size or it could be an oligomeric chain. The tail group can be a hydrocarbon, fluorocarbon, or a siloxane. It can contain straight chains, branched or ring structures, multiple chains, etc. Surfactant molecules with two head groups (Bola surfactants) are also available and there are dimeric surfactants with two head groups and two tail groups with a covalent linkage connecting those (Gemini surfactants). Furthermore, the head and the tail groups can be polymeric in character, as in the case of block copolymers. This variety in the molecular structure of surfactants allows for extensive variation in their solution and interfacial properties and their practical applications. Therefore, it is not surprising that the drive to discover the link between the molecular structure of the surfactant and its physicochemical behavior has had a long history.

The existence of surfactant molecules in the form of self-assembled aggregates was first suggested by McBain in 1913 [1] based on his studies on how the conductivity of a solution of soap molecules changes with the concentration. Soap solutions exhibit even lower osmotic activity than would be predicted if one assumed that soap existed in solution as simple undissociated molecules. Soap solutions also conduct the electric current far better than would be expected from the observed osmotic effects. Attempting to explain these anomalies, McBain, in 1913, suggested that the fatty soap ions aggregated in solution. Such colloidal aggregations of ions, which were termed micelles, would explain both the low osmotic activity and relatively high conductivity of soap solutions.

Understanding the aggregation properties of surfactant molecules has nearly a hundred years of history. The early work, until about 1950, was significantly focused on experimental methods to identify the size and shape of the aggregates. McBain [2–5], Adam [6], Harkins [7–11], Hartley [12–15], and Philippoff [16,17] are among the pioneers who proposed different structural models for micelles. The x-ray diffraction technique was extensively applied and there were many qualitative structural models proposed for the aggregates.

The first theory, published in 1949 by Debye [18–20], explained why micelles form and why there are finite-shaped micelles. In the period between 1950 and 1956, this work stimulated a number of theoretical studies by Hobbs [21], Ooshika [22], Reich [23], and Halsey [24], who attempted to rectify some of the fundamental theoretical aspects as to how an equilibrium system should be described and also drew attention to the role of surface energy, which was missing in the Debye model. From 1955 to 1965, further advances in theory emerged and were guided by the methods of

statistical mechanics. Specifically, the theories of Hovee and Benson [25] and Poland and Scheraga [26,27] have provided some key concepts that have eventually been integrated into the current models. Also during this time, a light-scattering technique was applied to surfactant solutions and experimental evidence for the formation of rodlike micelles was generated.

The work of Poland and Scheraga explicitly introduced the role of hydrophobic interactions in micelle formation. This concept was quantitatively included in the free energy model proposed by Tanford [28–30] during 1970 to 1974. Tanford's model had the simplicity of the earlier theory of Debye, and was also consistent with a rigorous statistical thermodynamic formulation of the aggregation process occurring in the surfactant solution. The free energy model incorporated all important physical chemical factors and provided an explanation for why micelles form, why they grow, and why they remain finite in terms of clearly identified opposing interactional efforts. Israelachvili et al. [31] used the framework of the Tanford free energy model along with molecular packing considerations inside surfactant aggregates to develop a geometry-based approach to predict the formation of different shapes of aggregates. They were able to explain the formation of spherical and cylindrical micelles and spherical bilayer vesicles, as well as transitions between these structures based on a combination of general thermodynamic principles, Tanford's free energy model, and the geometric constraints imposed by molecular packing considerations. At this stage, one could argue that the general principles of surfactant self-assembly were sufficiently well-established due to the contributions of Tanford and Israelachvili et al., in particular (Figure 1.1).

In 1976, Kash Mittal organized a symposium on *Micellization, Solubilization and Microemulsions* [32–37], which became the precursor to the current biennial symposia *Surfactants in Solution*. These series of symposia have given impetus to practically all of the subsequent research in surfactant science and technology. In addition to stimulating theoretical work, the *Surfactants in Solution* symposia, since 1976, have also contributed to the extensive development of novel applications using surfactants beyond the classic areas of detergency, emulsions, foams, and dispersions. Chief among these is the use of surfactants for material synthesis, especially the use of reverse micelles as nanoreactors for nanoparticle synthesis including metal oxides, metals, and quantum dots and the use of surfactant liquid crystals as templates for the synthesis of mesoporous materials that vastly extended the pore size beyond the small range possible with zeolites.

The period following Tanford's work has seen a number of key theoretical advances. First, theoretical models began to be developed with a view to a priori predict the self-assembly properties from the molecular structure of the surfactant. Second, theoretical models began to be applied to mixtures of surfactants and also to surfactants that had hydrophobicity arising from

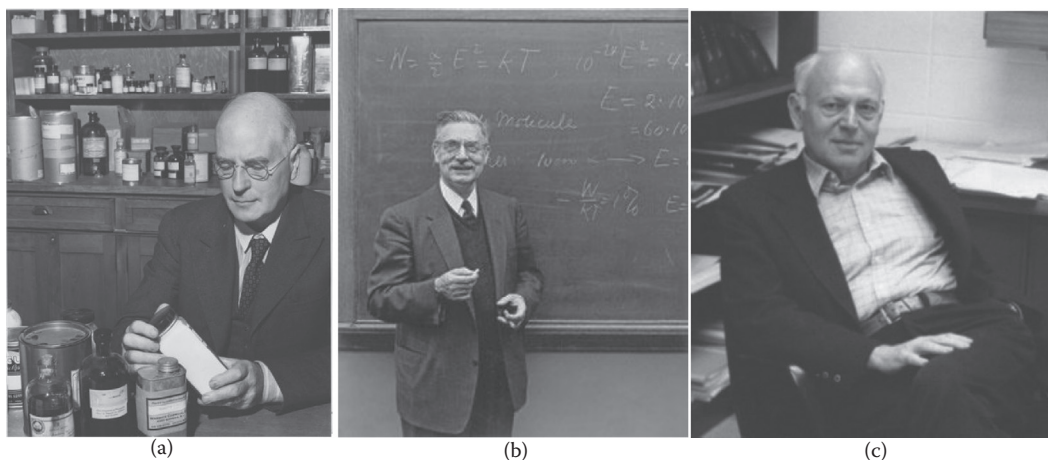


FIGURE 1.1 (a) James W. McBain. (Courtesy of Stanford University.) (b) Peter Debye. (Courtesy of Cornell University Archives.) (c) Charles Tanford. (Copyright 2009, The Protein Society.)

fluorocarbons and siloxanes. Third, self-assembly phenomena such as solubilization and micro-emulsions were described using theoretical approaches used for surfactant aggregation so that a unified view of self-assembly in multicomponent systems was made possible. Fourth, some key features of the free energy models, including the calculation of electrostatic interactions in ionic surfactants, and treatment of how hydrophobic chains pack and arrange inside aggregates of different shapes, were more fundamentally treated. Fifth, the theory of self-assembly was quantitatively applied to novel surfactants such as Bola surfactants and Gemini surfactants. Sixth, self-assembly phenomena at gas–liquid and solid–liquid interfaces began to be modeled. Finally, the free energy models of the analytical form were improved and sometimes combined with free energy models developed by molecular dynamic simulations so that the predictive models can be truly *a priori*.

In this chapter, we focus mainly on the theoretical evolution of free energy models for surfactant self-assembly. The models chosen for discussion are important in the sense that they have affected the evolution of theory and have also influenced our own work in developing predictive models for a range of self-assembly phenomena. Because of the structure of this chapter, a number of scientists who have contributed to experimentally identifying important phenomena or theoretically modeling one or another specific feature of the self-assembly will go unmentioned. Their important contributions and influence over the evolution of theory are not to be ignored and hopefully are visible through the extensive citations of their work in our previous theoretical articles.

1.2 EARLY QUALITATIVE STRUCTURAL MODELS OF MICELLES

The early discussions on aggregate shapes (Figure 1.2) focused on two types proposed by McBain [4,5], a lamellar (disk) aggregate with 50 to 100 molecules and a small oligomeric surfactant cluster with approximately 10 molecules. The lamellar micelle consists of two layers of soap molecules or ion pairs partially dissociated and arranged side by side, with the two hydrocarbon layers inside. Harkins and coworkers [7–10] interpreted their x-ray results as confirming the existence of the lamellar McBain micelle. Furthermore, Hess and coworkers proposed the existence of McBain lamellar micelles that repeat in parallel arrangement, separated by layers of water thus giving an x-ray long spacing equal to twice the length of the molecule plus that of the layer of water [38,39]. This micelle was referred to as the Hess micelle (Figure 1.2).

Harkins considered how molecular shape influences molecular packing at interfaces [6]. He initially favored the lamellar aggregate model and also proposed a cylindrical lamellar form in which

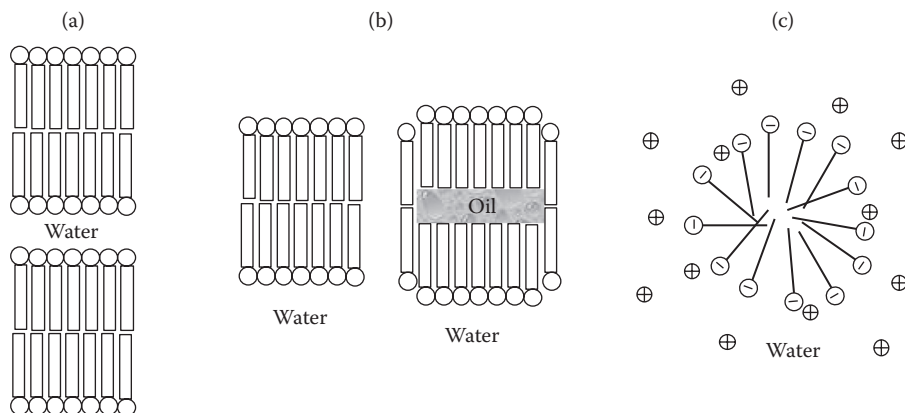


FIGURE 1.2 (a) Hess lamellar micelle made of two McBain lamellar micelles; (b) Harkins cylindrical micelle model showing his idealized cross-section of a soap micelle without solubilized oil and with solubilized oil; (c) Hartley model of a spherical micelle.

the surfactant molecules are oriented parallel to the axis of the cylinder, with the head groups constituting the two end surfaces of the cylinder (the cylinder being merely a small section of the lamellar aggregate) [7–9]. Harkins also suggested that although a cylinder seems to represent most of the properties of the micelle, it is imperfect in that it represents too large an interface at the side between hydrocarbon groups and water. Thus, it does not seem improbable that a model, which lies between a cylinder and a cylindrical type of spheroid, may be found to more accurately represent the energy relationships. This would amount to a distortion of the side of the cylinder with which polar groups cover (to some extent) the nonpolar hydrocarbon chains [10].

