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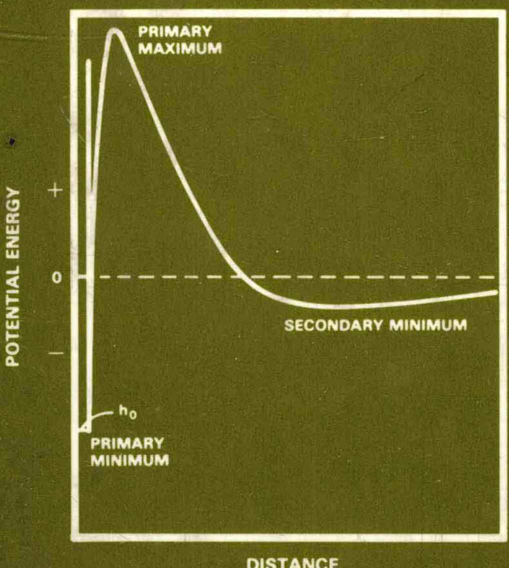

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Preface

Surfactants are an interesting class of materials, and it is their dual characteristics (hydrophilic-lipophilic nature) that make them so useful. Surfactants play an important role in many processes ranging from the very mundane (washing cloth) to the very sophisticated (microelectronics). In the last several years, there has been a great deal of research activity in understanding the role of surfactants in multi-billion-dollar chemical and processing industries. Rates of organic reactions have been shown to be accelerated by many orders of magnitude by carrying out the reactions in appropriate micellar or microemulsion media. New examples include the application of surfactants in unit operations for industrial separations, environmental protection, pharmaceuticals, herbicides and pesticides, engineered materials, and enhanced oil recovery. (The reader is referred to Volume 26 of this series, *Surfactants in Emerging Technologies*, edited by Milton J. Rosen.) All these new developments in the field of surfactants obviously cannot be covered in one volume. However, we have made an attempt to focus on a few of the recent developments in industrial applications of surfactants and to bridge the gap from engineering science to application technology.

In recent years, there has been more involvement by chemical engineers and applied chemists in the process application of surfactants and hence greater willingness on their part to address this important subject. Therefore, it should not be very surprising that most of the contributors to this volume are engineering scientists.

The various chapters may be outlined as follows. The field of surface rheology has largely developed over the past two decades. Edwards and Wasan, in the first chapter, introduce the reader to surface rheological properties such as surface shear and dilatational viscosities and elasticities of fluid-fluid interfaces containing surfactants by using a simplified "pillbox" approach. They then proceed to show the importance of these properties in practical dynamic surface problems with particular emphasis on the role that the dilatational surface properties play in a number of applications involving the use of surfactants such as foam rheology, foam flow in enhanced oil recovery, and foam and emulsion stability.

Distillation is a complex vapor-liquid contacting operation, but it lies at the heart of many process industries. Berg describes the observed effects of surfactants in distillation processes. Surface-tension effects, and their modification by surface-active agents, play a significant role in the performance of distillation equipment. Traces of surfactants have been shown to be capable of improving the performance of packed distillation towers by as much as 80%. Enhancement is achieved through the stabilization against rupture of the thin films of reflux liquid flowing over the irrigated packing, thereby increasing available interfacial area. Similar area increases can be achieved for tray columns through the stabilization of froths. These effects are described, explained, and quantified by both hydrodynamic analyses and laboratory experiments using bench-scale equipment.

Scamehorn and Harwell provide an in-depth examination of how surfactant systems can be used in the treatment of aqueous process streams to achieve important industrial separations. Five important separation techniques are examined, namely, micellar-enhanced ultrafiltration, foam separations, surfactant-enhanced carbon regeneration, extraction into reverse micelles, and admicellar chromatography. These methods are of special interest because they typically require low energy for operation. They are also quite useful in selectively removing organics or multivalent ions from water, in addition to other separations. Accordingly, surfactant-based separations are useful for separating contaminants or for enrichment of value components. Technologies in which these techniques may be widely used include biotechnology applications, pollution control or waste water treatment, and separation of metals.

