This volume is loosely based upon papers presented and topics discussed at several recent international meetings. The first of these meetings was the international symposium on Interfacial Structure held in conjunction with the 210th National Meeting of the American Chemical Society on August 20-25, 1995 in Chicago. The second of these was the 1996 Chemistry at Interfaces Gordon Research Conference held July 21-26, 1996 in Meriden, New Hampshire. Additional contributors to this volume were selected because of work they presented at the 11th Surfactants in Solution conference held June 9-13, 1996 in Jerusalem or because their work was known to the Editor. All of the papers included in this volume, however, are of more recent vintage, and were written in the fall and early winter of 1996. The subject of this volume is limited in that it addresses amphiphiles at liquid/air, liquid/liquid, and liquid/solid interfaces, with little attention paid to vapor/solid interfaces. This subject is an important focal point for examining physical phenomena that occur in colloidal systems such as micellar solutions, microemulsions, emulsions, dispersions, slurries, etc., as well as flows at and wetting of macroscopic interfaces. This volume hopefully will serve to summarize our current understanding of interfacial structure at the molecular level in these systems, and the relation of this structure to chemical and physicochemical phenomena. Simulations and experiments are becoming complementary approaches to investigating the structure of these interfacial systems, and a balanced presentation of these various approaches has been attempted.

Invaluable support for these meetings was provided by the Division of Colloid and Surface Chemistry of the American Chemical Society, Eastman Kodak Company, 3M Specialty Chemicals Division, the Petroleum Research Fund of the American Chemical Society, Chemical Transport & Separations Division of the National Science Foundation, and the Chemistry Division of the Army Research Office. This support was very helpful in assisting with the travel expenses of distinguished scientists from Asia, the middle east, and Europe, and in making it possible for a significant number of graduate students and postdoctoral research associates to attend these meetings.

The contents of this volume have been distributed among six sections. The first of these sections, Liquid/Liquid Interfaces, is the least well characterized interface in colloid science. The first two papers by Brevet and Girault and by Richmond and co-workers give a comprehensive review of the great progress made recently in the application of two-photon processes in the analysis of molecular orientation and conformation at oil-water interfaces. The paper by Volkov and Deamer reviews theoretical aspects of charge transfer at oil-water interfaces, and discusses experimental interfacial catalytic systems. Pohorille, Wilson, and Chipot provide a comprehensive review of simulation studies of water-oil interfaces and present some exciting new results on surface segregation, highlighting the importance of electric dipoles in the genesis of interfacial activity. Murray presents some novel Langmuir trough studies applied both to oil-water and to air-water interfaces. Andelman and Diamant present an elegant variational study of the derivation of kinetics at liquid-liquid interfaces, and their work will interestingly be compared to the experimental study of Pitt at the end of this volume and the lattice-gas simulations of Khan and Shnidman. Stauffer alludes to the inclusion of amphiphiles in an Ising-like treatment, and this allusion is illustrated by Khan and Shnidman later in this volume.

The second section on Vesicles, Bilayers, and Membranes addresses the most biologically relevant area for amphiphiles. Chaimovich introduces the section with an interesting survey of chemical factors affecting transport through liposomes and bilayers. Beyer introduces a mechanism for bilayer formation from micelles, and Klopfer and Vanderlick present a molecular dynamics study illustrating how small nonionic amphiphilic structure can lead to the selection of bilayer structure over micellar structure. McIntosh and Simon present a comprehensive review of work done on the experimental characterization of fluctuations in lipid bilayers, and Berkowitz and coworkers articulate various approaches to defining the role of hydration forces in the interactions of such bilayers. Stouch reviews the key physical features affecting transport and partitioning in bilayers, and atomic-level molecular dynamics simulations of such bilayers. Green
and Lu review studies applied to trying to model transport through membrane pores.