Philippoff [16,17] analyzed osmotic activity, specific conductivity, and x-ray data obtained at various electrolyte and surfactant concentrations and for various surfactant tail lengths and identified two regimes with respect to micellar shapes. In the first regime, which corresponds to zero or small amounts of electrolytes, micelles are practically spherical in the sense that they need not be true spheres but can be cubes, short cylinders, prisms, or spheroids. In the other regime, which corresponds to large electrolyte concentrations and longer tail lengths of surfactants, the aggregates are anisometric and large. Philippoff considered that it is improbable for small micelles to reorganize into large micelles with increasing salt and surfactant concentrations and therefore postulated the large structures to be secondary aggregates of the preformed primary micelles.

As opposed to the lamellar structures, Adam [6] arrived at spherical micellar structure based on how molecules pack at interfaces depending on their molecular shapes. Adam suggested that “molecules larger at their polar ends will naturally pack into a curved film having the hydrocarbon side concave and the water-attracting side convex.” Hartley [12–15] proposed the existence of larger spherical micelles with approximately 50 surfactant molecules. Hartley 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.” Harkins, who initially supported the lamellar micelle model and also proposed a cylindrical–lamellar structure, eventually considered the possibility of spherical shape for micelles [11]. Corrin demonstrated [40] from an analysis of the x-ray diffraction data from the Harkins laboratory that a lamellar model is not required to explain the x-ray diffraction patterns obtained from solutions of long-chain ionic surfactants. Qualitatively, the diffraction patterns could be satisfactorily interpreted by a model of spherical micelles whose relative position can be represented by a radial distribution function. He argued that although this does not prove the validity of the spherical micelle model, it indicates that x-ray measurements alone do not allow one to decide between the lamellar and spherical models.

During that stage of development in surfactant research, no definitive theory of micelle formation yet existed. The following statement from Philippoff [17] in his 1951 article makes the case. “Having reviewed the field, we can make only the negative statement that there is at present no theory to account for the causes of micelle formation which can interpret the whole of the experimental evidence. Micelle formation is independent of the sign of the charge of the micelle forming ion. Micelles are partially ionized, therefore a theory must account for this. Micelles form with nonionizing detergents in water, and with some ionizing detergents in hydrocarbons (aerosol OT, diethyl hexyl sodium sulfosuccinate), showing that a charge is not essential for the phenomenon. A straight-chain compound is not necessary for micelle formation. Sodium deoxycholate with a single ionizing group on a sterol skeleton forms micelles as well as divalent aerosol OT in hydrocarbons with four branched chains to one ionic group. The commercially important micellar arylalkyl sulfonates have a complicated structure of the hydrocarbon part of the molecule. Likewise, an extended hydrophilic group as in the polyethylene oxide derivatives is not prohibitive even to x-ray structures. Tween 40, polyethylene oxide sorbitan monopalmitate, with even three hydrophilic chains, forms micelles. Mixed micelles are also readily formed by detergents of the same general structure, differing only in chain. The only common principle left is the segregation of the hydrophilic and hydrophobic parts of a molecule.” It is in this context, that theories began to be developed to explain one or more features of surfactant aggregates.

1.3 FIRST QUANTITATIVE THEORY OF MICELLE DUE TO DEBYE

The first quantitative, molecular theory of the formation of micelles was proposed by Debye [18–20]. He considered ionic surfactants consisting of a hydrocarbon chain with a charge at one end. To create a micelle with the lamellar form proposed by McBain, Debye proposed accounting for two different kinds of energy. There is a gain in energy because a number of hydrocarbon tails are removed from the surrounding water and brought into contact with each other in the micelle. He considered the molecular forces of importance in this process to be relatively short-range forces of the van der Waals kind. To bring the charged ends of the monomers nearer to each other on both flat surfaces of the lamellar micelle requires energy to overcome the long-range electrical forces. Accordingly, Debye concluded that the interplay between short-range van der Waals forces and long-range electrostatic forces are responsible for the equilibrium structure of the micelle.

1.3.1 MONOMER–MICELLE EQUILIBRIUM AND CRITICAL MICELLE CONCENTRATION

Debye started with the classic mass action equilibrium between simple ions and micelles. Consider the following reversible association equilibrium between fatty soap ions A (monomers) and micelles A_g , where g is the number of fatty ions present in a micelle and K_g is the equilibrium constant for the monomer–micelle association:



If X_g denotes the concentration of micelles, X_1 the concentration of unaggregated paraffin chains, and X_T the total concentration of fatty ions, with all concentrations expressed in mole fractions, then

$$X_T = X_1 + gX_g \quad (1.2)$$

Denoting the micellization equilibrium constant K_g in terms of a concentration X_C in the form, $K_g = X_C^{1-g}$, the application of the mass action law assuming unit activity coefficients leads to

$$X_g = K_g (X_1)^g = X_C \left(\frac{X_1}{X_C} \right)^g, \quad X_T = X_1 + gX_C \left(\frac{X_1}{X_C} \right)^g \quad (1.3)$$

From this mass action law, for large enough g , one can see that when $X_1 < X_C$, the micelle concentration X_g will remain negligibly small and X_T will be practically equal to X_1 . To prevent the divergence of the right-hand side of the equation, it is clear that X_1 will become equal to X_C but never exceed it. Therefore, when micelles form, X_1 will be practically equal to X_C . These considerations indicate that if g is large enough, the soap is practically unaggregated up to the concentration X_C and, above that concentration, all excess soap will appear in the form of micelles. On this basis, one can identify X_C as the critical micelle concentration (cmc).

1.3.2 WORK OF FORMATION OF MICELLE

To estimate the energy change on micelle formation, Debye considered the work necessary to create an aggregate from single molecules. One part of this work is electrical and it was estimated as follows. The total charge on the micelle surface will be proportional to $\sigma_e R^2$, where R is the radius of the micelle surface viewed as a circular disk and σ_e is the constant surface charge density. The potential at the rim of the disk will be proportional to $\sigma_e R$. Therefore, for a differential change in the disk radius R , the change in surface charge is $2\pi R dR \sigma_e$ and additional work should be done against the Coulomb

forces proportional to $R^2 dR\sigma_e^2$. The total electrical work involved in building up the disk is thus proportional to R^3 . Because the surface area R^2 is proportional to the number of molecules g constituting the micelle, the electrical energy to be overcome in creating a micelle of size g is

$$W_e = g^{3/2} w_e \quad (1.4)$$

where w_e is a fundamental electrical energy (absorbing all other constants independent of the size g). Due to the long-range character of the electrical forces, this work increases faster than the number of molecules in the micelle. The second work is related to the energy gained by bringing g hydrocarbon tails in contact (which involves only short-range molecular forces) with one another. It was represented as

$$W_m = -g w_m \quad (1.5)$$

with the introduction of another fundamental molecular energy w_m . The negative sign indicates that this energy represents a favorable process of bringing the surfactant's tail from contact with water to contact with other tails.

1.3.3 EQUILIBRIUM MICELLE

The total energy $W = W_e + W_m$ has a minimum for a certain value $g = g_o$ and at this point, the energy W_o of the micelle is negative. This means that the micelle is more stable than g_o separate molecules and that work is required to either increase or decrease the equilibrium number g_o . The energy contributions W_e and W_m and the total energy W are shown in Figure 1.3 as functions of micelle aggregation number g . The total energy W is negative with a shallow minimum W_o at g_o .

From the minimization of the total energy W , one gets the equilibrium aggregation number g_o and the energy W_o corresponding to this equilibrium aggregate.

$$g_o = \left[\frac{2}{3} \frac{w_m}{w_e} \right]^2, \quad W_o = g_o^{3/2} w_e - g_o w_m = -\frac{1}{3} g_o w_m \quad (1.6)$$

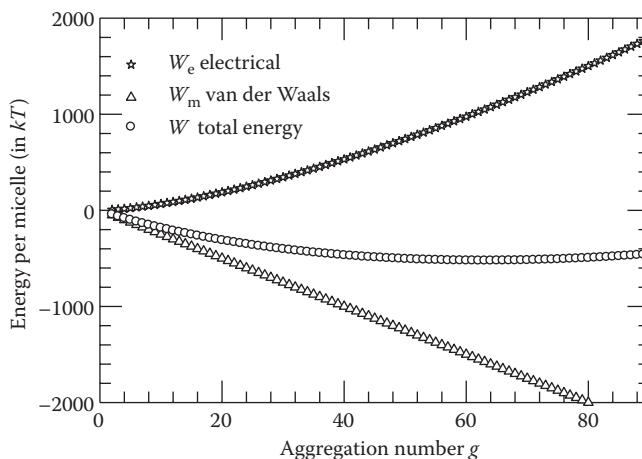


FIGURE 1.3 Debye model energy contributions to micelle formation. The electrostatic energy increases faster than the increase in the van der Waals energy as g increases and thereby contributes to the finite size of micelles.

Equating the energy of formation of the equilibrium micelle to the equilibrium constant for the aggregation in the mass action model, and recognizing that the number of molecules g_o in the equilibrium aggregate will be much larger than 1, one gets an expression for the cmc.

$$W_o = -kT \ln K_g = (g_o - 1) kT \ln X_C \approx g_o kT \ln X_C$$

$$kT \ln X_C = \frac{W_o}{g_o} = -\frac{1}{3} w_m \quad (1.7)$$

Knowing the fundamental energy constants w_m and w_e , one can determine the equilibrium micelle size g_o from Equation 1.6 and the critical concentration X_C from Equation 1.7. Alternatively, knowing the experimentally determined micelle aggregation number and the cmc, one can determine the fundamental energy constants w_m and w_e appearing in the Debye model.