Li invented the liquid surfactant membrane concept in 1968. Over the last 20 years, considerable efforts by chemists and chemical engineers have been devoted to developing the liquid surfactant membranes for many potential applications, including separation of hydrocarbons, hydrometallurgy, waste water treatment, biomedicine, and biochemical engineering. To date, this concept has been successfully commercialized for the extraction of metals. Gu, Wasan, and Li specifically review the various extraction systems for metal ion recovery and the dominant mechanisms for their extraction.

Sonntag examines the use of surfactants in the aqueous separation of two important fatty acids, oleic and stearic acids, from mixtures of tallow fatty acids. He includes a discussion of some fundamental properties such as adsorption, wetting, and hydrophilization in treating his topic. Aqueous emulsion separations are shown to offer advantages over solidification and solvent crystallization methods based on melting-point differences. Adsorption and wetting are shown to be especially important in separating oleic from stearic acid. Successful separations are achieved by treating the fatty acid mixtures with solutions of 0.5% (by weight) sodium lauryl sulfate and 2% (by weight) magnesium sulfate, followed by centrifuging or rotary vacuum filtration. Surfactant concentrations are regarded as critical since highly emulsified mixtures are found to separate only with great difficulty. The results are discussed in relation to key surface and wetting phenomena.

Somasundaran and Ramachandran review the role of surfactants in flotation, an important unit operation. The principles that govern surfactant adsorption and particle-bubble attachment are discussed with relevant examples from the literature. Selective adsorption of surfactants on particles is dependent on the surface and solubility properties of the solid and the solution chemistry of the surfactants, as well as on the dissolved inorganics and polymers present in the system. The importance of the interactions of the different species of the surfactants with inorganics, as well as with polymers in bulk and at various interfaces, is emphasized. Effects of the different variables such as pH, ionic strength, and temperature are also discussed.

A second chapter by Sonntag deals with the role of surfactants in herbicide emulsions. Surfactants are shown to play a vital role in weed control technology by increasing the effectiveness of herbicides. The action of surfactants relates to their ability to accomplish a more uniform distribution over the surface of leaf foliage (and also by increasing penetration). Factors affecting surfactant usefulness in herbicide dispersion include surface activity (surface-tension lowering), wetting properties, contact angle, micelle formation, and hydrophobic-lipophilic balance (HLB), particularly for nonionic surfactants. The increased use of vegetable oils in herbicide dispersions as replacements for hydrocarbons (and water) is discussed in developing an understanding of these complex systems. Factors favoring use of vegetable oils such as soybean oil include ready availability, improved functionality, and better environmental acceptance. Such factors tend to override costs in many situations.

Kine and Redlich provide a thorough treatment of the role of surfactants in emulsion polymerization. The product of such polymerization is termed "emulsion polymer," a latex or a polymeric dispersion, and consists of minute plastic spheres (10^{-4} mm in diameter) dispersed in a continuous phase, usually water. Each cubic centimeter of latex contains about 100 trillion of these spheres, and each sphere has a layer of a surface-active moiety on its surface. The use of surfactants is shown to be vital in the preparation of the emulsion polymer and, at times, of even greater importance in its formulation and application (e.g., in protective coatings). Factors affecting the preparation of the dispersion, the resulting physical properties, and ultimate application are discussed in developing a greater understanding of interrelationships. Whenever possible, the authors strive to develop both theoretical and practical implications pertinent to various industrial applications. Such applications of emulsion polymers include use in soil stabilizers, protective coatings, sealants, adhesives, tile and paper finishing agents, and specialty concretes, and for the treatment of automotive and aircraft tires.