Micellar Aggregation is the focal point of the third section. Care and coworkers lead off with a paper modeling micellar aggregation on a lattice. They examine relatively short-chain surfactants, and calculate the thermodynamics, shapes, and aggregate-size distributions. Mattice and coworkers present a comprehensive review of their work modeling the formation of association colloids of triblock copolymers. They also use a lattice approach. Shelley, Sprik, and Klein outline key issues to consider in molecular dynamics modeling of micellization and other structured surfactant-water phases. They find that inclusion of polarizability results in counter ions being heavily solvated, but that the water-hydrocarbon interface and the electrical double layer at the surfactant-water interface is clearly distinguishable irrespective of polarizability assumptions. Mavelli presents an exciting new application of stochastic dynamical modeling in illustrating surfactant aggregation. Texter and coworkers present a review of experimental studies directed at examining the role of cosurfactants in modifying reverse micelle aggregation and the onset of percolation processes therein.

The fourth and fifth sections deal with amphiphiles at solid-liquid interfaces. Section four on Amphiphiles at Electrode Surfaces contains a collection of important applications. The first by Rusling illustrates how surfactant films on electrode surfaces may be fabricated to electrocatalyze a variety of reactions. Koglin and coworkers provide some exciting new surface enhanced Raman spectroscopy results that contravene some of the reigning dogma on how cationic surfactants assemble on anionic surfaces. Kaifer presents a concise review of self-assembled monolayers on electrodes derivatized with thiolates and containing preformed binding sites. Somewhat similarly, the paper by Baszkin and coworkers in the last section investigates the incorporation of cyclodextrins into phospholipid monolayers. Bizzotto and Lipkowski comprehensively review nonionic amphiphile adsorption on electrodes and show how hemimicellar and micellar formation, adsorption, and desorption processes may be studied experimentally. The fifth section on Adsorption at Solid/Liquid Interfaces commences with an important review by Thomas on the resolution of surfactant structure by neutron reflectivity. Manne follows with a review of recent, exciting force microscopy results that go further to upset some of the dogma on surfactant hemimicelle formation, and yield some direct morphological evidence for hemimicellar structure. Balazs and coworkers present a self-consistent field treatment of polymers tethered to solid surfaces, and explore association structures formed by these polymers in various solvents. Grainger reviews polymeric thin film formation by adsorption from solution using chemisorption and using stratified polyelectrolyte layers. Khan and Shnidman present a lattice gas treatment of capillary dynamics, and include the effects of amphiphiles. Some formal similarity with the treatments of Daimant and Andelman and of Stauffer in the first section exist in the formalism adopted to attack these flow problems. Cohen and coworkers present a review of small angle x-ray scattering in the analysis of adsorbed layers surrounding colloidal particles.

Section six is devoted to Amphiphiles at Vapor-Liquid Interfaces. Zasadzinski and coworkers present a review of lung surfactant protein and the effects of such protein on altering phase structures in palmitic acid monolayers. They articulate some of the minimal functional requirements for such protein, with a view to expediting the design and synthesis of less expensive replacements for human lung surfactant. Siepmann reviews vapor-liquid phase equilibria and examines by Monte Carlo methods the suitability of two different force fields in modeling such equilibria. Goedel shows how hydrophobic polymers may be assembled at the air-water interface to prepare models of polymer “melt brushes”. The experimental approach is viable for preparing nanometer thick coatings. Baszkin and coworkers examine the miscibility of two phospholipids with lipid-derivatized β-cyclodextrin and with lipid-derivatized poly(ethylene oxide). While Murray's paper on protein dynamics appears in the first section, it is equally directed to air-water interfaces, and it will be interesting to see if these protein dynamics can meaningfully be treated by models developed for more classical surfactants. Abbott reviews recent applications of electrochemically active surfactants in modifying interfacial tension, and illustrates some exciting electrochemical engineering in deducing structural features that facilitate control of surface adsorption. This work also defines a mechanism whereby localized release of surfactants may be utilized in the localized permeabilization of membranes. The paper by Pitt presents exciting experimental results for different classes of surfactants in the development of an understanding of key features that control dynamic interfacial tension and the factors important in modifying the efficiency of dynamical surface tension lowering. Correlation of these data with various models put forth by Diamant and Andelman earlier in the volume will help refine our perspective of the modeling of these systems.