Debye evaluated the physical relevance of the characteristic energy parameters in his model by considering that for dodecylamine hydrochloride at 25°C, the experimental cmc is 0.0131 M (converts to mole fraction $X_C = 2.36 \times 10^{-4}$) and the aggregation number is $g_o = 66$. For these experimental values, the model shows, $W_o/g_o = 8.36 kT$, $w_m = 25 kT$, and $w_e = 2.2 kT$. He noted that the heat of vaporization per dodecane molecule is $25 kT$, and that it has a correspondence to the characteristic short-range energy parameter w_m . He calculated w_e for a disk covered with a constant charge density in a medium of dielectric constant ϵ , to be

$$w_e = \frac{4}{3} \sqrt{\frac{2}{\pi}} \frac{e^2}{\epsilon \sqrt{a}} \quad (1.8)$$

where a is the area per head group and e is the electronic charge. Taking the estimate of Harkins et al. [8] that the surface area occupied by one head group at the aggregate surface is $27 \text{ \AA}^2$, and assuming for the effective dielectric constant (the average of water and that of a hydrocarbon), he obtained $w_e = 2.8 kT$ compared against $2.2 kT$ obtained from the experimental cmc and micelle size data.

1.3.4 SIZE VARIANCE OF EQUILIBRIUM MICELLE

Debye also made an assessment of the distribution of micelle aggregation numbers by expressing the total energy W of the micelle in the vicinity of $g = g_o$ as a function of $(g - g_o)$. From a Taylor expansion of the energy function W around g_o , he obtained

$$W = \left[W + (g - g_o) \frac{\partial W}{\partial g} + \frac{(g - g_o)^2}{2} \frac{\partial^2 W}{\partial g^2} \right]_{g_o} = W_o \left[1 - \frac{3}{4} \left(\frac{g - g_o}{g_o} \right)^2 \right] \quad (1.9)$$

This equation is rearranged to obtain the fluctuation in the micelle aggregation number

$$g - g_o = g_o \sqrt{\frac{4}{3} \frac{W - W_o}{W_o}} \quad (1.10)$$

Introducing natural thermal fluctuations into this expression, $W - W_o = kT$ and Equation 1.6 for W_o , Debye showed that the fluctuation in the micelle aggregation number is

$$g - g_o = \sqrt{4 g_o \frac{kT}{w_m}} \quad (1.11)$$

For the experimental values of g_0 and w_m determined for the dodecylamine hydrochloride surfactant, $g - g_0$ is of the order of 3.3, indicating that the micelle aggregation number is relatively narrowly dispersed.

Debye's first theoretical model thus introduced the concept of opposing forces (long-range electrical versus short-range van der Waals). It showed the driving force for micelle formation to be the attractive van der Waals interactions whereas the finite size of the micelle is determined by repulsive electrostatic forces. It identified a cmc with the recognition that it remains practically constant. From the minimization of the energy of a single micelle, it showed that the micelles are small. From the Taylor expansion analysis of the total energy, the model suggested that the small micelles are narrowly dispersed in their sizes. Because the model was based on minimizing the energy of a single micelle, it can be viewed as a precursor to what later evolved as the pseudophase model of micelle formation. However, it is different from the pseudophase model because in a pseudophase, the energy of a molecule that constitutes the pseudophase is a minimum whereas in the Debye model, the energy of the micelle (and not of a single soap molecule within it) is a minimum.

1.4 EVOLUTION OF THEORIES ADDRESSING THE SHORTCOMINGS OF THE DEBYE MODEL

The pioneering theory of Debye stimulated other theoretical studies on micellization; some of which attempted to improve on the Debye theory without questioning the basic model whereas others attempted to correct some of the critical omissions of the Debye theory. Debye had already noted that the role of the addition of electrolyte to the surfactant solution needed to be worked out. He argued that because in an electrolyte solution, every charge will be surrounded by an excess of ions of the opposite sign, its electrical action will be screened out for larger distances. Therefore, an added electrolyte will screen the action of the charges on the micelle, reduce the electrical work W_e , and therefore increase the equilibrium size of the micelle. This analysis was quantitatively developed by Hobbs [21], who extended the Debye theory to a solution containing electrolytes by applying the Debye–Hückel approximation to estimate the salt-induced change in the ionic interaction energy. He obtained expressions for the increase in the micelle size and decrease in the cmc as a function of the added salt concentration. However, the validity of the Debye model was not questioned. Hobbs also estimated the electrostatic interactions between the two charged surfaces of the lamellar micelle. In the absence of any salt, he estimated that these interactions may account for 20% of the total electrostatic energy and could thus reduce the equilibrium micelle size and increase the cmc.

Ooshika [22] and Reich [23] questioned some of the fundamental concepts underlying the Debye theory. In building a theory based on McBain's lamellar aggregate, Debye did not include any energy contribution to account for the fact that the curved surface of the aggregate is exposed to water. The need for adding such a surface energy component to the micelle energy was pointed out by Ooshika and Reich. Ooshika showed that it is the surface energy, rather than the van der Waals interactions between tails proposed by Debye, which opposes the repulsive head group interaction energy in determining the size of the micelle. Ooshika and Reich also questioned the validity of minimizing the energy of a single micelle as a criterion for equilibrium rather than minimizing the energy of the entire system, which would also include the solution entropy.

1.4.1 OOSHICA MODEL

Ooshika [22] pointed out that in the equilibrium state, there must be aggregates of various sizes and shapes, and their distribution is to be determined by statistical mechanics. However, if the size (aggregation number) of a micelle is large, the mixing entropy of the micelles in the solution is negligible when compared against that of monomers, and the cmc may be regarded as

the point where a kind of phase change occurs (a view recognized as the pseudophase model for micelles). Therefore, the cmc is not appreciably affected by the distribution of the micelle sizes. The finiteness of micelles at the cmc has been attributed by Debye to the counterbalance of the van der Waals attractive energy of the hydrocarbon tails and the Coulomb-repulsive energy of the polar heads. Ooshika argued that in ordinary phase changes, the phase that has a lower free energy tends to grow infinitely because of the surface energy and not because of the additive van der Waals energy. Hence, it is clear that one must add to the free energy of micelle formation, the surface energy between the micelle and water. The surface energy of the micelle is proportional to the circumferential area $2\pi RH$ that is exposed to water, where H denotes the thickness of the lamellar aggregate. Because the volume $\pi R^2 H$ of the micelle is proportional to the aggregation number g , the circumferential area $2\pi RH$ will be proportional to $g^{1/2}$. Adding this contribution to the energy model of Debye, Ooshika proposed

$$W = W_e + W_m + W_s = g^{3/2} w_e - g w_m + g^{1/2} w_s \quad (1.12)$$

where w_e and w_m are constants determined by particular surfactants as defined earlier, and w_s is a characteristic surface energy constant.

To take into account the system entropy contribution to the total free energy, Ooshika considered the system composed of N_1 soap molecules in the solution, N_2 soap molecules incorporated into the micelles, and N_w water molecules. The free energy of mixing of these components in the solution is written as

$$F_{\text{mix}} = -kT \left[N_1 \ln \frac{N_1}{N_w + N_1 + \frac{N_2}{g}} + N_w \ln \frac{N_w}{N_w + N_1 + \frac{N_2}{g}} + \frac{N_2}{g} \ln \frac{N_2/g}{N_w + N_1 + \frac{N_2}{g}} \right] \quad (1.13)$$

$$F_{\text{mix}} \approx -kT \left[N_1 \ln \frac{N_1}{N_w + N_1} + N_w \ln \frac{N_w}{N_w + N_1} \right]$$

where k is the Boltzmann constant and T the absolute temperature. The three terms appearing in the first equality in Equation 1.13 represent the entropic contributions from the monomeric surfactant, solvent water, and micelles, respectively. Because the aggregation number g is appreciably larger than 1, the number of micelles N_2/g will be much smaller than N_1 and N_w . Therefore, the first equality in Equation 1.13 can be simplified to obtain the second equality as shown. Effectively, the relatively smaller contribution from the entropy of micelles is neglected. Combining the interaction energy (Equation 1.12) and the free energy of mixing (Equation 1.13), Ooshika obtained (for the free energy of the system) the expression,

$$F = -kT \left[N_1 \ln \frac{N_1}{N_w + N_1} + N_w \ln \frac{N_w}{N_w + N_1} \right] + N_2 \left(\frac{W}{g} \right) \quad (1.14)$$

The cmc, $X_C = N_1/(N_1 + N_w)$ and the equilibrium micelle size (the aggregation number g_o) are determined by minimizing the total free energy with respect to the independent variables N_1 and g , holding the total soap molecules $N_1 + N_2$ and water molecules N_w at constant values, respectively. One obtains,

$$kT \ln X_C = \frac{W_o}{g_o}, \quad g_o = \frac{w_s}{w_e} \quad (1.15)$$

Introducing the expression for W_o (Equation 1.12 with $g = g_o$) in Equation 1.15, the cmc can be expressed as

$$kT \ln X_C = 2\sqrt{w_e w_s} - w_m, \quad g_o = \frac{w_s}{w_e} \quad (1.16)$$

Clearly, in contrast with the Debye theory, the equilibrium micelle size g_o is obtained from the counterbalance of the surface energy and the electrostatic head group interactions. Correspondingly, the cmc also shows an explicit dependence on the surface energy.

1.4.2 REICH MODEL

The Debye and Ooshika models, in which the electrostatic head group interactions play a central role, are not applicable to nonionic detergents. Reich [23] proposed that a general theory of micelles should be developed, starting from a treatment of nonionic surfactants for which the electrostatic interactions are not relevant. He also criticized the Debye theory for the same reasons as Ooshika, namely, the stable micelle size must be that which results in minimum free energy for the system and not the work of formation of a micelle. He argued that the growth of micelles will involve a decrease in the total number of independent species (singly dispersed surfactant molecules and micelles) in the system, and hence will involve a decrease in total system entropy, which must be taken into account. Furthermore, Reich suggested that the van der Waals energy of hydrocarbon chain per surfactant molecule must increase as the micelle grows, arguing that if it remained constant, as in the Debye model, then growth beyond a dimer would not occur. This last feature is an early recognition by Reich of the need for cooperativity of aggregation, characteristic of micelle formation, and is discussed in detail in Section 1.8.