The late Dr. J. Schulman, mentor of Shah, coined the word "microemulsion." A microemulsion can be defined as a thermodynamically stable, isotopically clear dispersion of two immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film of surface-active molecules. Since the introduction of microemulsions in 1943, significant advances have been made to explain the formation, structure, properties, and phase behavior of microemulsions. Leung, Hou, and Shah review the various theoretical and experimental aspects, as well as novel applications of microemulsions.

The last chapter, by Woods and Diamadopoulos, reviews the fundamentals of surface phenomena that affect stability of dispersions. Included are equilibrium theories of electrochemical double layer and adsorbed macromolecule and rate theories of coalescence, adsorption, and coagulation. Eleven strategies that affect stability are outlined. The role of surfactants, inorganics and polymers, and solubility are discussed. Methods are given to predict the drop size and to characterize dispersions. Overall strategies and rules of thumb for separation dispersions are presented. Details are given for chemical destabilization, coagulation and flocculation, and deep-bed filtration and flotation. Numerous practical sample calculations are given.

We wish to thank all the authors for their contributions and for providing us with the summaries of their work that are included in this preface. We have attempted to cover some recently selected developments to highlight the importance of surfactants and surface phenomena, and the use of surfactants and the role they play in various applications. We hope this volume, although far from being comprehensive, will be judged as definitive and will stimulate other works to further enhance our knowledge in this technologically important field.

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Contents

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Dilatational Properties of Adsorbed Surfactant Interfaces and Their Applications

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I. INTRODUCTION

The adsorption of surfactant at a fluid-fluid interface has long been known to alter equilibrium interfacial properties. However, in practice, equilibrium is an inevitable abstraction: the limiting case of actual dynamic processes which occur near, at, and across an interface. Dynamic interfacial properties, which are required to quantify practical dynamic surface problems, are less well known.

Dynamic interfacial properties may be classified in terms of shear properties and dilatational properties. The former, which typically include the surface shear viscosity and the shear elasticity, have been shown relevant to such dynamic phenomena as foam and emulsion stability, coalescence, and interfacial mass transfer [1–3].

We have recently undertaken a fundamental research program to investigate the less understood but more significant dilatational properties, such as the dynamic surface/interfacial tension, the dilatational modulus, and the surface dilatational viscosity. Our objective in this research has been first, to develop techniques to measure the dilatational properties, and second, to investigate (both experimentally and theoretically) the correlation between the dynamic surface/interfacial properties and foam rheology, foam flow in EOR processes, foam stability, and emulsion stability.

In this chapter we summarize the current results from our research efforts, beginning with a simple derivation of the relation between surface and bulk-phase hydrodynamics (in which context dynamic surface properties are defined), followed by a detailed consideration of surface dilatational properties, and concluding with the various theoretical and experimental results that we have obtained for dilatational surface properties and their application to dynamic interfacial phenomena.

II. DYNAMIC SURFACE PROPERTIES (SURFACE RHEOLOGY)

Surface rheology is the study of interfacial response to deformation. Often we consider the deformational response of the surface as defined by a single stress coefficient: the surface tension. However, when surfactant adsorbs to the fluid-fluid interface, an intrinsic rigidity may arise, introducing beyond the tensile response to deformation, a damping or viscous response which cannot be defined completely by the surface tension, requiring coefficients of surface viscosity.

Although the origin of surface tension and surface viscosities is quite intuitive, the surface stress equations that relate these stress coefficients to the deformational response of the surface soon lose intuitive appeal, particularly when the surface becomes curved. Therefore, to advance an intuitive understanding of surface rheology we will throughout this section consider the rheology of the planar fluid surface. The reader interested in the rheology of curved fluid surfaces is referred to Refs. 4 and 5.

Consider, then, a rectangular fluid element containing a portion of two continuous fluid phases, as in Fig. 1. The thickness of the element (2ℓ) is sufficiently small that the inhomogeneous layer of fluid between the two fluid phases loses any discontinuous appearance. This inhomogeneous layer, the interfacial region, is completely contained between the surfaces $z = \pm\ell$.