John Texter
CONTENTS

Preface ......................................... V

Liquid/Liquid Interfaces

P. F. Brevet, H. H. Girault: Optical SHG measurements of amphiphiles at liquid/liquid interfaces 1
A. G. Volkov, D. W. Deamer: Redox chemistry at liquid/liquid interfaces 21
A. Pohorille, M. A. Wilson, C. Chipot: Interaction of alcohols and anesthetics with the water-hexane interface: a molecular dynamics study 29
B. S. Murray: Dynamics of proteins at air-water and oil-water interfaces using novel Langmuir trough methods 41
H. Diamant, D. Andelman: Adsorption kinetics of surfactants at fluid-fluid interfaces 51
D. Stauffer: Oil-water interfaces in the Ising-model 60

Vesicles, Bilayers, and Membranes

H. Chaimovich, I. M. Cuccovia: Quantitative analysis of reagent distribution and reaction rates in vesicles 67
K. Beyer: Packing and bilayer-micelle transitions in mixed surfactant-lipid systems as studied by solid state NMR 78
K. J. Klopfer, T. K. Vanderlick: Self-assembly of volatile amphiphiles 87
T. J. McIntosh, S. A. Simon: Experimental tests for thermally-induced fluctuations in lipid bilayers 95
J. Lu, M. E. Green: Solute transport and partitioning in lipid bilayers: molecular dynamics simulations 116

Micellar Aggregation

C. M. Care, T. Dalby, J-C. Desplat: Micelle formation in a lattice model of an amphiphile and solvent mixture 130
J. C. Shelley, M. Sprik, M. L. Klein: Structure and electrostatics of the surfactant-water interface 146
F. Mavelli: Stochastic simulations of surfactant aggregation kinetics 155
J. Texter, B. Antalek, E. Garcia, A. J. Williams: Cosurfactant facilitated transport in reverse microemulsions 160

Amphiphiles at Electrode Surfaces

J. F. Rusling: Catalytically active, ordered films of proteins, surfactants and polyelectrolytes on electrodes 170
Adsorption properties of two cationic surfactant classes on silver surfaces studied by means of SERS spectroscopy and ab initio calculations ........................................ 181

Electrodes derivatized with mono- and multilayer assemblies containing preformed binding sites .......................................................... 193

Amphiphiles at electrified interfaces ................................................... 201

Adsorption at Solid/Liquid Interfaces

Neutron reflection from surfactants adsorbed at the solid/liquid interface .......................................................... 216

Visualizing self-assembly: force microscopy of ionic surfactant aggregates at solid-liquid interfaces .......................................................... 226

Forming patterned films with tethered polymers .................................. 234

Synthetic polymer ultrathin films for modifying surface properties .......... 243

Molecular mean-field models of capillary dynamics ................................ 251

Probing the structure of inhomogeneous colloidal particles by small-angle x-ray scattering .......................................................... 261

Amphiphiles at Vapor-Liquid Interfaces

Protein and lipid interactions in lung surfactant monolayers .................. 268

Monte Carlo calculations for vapor-liquid phase equilibria in Langmuir monolayers .......................................................... 280

Hydrophobic polymers tethered to the water surface ........................... 286

The effect of the chemical nature of grafted chains on the interfacial miscibility of amphiphiles .......................................................... 294

Active control of interfacial properties of aqueous solutions using ferrocenyl surfactants .......................................................... 300

The efficiency of dynamic surface tension reductions within homologous series of surfactants in aqueous gelatin solution .......................... 307

Pure and mixed chlorophyll a Langmuir and Langmuir-Blodgett films: Structure, electrical and optical properties .................................... 318

Author Index ....................................................................................... 327

Subject Index ..................................................................................... 327