Reich expressed the free energy of the system described by the equilibrium relation in Equation 1.1 as

$$\ln X_g = \ln K_g + g \ln X_1 = -\frac{\Delta G^\circ}{kT} + g \ln X_1 = \frac{T\Delta S^\circ - \Delta E^\circ}{kT} + g \ln X_1 \quad (1.17)$$

where ΔS° and ΔE° are the entropy and enthalpy changes associated with micelle formation. For calculating ΔS° , he assumed a constant entropy change s per molecule, on micelle formation, which is independent of the size of the micelle. To calculate the energy change ΔE° for the nonionic detergent, he considered the changes experienced by the aliphatic hydrocarbon tail of the detergent on micelle formation. For an aliphatic hydrocarbon tail in water, the molecule will show a tendency to fold up so that the segments of the chain can escape from water and remain in contact with each other. He assumed that each hydrocarbon tail was a tightly packed sphere, excluding any water and with a surface area A_H . Of this surface area A_H , a portion a_p is covered by the polar group, whereas the remainder, $A_H - a_p$, will be the exposed hydrocarbon surface. The surface energy of this single molecule is denoted by Υ . Micelle formation causes a fraction of the original exposed hydrophobic surface to be protected from water. This protected fraction multiplied by $(-\Upsilon)$ provides the surface energy change on aggregation. For g surfactant molecules in the nonaggregated state, the exposed hydrocarbon surface area is $g(A_H - a_p)$. For g molecules in spherical micelles, the exposed hydrocarbon surface area is $(g^{2/3}A_H - ga_p)$. Therefore, the fraction of hydrocarbon surface exposed to water that is eliminated on aggregation is $(gA_H - g^{2/3}A_H)/(gA_H - ga_p)$. Reich defined aggregates of the size g_{com} at which the surface becomes completely covered with polar groups as “complete micelles,” namely,

$$\frac{gA_H - g^{2/3}A_H}{gA_H - ga_p} = \frac{A_H}{A_H - a_p} (1 - g^{-1/3}) = 1 \quad \text{at} \quad g = g_{com} \quad (1.18)$$

If an aggregate grew larger than the complete micelle size and still remained spherical, the surface would not be able to accommodate all the polar groups. Some polar groups would have to be buried in the interior (this is unlikely energetically). Such large aggregates would presumably be flattened sufficiently to create enough extra surface to accommodate all the polar groups. Thus, as g increases beyond the complete micelle size g_{com} , the aggregates become larger and flatter. The fraction of the hydrocarbon surface eliminated remains at 1.

Accordingly, for values of g less than that of the complete micelle, Equation 1.17 becomes

$$\ln X_g = \frac{Tsg + gY \left[\frac{A_H}{A_H - a_P} \right] \left[1 - g^{-1/3} \right]}{kT} + g \ln X_1 \quad (1.19)$$

whereas for values g exceeding that of the complete micelle (fractional surface removed is 1 in this case), it becomes

$$\ln X_g = \frac{Tsg + gY}{kT} + g \ln X_1 \quad (1.20)$$

Reich was able to calculate and plot a micelle size distribution based on the above equation for a nonionic surfactant. To estimate the entropy change s per molecule, he calculated the standard entropy change for condensing a hydrocarbon molecule from vapor state to liquid state, holding the density constant. He recognized that there would be some contribution from the entropy change associated with the polyoxyethylene type head group of the surfactant, although it could not be estimated. He calculated the energy parameter Y from consideration of the macroscopic interfacial free energy for a hydrocarbon.

The calculated size distribution function (Figure 1.4) showed (i) how the concentrations of the micelles of sizes different from the complete micelle fall off sharply; (ii) how the chemical potential of the surfactant, or explicitly, the concentration of the unaggregated surfactant controls the micelle

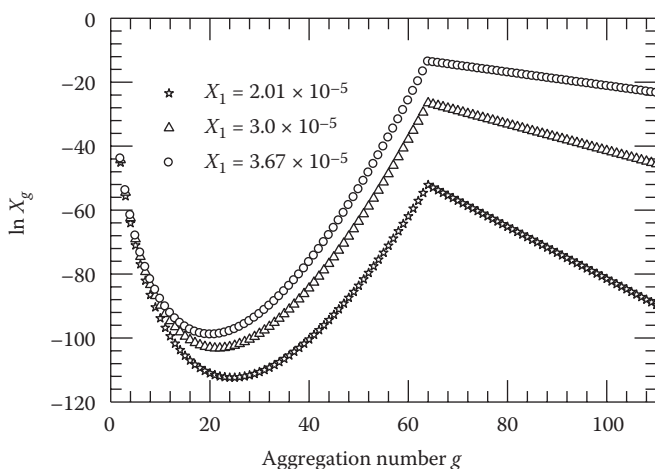


FIGURE 1.4 Size distribution of micelles calculated by the Reich model for a nonionic detergent at different monomer concentrations. Parameters used in the computations are $A_H = 4a_P$, $s = -20$ k, and $Y = 30$ kT, all taken from the article by Reich. (From I. Reich, *J. Phys. Chem.*, 60, 257–262, 1956.)

size distribution; (iii) the sharpness of the cmc and the narrow size distribution of the micelles; and (iv) that the size of the complete micelle depends on the ratio a_p/A_H . All these features are qualitatively valid for what we know to be the properties of nonionic detergents. However, because of the definition of the complete micelle, the most probable micelle size always remained that of the complete micelle without being affected by the total surfactant concentration.

Reich also discussed the problem of the McBain micelle. In this case, the micelle is assumed to grow in two dimensions, with the hydrocarbon chains aligned parallel to each other and the polar groups covering the flat faces. Irrespective of the size of such an aggregate, the hydrocarbon–water interface will never be eliminated completely because the detergent molecules at the edge will have their hydrocarbon chains exposed to water. In developing an expression for the energy change in the McBain micelle, which follows similar considerations as the spherical micelle, Reich showed that the formation of the McBain micelle would indeed correspond to a condition of phase separation, a conclusion that we currently understand for lamellar aggregate shapes.

1.5 EMERGENCE OF A THEORY FOR RODLIKE MICELLES

Early discussions on micelle shapes did not include consideration of the rodlike micelles as we recognize them presently. Philippoff [17] analyzed osmotic activity, specific conductivity, and x-ray data obtained at various electrolyte and surfactant concentrations and for various surfactant tail lengths and identified two regimes with respect to micellar shapes. In the first regime, which corresponds to zero or a small amount of electrolyte, micelles are practically spherical in the sense that they need not be true spheres but can be cubes, short cylinders, prisms, or spheroids. In the other regime, which corresponds to large electrolyte concentrations and longer tail lengths of surfactants, the aggregates are anisometric and large. Philippoff considered that it is improbable for small micelles to reorganize into large micelles with increasing salt and surfactant concentrations and therefore postulated the large structures to be secondary aggregates of the preformed primary micelles.

The formation of rodlike micelles as we understand them currently was first proposed by Debye and Anacker [41] based on light scattering measurements on solutions of cationic alkyl trimethyl ammonium bromides in the presence of added salt, KBr. They concluded that the dissymmetry measurements were not in agreement with the formation of spherical micelles and cylindrical lamellar micelles but agreed with micelles being very large and rodlike at high concentrations of added salt. They proposed that “the cross-section of the rod would be circular with the polar heads of the detergent lying on the periphery and the hydrocarbon tails filling the interior. The ends of such a rod would most certainly have to be rounded off with polar heads.” They observed that the effect of salt on micelle growth was more significant, the longer the tail length of the surfactant. A number of studies that followed confirmed the formation of such large rodlike micelles, as summarized in the article by Anacker [42].

The polydispersed nature of rodlike micelles was first recognized by Scheraga and Backus [43]. They conducted flow birefringence measurements in solutions of cetyltrimethylammonium bromide (CTAB) and concluded that large asymmetrical aggregates are formed whose length increases with increasing salt concentration. More importantly, they found that a monodispersed aggregate model does not describe the experimental data and that aggregates must be highly polydispersed. They provided an interpretation for this size distribution by arguing that for spherical micelles formed at low salt concentrations, relatively high energies are involved (based on Debye’s theory) if the micelle size is to be changed by more than two or three monomers. Hence, the small micelles should have narrow size distributions. In contrast, at high salt concentrations, the charged groups become shielded so that it does not require much work to be done to bring up more molecules. This would increase the mean micelle size and also lead to a high polydispersity. They also speculated as to the bending and flexibility of the micelles, although these features were not explored.

The existence of viscoelastic behavior in surfactant solutions was first discovered by Pilpel [44,45], based on rheological studies on aqueous solutions of sodium and potassium oleate in the presence of electrolytes. He interpreted the viscoelasticity as arising from a change in shape of the aggregates, with the small soap micelles formed at low electrolyte concentrations transforming to long interlinked cylinders at high electrolyte concentrations.

1.5.1 HALSEY MODEL

The first theoretical concept to describe rodlike micelles was proposed by Halsey [24]. As discussed previously, two factors that limit the growth of micelles and permit them to exist without phase separation had been proposed: one is the geometrical limit of chain length proposed by Hartley as the limiting radius of spherical micelles and the other is the repulsive interactions between the head groups at the micelle surface proposed in the Debye model (applied to the McBain–Harkins cylindrical portion of a lamellar micelle). Halsey [24] examined the growth of micelles avoiding both of these limitations, which resulted in finite stable aggregates without causing phase separation. Using Debye's approach, Halsey compared the energetics of one-dimensional growth of micelle as a disk and as a rod.

Halsey calculated the electrical potential at a small distance z from the end of a long rod of length $L = nz_0$, where z_0 is a characteristic distance between charges and w_e is the characteristic electrical energy appearing in the Debye model for electrostatic head group interactions. For large n , the potential will be

$$w_e \int_{z_0}^{nz_0} \frac{dz}{z} = w_e \ln n \quad (1.21)$$

The total electrical work of forming a cylindrical micelle of size g is given by

$$W_e = \int_1^g w_e \ln n \, dn = w_e [g \ln g - g + 1] \quad (1.22)$$

Comparing this expression for electrical energy of cylinders with the Debye expression (Equation 1.4) $W_e = w_e g^{3/2}$, for lamella, Halsey noted that the function $(g \ln g - g + 1)$ varies more slowly than $g^{3/2}$ as g increases. Therefore, he concluded that for large g , a rodlike micelle will correspond to lower energy and hence the more stable aggregate compared with a disk. He argued that because the surfactant molecules approaching one end of a long rod would feel only the near end, the rod length should have no effect on the total energy. This would make the length of the rod to be infinite. Because this is not the case, he proposed that the finite size of the micelles can be explained by the analogy between rodlike micelles and a one-dimensional gas (molecules fixed on a string like beads). Just as a one-dimensional gas does not condense whatever may be the nature of interactions, the rodlike micelles remain finite and do not cause phase separation. The micelles can be polydispersed analogous to the distribution of a linear polymer in equilibrium with the monomer. As for the other two smaller dimensions of the rodlike micelle, Halsey observed that one dimension must be limited by the length of the hydrocarbon chain and the second can either be limited by electrical forces (as in the Debye model) or by the length of the hydrocarbon chain (based on the structural description proposed by Hartley). Halsey's conclusions as to the large micelles being cylindrical, finite in size, polydispersed, and that such micelle formation is different from phase separation remain valid today.

1.6 STATISTICAL MECHANICAL THEORIES OF MICELLES

With the development of fundamental statistical mechanical models describing liquid state, such formalisms were also applied to describe the formation of micelles. Two of the significant contributions are due to Hoeve and Benson [25] and Poland and Scheraga [26,27] because, in both of their models, the free energy of formation of micelles was decomposed into many individual contributions identified in molecular terms similar to more recent predictive theories. These studies more clearly enumerated the various factors contributing to the free energy of micellization, including the hydrophobic effect associated with the transfer of surfactant tail from water to micelle and the surface energy associated with the exposed hydrophobic surface of the micelle.

1.6.1 HOEVE AND BENSON THEORY

In Hoeve and Benson's treatment [25], the micelles are thought to be aggregates of the hydrocarbon parts of the molecules, with the polar parts on the outside of the aggregate in contact with water. It was assumed that a spherical shape persists until the micelle becomes large enough that the radius of the sphere would exceed the maximum length of the hydrocarbon part of the molecule. When that occurs, the micelle is assumed to become flatter, leaving the polar parts fully hydrated and an oblate spherocylinder shape was assumed. The interior of the micelle is assumed to have properties similar to that of a liquid hydrocarbon. It is assumed that the system may be treated by classic partition functions, apart from contributions of vibrations, which are considered to be quantized and separable.

Aggregates of all sizes g are assumed to exist, with N_g being the number of aggregates of size g . For solutions of nonionic detergents in water, the most probable micelle size distribution is determined by minimizing the free energy F or maximizing the canonical partition function Q of the solution (note, $F = -kT \ln Q$). Hoeve and Benson obtained

$$\begin{aligned} \ln N_1 &= \ln \left(\frac{Q_1 V}{\Lambda_1^3} \right) + \lambda, & \ln N_g &= \ln \left(\frac{Q_g V}{\Lambda_g^3} \right) + \lambda g \\ \ln N_g &= \ln \left(\frac{Q_g V}{\Lambda_g^3} \right) - g \ln \left(\frac{Q_1 V}{\Lambda_1^3} \right) + g \ln N_1 \end{aligned} \quad (1.23)$$

where V is the system volume over which all the aggregates translate, Q_1 and Q_g are the internal partition functions for the unaggregated molecule and an aggregate of size g , Λ_1 and Λ_g are factors appearing in the external translational/rotational partition functions for the monomer and aggregate, and λ is the Lagrange multiplier that links the two equations providing an expression for the size distribution of aggregates. The translational/rotational terms Λ_1 and Λ_g are given by

$$\begin{aligned} \Lambda_g &= \Lambda_g^{\text{trans}} \Lambda_g^{\text{rot}} = \left(\frac{h^2}{2\pi m g k T} \right)^{1/2} \left(\frac{h^2}{2\pi I_g k T} \right)^{1/2} \\ \Lambda_1 &= \Lambda_1^{\text{trans}} \Lambda_1^{\text{rot}} = \left(\frac{h^2}{2\pi m k T} \right)^{1/2} \left(\frac{h^2}{2\pi I_1 k T} \right)^{1/2} \end{aligned} \quad (1.24)$$

where m is the mass of a surfactant molecule, h is the Planck constant, and I_1 and I_g are the average moments of inertia of a monomer and aggregate of size g , respectively.

To evaluate Q_g for the aggregate, multiple contributions were considered. First, the assumption that the interior of a micelle is liquid in character was used. Hoeve and Benson suggested that

because paraffinic hydrocarbons are not appreciably curled up in the liquid state, the contributions to the partition function of a hydrocarbon liquid are separable, and they wrote down the following liquid state contribution to Q_g .

$$Q_g^{\text{liq}} = \frac{1}{g!} \left[\left(\frac{2\pi m g k T}{h^2} \right)^{3/2} V_f \left(\frac{2\pi I_h k T}{h^2} \right)^{3/2} 8\pi^2 \gamma \right]^{g-1} q_h^g \quad (1.25)$$

Here, I_h is the moment of inertia of the hydrocarbon chain, q_h is the vibrational partition function for the chain, V_f is the free volume within the liquid phase where molecular translation occurs, and γ is the rotational free angle ratio accounting for the hindered rotation in the hydrocarbon liquid.

A second contribution comes from the recognition that the aggregate is a small liquid drop and therefore has a surface contribution. For a spherical drop of g molecules, with each molecule having a surface area A_H , the drop surface area is $g^{2/3} A_H$. The surface area A_H is calculated from the radius r_o of a hypothetical sphere whose volume is identical to that of the surfactant tail. Hoeve and Benson proposed the surface contribution as the product of the surface area and a characteristic interfacial energy σ between the drop and water.

$$Q_g^{\text{sur}} = \exp - (A_H g^{2/3} \sigma) = \exp - (4\pi r_o^2 g^{2/3} \sigma) \quad (1.26)$$

Hoeve and Benson then considered a third contribution to account for the constraint that in the micelle all ends of the hydrocarbon chains to which the polar heads are attached must be at the surface of the micelle, whereas in the liquid drop, the corresponding ends may occupy any position within the drop. The contribution of bringing the chain ends to the surface, resulting in head group crowding, was approximated as follows. Before bringing the ends to the surface, the free volume available for them is proportional to the micellar core volume $V_g = g v_o$, with v_o denoting the volume of a surfactant tail. After bringing the ends to the surface, the free volume is proportional to the free surface area available for them, which is assumed to be the difference between the surface area of the spherical micelle A_g and the space $g a_p$ occupied by the g head groups already at the surface, that is, $A_g - g a_p$. Consequently, this contribution was written as proportional to the free volume restriction on micelle formation.

$$Q_g^{\text{crowd}} = C \left(\frac{A_g - g a_p}{V_g} \right) \quad (1.27)$$

Finally, a fourth contribution was recognized for nonionic surfactants with polar parts that are long polar chains (such as in the most common nonionic surfactant family with oligoethyleneoxide head groups), which strongly interact with the solvent and possess internal degrees of freedom. Using q_p , they denoted the contribution of the polar head due to internal vibrations and rotations and interactions with the solvent. Therefore,

$$Q_g^{\text{head}} = (q_p)^g \quad (1.28)$$

Combining all of these contributions, one can write

$$Q_g = Q_g^{\text{liq}} Q_g^{\text{sur}} Q_g^{\text{crowd}} Q_g^{\text{head}} \quad (1.29)$$

Following the same approach as for the micelle, Hoeve and Benson considered an expression for the partition function Q_1 of the monomer. In evaluating Q_1 , the contributions from the polar part and the hydrophobic chain were separated, which is similar to what was done for the aggregate. Because the polar parts are assumed to remain in the water phase, q_p has the same contribution per molecule for micelles and for the single molecule. Similarly, the internal vibrational contribution q_h is also the same for the monomer as for the molecule in an aggregate. However, the contribution of the hydrocarbon part interacting with the surrounding water could not even be approximately evaluated. They recognized that structural effects exist in the water surrounding the hydrocarbon parts of the single molecules, and that the model of a liquid drop cannot be valid here. It was felt that only after gaining a better understanding of these effects could the contribution of the hydrocarbon part be quantitatively obtained. Keeping it as an unknown molecular partition function q_w , the overall partition function of the monomer was written as

$$Q_1 = q_w q_h q_p \quad (1.30)$$

By introducing the partition functions (Equations 1.29 and 1.30) in the expression for aggregate size distribution (Equation 1.23), Hoeve and Benson were able to identify some general features of the micellization of nonionic surfactants.

The illustrative size distribution curves they calculated for two different monomer concentrations are shown in Figure 1.5. The size distribution function was calculated showing a minimum and maximum in the size distribution and without the piecewise continuity introduced by Reich because of his postulate of a complete micelle. As a result, the maximum in the size distribution could be seen to change with increasing surfactant concentration, although only a little, and not fixed to one micelle size (g_{com} of the complete micelle) as in the Reich model. The cmc phenomenon is also evident because the amount of surfactant incorporated into the aggregates (excluding monomers) increases from approximately 10^{-8} to 2.64×10^{-4} and 21.2×10^{-4} for the three monomer concentrations shown in Figure 1.5. A small decrease in the monomer concentration close to the cmc makes the aggregate concentration close to zero. A small increase in the monomer concentration close to the cmc causes an order of magnitude increase in the amount of surfactants present as aggregates.

The work of Hoeve and Benson is important for many reasons. It was the first formal application of the statistical mechanical formulation to micelle formation, even though the need for such

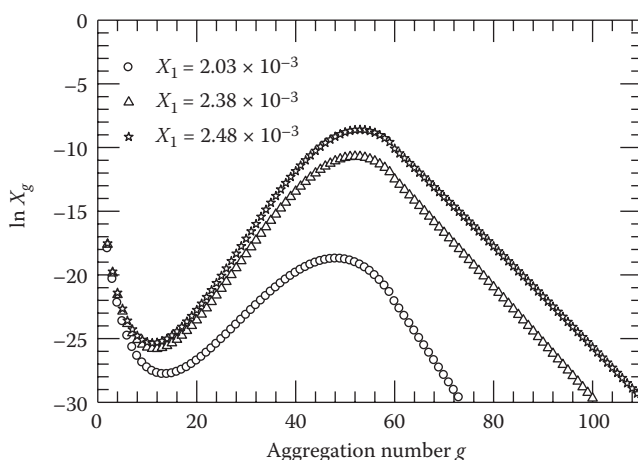


FIGURE 1.5 Size distribution of micelles calculated using the Hoeve and Benson model for a nonionic detergent at three different monomer concentrations. The parameters for the molecule used in the computations are identical to those used in the article by Hoeve and Benson [25].

an application was foreseen in the work of Ooshika, Reich, and Halsey. The formulation required the identification of multiple contributions to the partition function (or the free energy) and three important new contributions were identified compared with all previous studies that had identified van der Waals, electrical, and surface contributions. First, the treatment identified the importance of considering the molecular translational and rotational contributions, and these are part of the chain packing contributions we consider in current predictive theories. Second, by accounting for the crowding of head groups at the micelle surface for the nonionic surfactants, Hoeve and Benson were the first to propose a clear free energy contribution responsible for the finiteness of micelle size for nonionic surfactants. Third, Hoeve and Benson were the first to explicitly recognize that water structural changes will provide a critical contribution to the free energy and a more fundamental understanding of these structural changes is required before a quantitative predictive model of micelles can be developed. The subsequent work of Poland and Scheraga [26,27] and of Tanford [28–30] indeed emphasized detailed structural descriptions of these water structure changes and the quantitative and accurate estimation of the corresponding hydrophobic free energy.

Concerning ionic micelles, Hoeve and Benson noted that the micelles are highly charged and therefore the Debye–Hückel approximation is not adequate to describe ionic micelles. In applying the Poisson–Boltzmann equation, the challenge was to account for the fact that the counterions in the neighborhood of the micelle are crowded, even if the solution has a low concentration of ions. Another difficulty they pointed out related to the question of how “rough” the micelle surface is. Because the concentration of counterions is quite large in this region, the electrical free energy would be rather sensitive to the degree of roughness of the surface. These features relevant to the estimation of electrostatic interactions at the micelle surface remain unsatisfactorily explored even today and limit our ability to accurately predict aggregation properties in the presence of a variety of counterions, especially the counterion specificity in promoting a transition from spherical to rod-like micelles.

1.6.2 POLAND AND SCHERAGA THEORY

Poland and Scheraga [26,27] undertook the modeling of micelle formation as an illustration of the hydrophobic effect for which Nemethy and Scheraga [46–48] had developed a quantitative theory just a few years earlier. To simplify the calculations, instead of considering a size distribution of micelles, Poland and Scheraga [26] considered a system containing N surfactant molecules, present in the form of N_g micelles of size g . The equilibrium properties of the micelle were determined from the minimization of the free energy $F(g)$ of the system with respect to the micelle aggregation number g . Poland and Scheraga considered spherical micelles with polar heads on the surface and nonpolar tails in the interior partially coiled up (with some freedom of internal motion) and interacting with each other through hydrophobic bonds. The free energy of formation of these bonds was quantitatively estimated from the theory of hydrophobic bonding developed by Nemethy and Scheraga. They constructed a partition function Q_g for the micelle with g constituent molecules, by identifying an external contribution, an internal contribution, and a solvent interaction contribution.

$$F(g) = -kT \ln \left(\frac{Q_g^{N_g}}{N_g!} \right), \quad Q_g = Q_g^{\text{ext}} Q_g^{\text{int}} Q_g^{\text{sol}} \quad (1.31)$$

$$-\frac{F(g)}{NkT} = \frac{1}{g} \ln \frac{eQ_g}{N_g} = \frac{1}{g} \ln \frac{eQ_g^{\text{ext}}}{N_g} + \frac{1}{g} \ln Q_g^{\text{int}} + \frac{1}{g} \ln Q_g^{\text{sol}}$$

The external contribution is taken as the product of the classic partition functions for the translation and rotation of the micelle as a whole, similar to that in Hoeve and Benson’s theory.

$$Q_g^{\text{ext}} = \left[\left(\frac{2\pi m g k T}{h^2} \right)^{3/2} V_f \left(\frac{2\pi I_h k T}{h^2} \right)^{3/2} 8\pi^2 \gamma \right]^{g-1} \quad (1.32)$$

Here, I_h is the moment of inertia of the hydrocarbon chain, q_h is the vibrational partition function for the chain, V_f is the free volume within the liquid phase where molecular translation occurs, and γ is the rotational free angle ratio accounting for the hindered rotation in the hydrocarbon liquid.

The internal partition function corresponds to the internal freedom of the micelle arising from the motions of the hydrocarbon tails. A monomer molecule in a micelle will make two large contributions to the internal partition function. One is the motion of the monomer molecule as a whole within the micelle and the other is the internal rotation (including complex vibrations and torsional oscillations) in the hydrocarbon tails. Because the latter is included in the hydrophobic bond energy per molecule and is accounted for as part of the solvent contribution discussed below, only the contribution of the former had to be included in Q_g^{int} . To account for the internal motion of the monomer in the micelle, they considered two approaches. In one, a free volume viewpoint is taken and the internal motion is treated as a translation; in the other, the micelle is treated as a lattice and the permutations of monomers in the lattice are calculated. From both approaches, they obtained essentially the same dependence of Q_g^{int} on g . Taking the free volume approach,

$$Q_g^{\text{int}} = \frac{1}{g!} \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} V_f \right]^g, \quad V_f = V_{\text{sh}} \left(\frac{g-1}{g} \right) \quad (1.33)$$

In Equation 1.33, V_{sh} is the volume of a spherical shell within which all the head groups are constrained to translate and the factor $(g-1)/g$ represents the fact that the volume occupied by a molecule is not available to it for translation.

For calculating the solvent interaction partition function, they applied the results from the theory of hydrophobic bonding developed by Nemethy and Scheraga. In the monomeric state, the entire surface area of the surfactant tails comprises the hydrophobic surface exposed to water. In the micellar state, only the surface of the spherical micelle, excluding the space occupied by the head groups, comprises the hydrophobic surface exposed to water. Therefore, one can calculate the fraction θ_H of the total hydrocarbon surface involved in hydrophobic bonding, similar to that done by Reich. Poland and Scheraga expressed the solvent interaction contribution as the product of this fractional area of exposure θ_H involved in hydrophobic bonding and the hydrophobic bond energy ΔF_H per molecule. The hydrophobic bond energy per molecule had been estimated from Nemethy and Scheraga's theory of hydrophobic bonding as a function of temperature and the chain length of the molecule. The solvent interaction partition function is given by Equation 1.34. Here, for the hydrophobic bond energy, they used a temperature-dependent expression (which they established for amino acids) with the constants c_1 , c_2 , and c_3 taken to correspond to alanine-alanine bonds. The fractional area of exposure is approximated in the last step by neglecting the area a_p covered by the head group in comparison with the surface area A_H of a tail.

$$Q_g^{\text{sol}} = \exp \left[- \frac{g \Delta F_H}{RT} \theta_H \right], \quad \Delta F_H = c_1 + c_2 T + c_3 T^2 \quad (1.34)$$

$$\theta_H = \frac{g A_H - g^{2/3} A_H}{g A_H - g a_p} = \left[\frac{A_H}{A_H - a_p} \right] [1 - g^{-1/3}] \approx [1 - g^{-1/3}]$$

Poland and Scheraga [27] also extended their treatment to ionic surfactants by including an electrostatic free energy for spherical micelles. They calculated this free energy by considering the Coulombic interactions between the charged head groups similar to the model of Debye, but applied to a spherical surface of radius R . As mentioned previously, the radius R is related to the aggregation number g through the relation $R = r_o g^{1/3}$, where r_o denotes the radius of a spherical hydrocarbon droplet whose volume is equal to that of a single surfactant tail. Therefore, the electrostatic partition function was represented as

$$Q_g^{\text{ele}} = \exp \left[\frac{ge^2}{2\epsilon R} \right] = \exp \left[\frac{ge^2}{2\epsilon r_o g^{1/3}} \right] \quad (1.35)$$

Combining the different free energy contributions, the overall dependence of the free energy $F(g)$ on the aggregation number has the form

$$\frac{F(g)}{NkT} = -\frac{1}{g} (\alpha - \ln X + 5 \ln g) + \frac{\Delta F_H}{RT} (1 - g^{-1/3}) - \beta + \frac{1}{3} \ln g + \gamma g^{2/3} \quad (1.36)$$

where α is extracted from the external free energy term (Equation 1.32), X is the surfactant concentration, β is extracted from the internal free energy term (Equation 1.33), and γ is extracted from the electrostatic energy term (Equation 1.35). Note that β and γ are relevant only for the micelle and will not appear in the free energy of a monomer.

Poland and Scheraga specified three conditions to obtain a stable micelle in a system containing N surfactant molecules: (C1) the free energy $F(g)$ of the solution of micelles must be an extremum ($\partial F/\partial g = 0$), (C2) the extremum must be a minimum ($\partial^2 F/\partial g^2 < 0$), and (C3) the free energy of the system of micelles $F(g)$ should be lower than the free energy of the system of monomers, $F(1)$. These three conditions lead to the following three constraints, respectively, on the hydrophobic bond energy, required for the formation of micelle of size g_o , where the last condition has been approximated taking into account that g_o is much larger than 1. Furthermore, if the third condition is made into an equality, it provides the relation for the cmc.

$$\begin{aligned} \text{C1: } \left(\frac{\partial F}{\partial g} \right) &= 0 & \left(-\frac{\Delta F_H}{RT} \right) &= g_o^{1/3} \left[\frac{3}{g_o} (\alpha - \ln X + 5 \ln g_o - 5) + 1 \right] + 2\gamma g_o \\ \text{C2: } \left(\frac{\partial^2 F}{\partial g^2} \right) &< 0 & \left(-\frac{\Delta F_H}{RT} \right) &< \frac{3}{2} g_o^{1/3} \left[1 + \frac{15}{g_o} \right] + 5\gamma g_o \\ \text{C3: } F(g) &< F(1) & \left(-\frac{\Delta F_H}{RT} \right) &> \left[\alpha - \ln X + \frac{1}{3} \ln g_o - \beta \right] + \gamma g_o^{2/3} \end{aligned} \quad (1.37)$$

The conditions for micelle formation based on the above equilibrium requirements are shown in Figure 1.6 as a relation between the hydrophobic bond energy and the micelle size. The first constraint in Equation 1.37 implies that, for a given concentration, micelles will be formed when the values of ΔF_H and g_o lie on the curve C1. The second constraint implies that micelles will form only for ΔF_H and g_o values, which lie below the curve C2. Because the surfactant concentration fixes the curve C1, curves C1 and C2 determine the values of the hydrophobic bond energy and the corresponding micelle size. The second constraint imposes a restriction on the magnitude of ΔF_H for micelle formation to occur. If the hydrophobic bond strength is too large, small oligomers would be preferred to micelles. For lower hydrophobic bond energy, the formation of small oligomers is

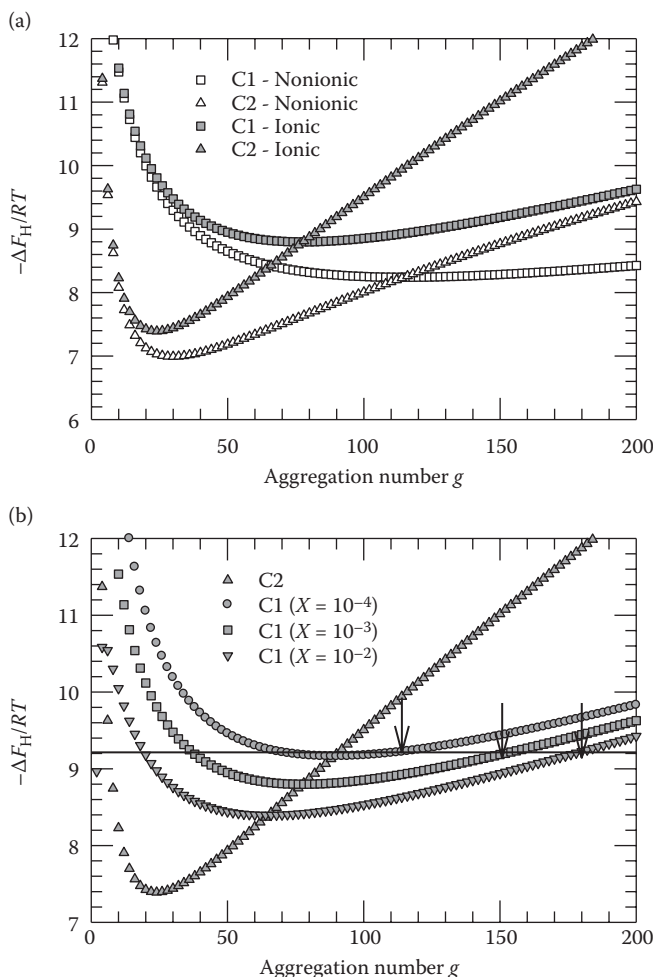


FIGURE 1.6 (a) Poland and Scheraga model predictions of conditions for micelle formation from ionic and nonionic surfactants at a surfactant concentration of $X = 10^{-3}$. Curves C1 and C2 are calculated using Equation 1.37 with the assumed model parameters of $\alpha = 1$, $\beta = 0.2$, and $\gamma = 0.003$. Micelle formation is allowed only for conditions below the curve C2. Equilibrium micelle size at the given concentration X can be found from the line C1 depending on the value of the hydrophobic bond energy of the surfactant. The leftward shift in the intersection of the curves C1 and C2 for the ionic surfactant imply that the equilibrium micelle size for the ionic surfactant will be smaller than that for the nonionic surfactant. (b) Shift in micelle size with a change in surfactant concentration for ionic surfactants. Curve C1 is calculated for three surfactant concentrations whereas curve C2 is independent of concentration. The arrows indicate the predicted equilibrium micelle size for the three concentrations, corresponding to the hydrophobic bond energy of 9.2 units. The micelle size increases with increasing surfactant concentration.

disallowed. Condition C3 indicates whether the concentration for which the curve C1 is constructed is above or below the cmc.

In the Poland and Scheraga model, the external, internal, and solvent interaction free energy contributions for the nonionic surfactants vary gradually when the aggregation number exceeds that of small oligomers, say 10. Correspondingly, the minimum in the free energy for nonionic surfactants is shallow resulting from a delicate balance between the slowly varying free energy contributions. In contrast, for ionic surfactants, the minimum is sharper because of the stronger dependence of the electrostatic energy on the micelle aggregation number. In the Poland and Scheraga treatment, the

hydrophobic effect was fully recognized and the first attempt to employ a reasonable quantitative estimate was made. The residual interfacial contact between the hydrocarbon tail and water was accounted for in the solvent interaction term as in the Reich model rather than treating it as a surface free energy as was done in the Hovee and Benson theory.

1.7 MICELLE SHAPE TRANSITIONS AND SIZE DISTRIBUTION

The free energy models constructed thus far have focused mainly on small micelles having either the lamellar-cylinder (McBain–Harkins micelle) or spherical (Hartley micelle) shape. Subsequent developments in the theory of micelle formation have attempted to construct a unified free energy model for the common aggregate shapes observed in surfactant solutions (Figure 1.7).

The small micelles are spherical in shape. When large rodlike micelles form, they can be visualized as having a cylindrical middle portion and parts of spheres as endcaps. The cylindrical middle and the spherical endcaps can have different diameters. When micelles can no longer pack into spheres (this happens for aggregation numbers for which a spherical aggregate will have a radius larger than the extended length of the surfactant tail), and if at the same time the rodlike micelles are not yet favored by equilibrium considerations, then small nonspherical globular aggregates form. Globular shapes such as prolate and oblate ellipsoids and shapes generated via ellipses of revolution have been proposed for these micelles. Some surfactants pack into a spherical bilayer structure called a vesicle, which 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 inner and outer layers of the bilayer can also be different from one another.

The multiple equilibrium model of micellization (Equation 1.1) can be formally applied to aggregates of any shape and size. Correspondingly, the equilibrium condition corresponding to the minimum of the free energy of a solution made up of monomers, aggregates of all sizes and shapes, and water molecules can be represented in the form shown in Equation 1.38, which stipulates that the chemical potential of the singly dispersed surfactant molecule is equal to the chemical potential per molecule of an aggregate of any size and shape. In the multiple equilibrium description, each aggregate of a given size and shape is treated as a distinct chemical component characterized by a chemical potential. The conditions corresponding to the formation of aggregates are usually in the

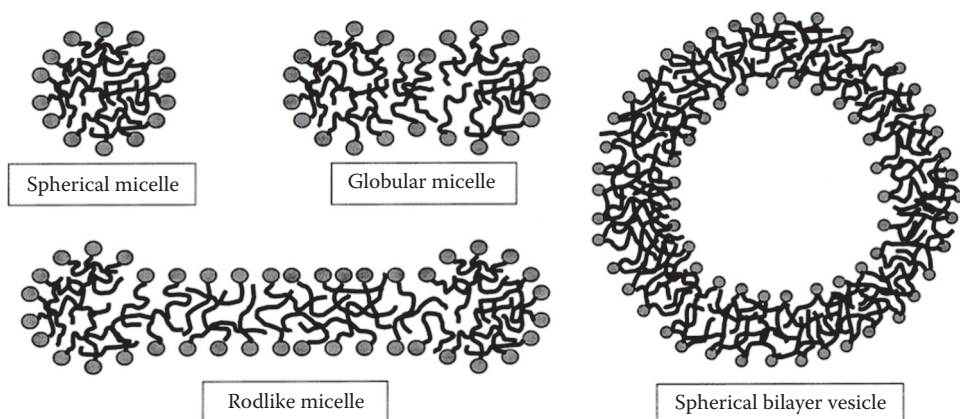


FIGURE 1.7 Schematic representation of surfactant aggregates in dilute aqueous solutions. The structures formed include spherical micelles, globular micelles, rodlike micelles with spherical endcaps, and spherical bilayer vesicles. One characteristic dimension in each of these aggregates is limited by the length of the surfactant tail.

realm of dilute solutions and, for these conditions, one can very simply relate the chemical potential of a component to the concentration of that component in solution, as shown in Equation 1.38.

$$\frac{\mu_g}{g} = \mu_1 \quad (1.38)$$

$$\mu_g = \mu_g^\circ + kT \ln X_g, \quad \mu_1 = \mu_1^\circ + kT \ln X_1$$

Here, μ_g° is the standard state chemical potential of the aggregate of size g having any shape, X_g is its mole fraction in solution, k is the Boltzmann constant, and T is the absolute temperature. The standard state of the solvent is defined as the pure solvent whereas the standard states of all the other species are taken to be infinitely dilute solution conditions. Combining the equilibrium condition with the concentration dependency of chemical potentials, we obtain the aggregate size distribution

$$X_g = X_1^g \exp\left(-\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right) = X_1^g \exp\left(-\frac{g \Delta\mu_g^\circ}{kT}\right) \quad (1.39)$$

Here, $\Delta\mu_g^\circ$ is the difference in the standard chemical potentials between a surfactant molecule present in an aggregate of size g and a singly dispersed surfactant in water. It is this free energy difference that is directly connected to the equilibrium constant K_g for micellization defined in Equation 1.1. To calculate the aggregate size distribution, we need an explicit equation for the standard state chemical potential difference $\Delta\mu_g^\circ$ or equivalently, the equilibrium constant for aggregation, K_g . Most of the theoretical studies in the last 30 years have focused on developing quantitatively accurate expressions for the dependence of this equilibrium constant on g .

Even in the absence of a free energy model for micellization, the thermodynamic relations provide many interesting results pertinent to the self-assembly process [49]. From the micelle size distribution, we can compute average aggregation numbers using the definitions

$$g_n = \frac{\sum g X_g}{\sum X_g}, \quad g_w = \frac{\sum g^2 X_g}{\sum g X_g}, \quad g_z = \frac{\sum g^3 X_g}{\sum g^2 X_g} \quad (1.40)$$

where g_n , g_w , and g_z denote the number-average, the weight-average, and the z-average aggregation numbers, respectively, and the summations extend from 2 to ∞ . The ratios g_w/g_n and g_z/g_w are unity for monodispersed systems and are equal to 2 and 3/2 for systems exhibiting very high polydispersity. Thus, either of these ratios can be used as an index of polydispersity. For a surfactant with any kind of head group, we can show [49] from the size distribution that the average aggregation numbers g_n and g_w depend on the concentration of the micellized surfactant (difference between the total surfactant concentration X_T and the cmc X_C) as follows:

$$\begin{aligned} \partial \ln g_n &= \left(1 - \frac{g_n}{g_w}\right) \partial \ln \sum g X_g, \quad \partial \ln g_w = \left(\frac{g_z}{g_w} - 1\right) \partial \ln \sum g X_g \\ g_n &\propto \left(\sum g X_g\right)^{\left(1 - \frac{g_n}{g_w}\right)}, \quad g_w \propto \left(\sum g X_g\right)^{\left(\frac{g_z}{g_w} - 1\right)}, \quad \sum g X_g = X_T - X_C \end{aligned} \quad (1.41)$$

This equation states that the average aggregation numbers g_n and g_w must increase appreciably with increasing concentration of the micellized surfactant if the micelles are polydispersed; the

average aggregation numbers must be virtually independent of the total surfactant concentration if the micelles are narrowly dispersed. Furthermore, Equation 1.41 shows that the exponent relating the average micelle size to the total surfactant concentration is a direct measure of the aggregate polydispersity. These are purely thermodynamic results independent of any free energy models for micellization. The conclusions of Debye as to the narrow distribution of small micelles and of Halsey on cylindrical micelles being polydispersed are consistent with these thermodynamic results, which are independent of any free energy model.

1.8 COOPERATIVE AND ANTICOOPERATIVE FREE ENERGY FUNCTION

Utilizing an increasing understanding of the energetic factors contributing to the micellization process, particularly with the recognition of hydrophobic interactions, Mukerjee was able to show how one part of the free energy function must promote the growth of the aggregate (the cooperative part) and another part of the free energy function must limit the growth and contribute to the finiteness of the aggregate (the anticooperative part) [36,50–53]. In developing his analysis, Mukerjee also discovered how very subtle changes in the two parts of the free energy function can affect the formation of spherical micelles versus rodlike micelles. As previously mentioned, Reich had already recognized the need for cooperativity in micelle formation for a micelle of some large enough aggregation number to form whereas the formation of dimers, trimers, and other small oligomers is prevented.

1.8.1 REPRESENTATION OF COOPERATIVITY

Mukerjee started with the representation of micelle formation as a stepwise association process.

$$A_1 + A_{g-1} \xrightleftharpoons{k_g} A_g, \quad K_g = \prod_{j=2}^g k_j \quad (1.42)$$

where k_g is the stepwise association equilibrium constant for the formation of a g -mer from the combination of a $(g - 1)$ -mer with a monomer. It is differentiated from the monomer–micelle equilibrium constant K_g defined in Equation 1.1 and is related to it as shown above. The stepwise association equilibrium constant is also directly linked to the free energy change $\Delta\mu_g^\circ$ through the relation

$$-kT \ln k_g = g\Delta\mu_g^\circ - (g-1)\Delta\mu_{g-1}^\circ = \frac{d(g\Delta\mu_g^\circ)}{dg}; \quad -kT \ln K_g = g\Delta\mu_g^\circ \quad (1.43)$$

Thus, the overall monomer–micelle equilibrium constant K_g is directly related to the magnitude of the free energy of micellization $g\Delta\mu_g^\circ$ whereas the stepwise association equilibrium constant k_g is related to the dependence of this free energy on g .

If k_g increases with g , then the larger aggregates are favored over the smaller ones and the system is considered to exhibit positive cooperativity. If k_g decreases with g , then the formation of larger aggregates is increasingly disfavored and the system is said to exhibit negative or anticooperativity. When k_g is independent of g , the association is said to be continuous and noncooperative. In this case, polydispersed aggregates form and their size distribution is monotonically decreasing.

The shielding of the hydrophobic part of the micellar core from water becomes more and more effective with every incremental addition of a surfactant to the micelle. Thus, the incremental change in free energy due to the hydrophobic interactions becomes more negative with increasing size of the micelles. This has the tendency to increase k_g with increasing g . However, as g increases, the micellar surface becomes increasingly crowded with the polar head groups of the surfactants.

Consequently, for every incremental addition of a surfactant to the micelle, the repulsion between the polar head groups increases. This has the tendency to decrease k_g with increasing g .

At the initial stages of aggregation, that is, for relatively small values of g , the incremental change in the hydrophobic interactions is greater than that in the head group repulsions. Hence, there is an initial region of positive cooperativity in which k_g increases with increasing g . Beyond some critical aggregation number, the incremental change in the head group repulsions exceeds that in the hydrophobic interactions. Therefore, beyond a maximum value corresponding to a critical aggregation number, k_g begins to decrease with g , signaling a region of negative cooperativity. When large cylindrical micelles begin to form, the incremental change in the surface area of the micelle per amphiphile becomes a constant. As a result, the incremental addition of a surfactant molecule to the micelle alters neither the incremental changes in the attractive hydrophobic interactions nor the repulsive head group interactions. Consequently, k_g becomes independent of g , indicating a final region of noncooperativity.

1.8.2 COOPERATIVITY AND FORMATION OF CYLINDRICAL MICELLES

Mukerjee [36,51] proposed an empirical equation (Equation 1.44) for the functional dependence of K_g and k_g on g to show that subtle changes in the anticooperative region determine whether small micelles or large cylindrical micelles form.

$$\begin{aligned}
 -\ln K_g &= \frac{g\Delta\mu_g^0}{kT} = 2(g-1)\ln(g-1) - 0.02(g-1)^2 + 2.7896(g-1) \\
 -\ln k_g &= \frac{d(g\Delta\mu_g^0 / kT)}{dg} = 2\ln(g-1) - 0.04(g-1) + 4.7896
 \end{aligned}
 \tag{1.44}$$

Specifically, he considered two situations differing from one another in the value of g where the anticooperative region ends and the noncooperative region begins, as shown in Figure 1.8. Mukerjee showed that when the anticooperative region extends to the aggregation number 116 and beyond, only small spherical or globular micelles with narrow size distribution form. The average size does not

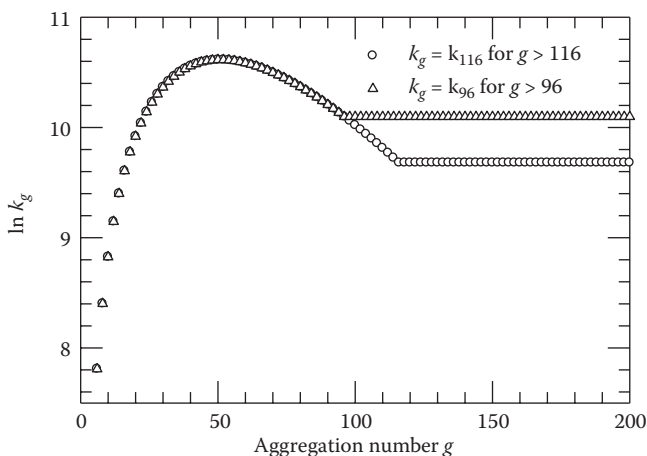


FIGURE 1.8 Schematic representation of the stepwise association equilibrium constant, showing the region of cooperativity and the region of anticooperativity. At large aggregation numbers, when cylindrical micelles form, the stepwise association constant becomes independent of size and is a constant, corresponding to a region of noncooperativity. The stepwise association equilibrium constant shown here is calculated using the empirical Equation 1.44 used by Mukerjee [36,51] to illustrate the phenomena.

change even when the total surfactant concentration is increased by orders of magnitude. In this case, the shallow free energy minimum and its range (determined by where the anticooperative region ends) are favorable enough for the stability of the smaller micelles and a transition to rods does not occur. On the other hand, when the anticooperative region ends at an aggregation number of 96, large polydispersed rodlike micelles form, which significantly change their average size with increasing surfactant concentration. In this case, the range of the shallow free energy minimum is not large enough to assure the stability of the small micelles and a transition to the large micelles occurs.

Mukerjee [50,51] was the first to treat the thermodynamics of rodlike aggregates by recognizing that two characteristic equilibrium constants are necessary to describe their formation. In the stepwise aggregation process, Mukerjee employed an equilibrium constant k_2 for the formation of a dimer that was different from the equilibrium constant k for the subsequent stepwise association for all aggregates larger than the dimer. From the equilibrium relations, Mukerjee showed how the weight average aggregation number g_w of the micelle is related to the concentration of the surfactant in solution and also the dependence of the cmc (X_C) on the equilibrium constants, as follows:

$$g_w = 2 \left(\frac{k}{k_2} \right)^{1/2} \left(\frac{X_T - X_1}{X_1} \right)^{1/2}, \quad X_C \approx X_1 = \frac{1}{k} \quad (1.45)$$

1.8.3 ALTERNATE REPRESENTATIONS OF CYLINDRICAL MICELLES FORMATION

The approach pioneered by Mukerjee is equivalent to the thermodynamic treatments presented in later studies by Tausk and Overbeek [54], Israelachvili et al. [31], Missel et al. [55], and Nagarajan [56] to describe the transition from spherical to rodlike micelles. Following the treatment presented by Israelachvili et al., starting from the proposed structure for rodlike micelles shown in Figure 1.7 with a middle cylindrical part and quasi-spherical endcaps, one can identify two characteristic equilibrium constants associated with the molecules in the cylindrical part and those in the endcaps, respectively. The standard chemical potential of a rodlike micelle of size g with g_{cap} molecules in the two spherical endcaps and $(g - g_{\text{cap}})$ molecules in the cylindrical middle can be written as

$$\mu_g^\circ = (g - g_{\text{cap}}) \mu_{\text{cyl}}^\circ + g_{\text{cap}} \mu_{\text{cap}}^\circ \quad (1.46)$$

where μ_{cyl}° and μ_{cap}° are the standard chemical potentials of the molecules in the two regions of the rodlike aggregate, respectively. Introducing the above relation in the aggregate size distribution (Equation 1.39), we obtain

$$X_g = \left[X_1 \exp \left(\frac{\Delta \mu_{\text{cyl}}^\circ}{kT} \right) \right]^g \exp \left\{ g_{\text{cap}} \left(\frac{\Delta \mu_{\text{cap}}^\circ - \Delta \mu_{\text{cyl}}^\circ}{kT} \right) \right\} \quad (1.47)$$

where $\Delta \mu_{\text{cyl}}^\circ$ and $\Delta \mu_{\text{cap}}^\circ$ are the differences in the standard chemical potentials between a surfactant molecule in the cylindrical middle or the endcaps of the rodlike micelle and a singly dispersed surfactant molecule. Equation 1.47 can be rewritten as

$$X_g = \frac{1}{K} Y^g, \quad Y = \left[X_1 \exp \left(\frac{\Delta \mu_{\text{cyl}}^\circ}{kT} \right) \right], \quad K = \exp \left\{ g_{\text{cap}} \left(\frac{\Delta \mu_{\text{cap}}^\circ - \Delta \mu_{\text{cyl}}^\circ}{kT} \right) \right\} \quad (1.48)$$

where K is a measure of the free energy penalty for the molecules present in the spherical endcap compared with those in the cylindrical portion. The average aggregation numbers can be computed from Equation 1.40 by analytically summing the series functions: