in great detail are also mentioned: the mean solute velocity, the Taylor/Aris dispersivity, and the effective volumetric reaction rate. Among the applications mentioned here we need to underline is that of the chromatographic separation. The key message that this textbook brings is eloquently emphasized in the preface: a systematic approach to derive macrotransport coefficients in terms of the solution of a corresponding microscale boundary-value problem. The authors consider it "one of the more physically self-consistent coarse graining theories existing in the transport phenomena literature." From a theoretical perspective, it is noted with respect to the system's macrotransport description that "(it) possesses a similar dual *Lagrangian/Eulerian* interpretation as that of the system's microtransport description." This duality is valid at the macro as well as at the micro level.

The book has three parts. The first (Chapters 1–9) deals with material dispersion theory, the second (Chapters 10 and 11) with nonmaterial (energy and momentum) dispersion theory, and the last one, the smallest (Chapters 12 and 13), with a short description of the foundations of macrotransport processes. Several applications are examined in detail throughout the book, starting in the first chapter with the original Taylor-Aris dispersion theory of a solute in the flow through a tube (Taylor, 1953, *Proc. Roy. Soc.*, **A219**, 186; Aris, 1956, *Proc. Roy. Soc.*, **A235**, 67) and progressively moving to more complicated ones in the subsequent chapters. Chapter 1 also provides an informal, nonmathematical overview of the key principles and primary applications of the macrotransport theory offering a good, clear description of the phenomena. After a brief literature survey, the key concepts/prerequisites for the theory are laid down. Both material and nonmaterial dispersion theory (exemplified through the discussion of momentum dispersion in porous media and suspensions) is introduced here. The Taylor dispersion emerges as the key concept resulting from the influence of external fields, rotation, velocity sampling due to differences in charges, sizes, shapes, and so on.

In all cases, the material is presented in a highly organized manner. First, the layout of the chapters is established according to criteria based on the principal characteristics of the problems under investigation. Prominent among those is the distinction between continuous (for example, capillary tube) and discontinuous (for example, porous media) applications discussed in Chapters 2–3 and 4, respectively. Other criteria include transport at the material interface separating two material media (Chapter 5), time periodicity in the flow (Chapter 6), the presence of coupling between the local- and global-space driving forces as realized by the hydrodynamic interaction between a particle and the wall or another particle in suspensions (Chapter 7), the presence of particle sources or sinks caused, for example, by chemical reactions (Chapter 8), and the presence of spatial periodicity (Chapter 9). This systematic presentation serves a dual role: it demonstrates potential applications more clearly and helps direct the reader to the appropriate location. In principle, after reading the introductory material in Chapters 1–4, the reader shall be able to read any other chapter in any order as needed.

In each chapter, the relevant system of partial differential equations, enabling the calculation of the macroscopic transport coefficients, is first systematically developed in the abstract local-global coordinate formalism for the specific class of macrotransport processes considered. The formal spatial axial-moment formulation originally developed by Aris (above citation) suitably modified is used for that purpose. The resulting equations are neatly summarized and the involved generic abstract variables tabulated for the benefit of the reader who is interested in solving the equations for a particular application rather than in their detailed mathematical derivation. This reader is especially further facilitated by meticulously going through the remainder of the chapter which deals with specific example applications where the before-mentioned theory is applied. Numerous figures, boxes, and each application equivalence table connecting the generic and the specific to that application variables further facilitate the understanding of the material. In this respect, the exercises at the end of every chapter become an integral part of the book directing and simultaneously helping the reader better understand the involved mathematical manipulations.

In conclusion, despite the mathematical complexity of the subject which is the biggest drawback of a more widespread use of the proposed theory, the authors, obviously very much aware of this fact, tried their best to overcome it through the exposition style (figures, boxes, and summaries), the organization of the material, a gradual introduction of the most difficult concepts, and many examples and exercises. They have admirably succeeded in this effort, and I therefore wholeheartedly recommend this textbook to anyone who is interested in transport phenomena in heterogeneous media.

Antony N. Beris
Chemical Engineering Dept.
Colburn Laboratory
University of Delaware
Newark, DE 19716

Surface and Colloid Science

Edited by Egon Matijevic, Vol. 15, Plenum, New York, 1993, 276 pp.

Surfactant technology is built on a vast body of scientific literature. The prospect of mastering even a part of that literature challenges the process engineer, industrial formulator, and academic researcher alike. Various textbooks introduce fundamental concepts and flag key papers, but forego excessive depth. Review chapters, such as those in the *Surface and Colloid Science* series, provide comprehensive coverage of more specialized topics.

Earlier volumes in this series included a number of chapters related to surfactants scattered among reviews of other areas. Volume 15 differs from its antecedents because it focuses primarily on one topic: association of surfactants or block copolymers as micelles. By and large, the six chapters in the volume avoid the well-covered topic of surfactant association in water; instead, they treat a variety of subjects of emerging importance in chemical technology. Three chapters provide extended introductions as well as comprehensive reviews; these should interest a wide audience. The other three chapters have more narrow foci and are highly recommended for specialists.

The first chapter, "Micelles of Block and Graft Copolymers in Solution" by Z. Tuzar and P. Kratochvil, stands out in its depth and breadth of coverage. The authors restrict their scope to association of diblock and triblock copolymers in dilute solutions, summarizing a large body of literature and formulating useful generalizations. After a brief review of characterization techniques, the chapter describes experimental work (primarily using radiation scattering) to determine micellar structure. A parallel section on theoretical models of copolymer micelles omits details but provides key predictions for association num-

bers, core radii, and shell thicknesses as functions of block molecular weights and other parameters.

The next section describes the evidence for micellization as a closed association process in which individual copolymer molecules exist in equilibrium with micelles having a large association number and narrow size distribution. This view allows experimentalists to quantify the thermodynamic driving forces for association. Unlike the entropically-driven process by which surfactants associate in water, the data imply that enthalpy changes drive block copolymer micellization in selective solvents.

The chapter concludes with a review of experiments on the kinetics of micelle formation and decomposition, hydrodynamic properties, photo-initiated core polymerization, and solubilization phenomena. The relative immaturity of these areas prevented the authors from making many generalizations at the time the chapter was completed. The intervening three years have brought substantial progress not documented in this review; a note added in proof gives a starting point for exploring the most recent literature.

"Surfactant Association in Nonaqueous Media," by A. J. I. Ward and C. du Reau, successfully reviews this topic and provides informative contrasts with micellization in aqueous media. The balanced treatment of reversed micelle formation recognizes that the existence of reversed micelles in some nonpolar solvents is still controversial. Experimental data generally indicate that dipole-dipole attraction between head groups drives association in nonpolar solvents, while unfavorable enthalpic interactions between solvent and tail groups favor association in polar solvents.

The review notes that, compared to micelles in water, reversed micelles in nonaqueous solvents have less well-defined critical micelle concentrations (CMCs) and take nonspherical forms more frequently. The suitability of closed vs. open association models for reversed micelles has not yet been resolved. Some experimental data (vapor pressure osmometry and dielectric dispersion) support open association models which predict the existence of dimers, trimers, etc. in addition to monomers and micelles. However, other experiments (light scattering, surface tension, and ^{1}H NMR, for example) detect CMCs and indicate closed association involving only monomers in equilibrium with micelles. Experiments using positron annihilation conclusively identify CMCs in some systems but not others.

The chapter ends with a discussion of relatively scarce data for liquid crystal and microemulsion formation in nonaqueous media. The review classifies the literature according to solvent: only ethylene glycol, glycerol, and formamide have been studied to date.

A short chapter entitled "Hydrotropes—Recent Developments," by D. Balasubramanian and S. Friberg, provides an excellent introduction to an area not yet familiar to most chemical engineers. Hydrotropes are compounds, normally neutral salts of organic acids, that increase the solubility of otherwise insoluble compounds in water. Hydrotropes including sodium benzoate, salicylate, and benzenesulfonate have been frequently studied. The review provides a clear distinction between solubilization by hydrotropes and surfactants: solubilization requires relatively large amounts of hydrotrope (20–30 wt. %), and hydrotropes can solubilize much greater amounts of solute than surfactants.

The chapter continues with an informative discussion of research that probes the underlying mechanisms of hydrotropy. Two mechanisms received early attention: "salting in," in which the hydrotrope dissociates to give ions that bind with water, thereby facilitating the dissolution of the solute, and cosolvency, wherein the nonpolar part of the hydrotrope increases the affinity of the water-hydrotrope mixture for the solute. More recent operational definitions of hydrotropy focus on structure formation in water-hydrotrope mixtures. Although the data show that hydrotropes do not micellize in the usual sense, other evidence supports molecular association in stack-like aggregates.

The most valuable section of this chapter discusses applications of hydrotropes. Early research focused on pharmaceutical applications, and hydrotropes continue to be used widely for drug solubilization. Other recent developments include hydrotrope-mediated rate enhancement of chemical reactions involving heterogeneous catalysts and biocatalysts, and use as agents in extractive separations and novel detergent formulations.

The chapter's final section returns to issues of structure and internal microenvironment within hydrotrope aggregates. Features similar to surfactant micelles can account for enhanced solubilization and reaction efficiencies, yet hydrotropy often displays solute selectivity not observed in surfactant solubilization. The authors conclude that "the thermodynamics of the aggregation process of hydrotropes needs to be delineated [before we] interpret hydrotropy in terms of the micellar paradigm."

Three other chapters in this volume will attract readers with more specialized interests. "Microemulsion Formation with some Typical Surfactants," by K. Ogino and M. Abe, reviews the authors' body of research on microemulsions involving sodium alkyl sulfates. Likewise, "Properties and Applications of Reversed Micelles," by K. Kon-no, focuses on the author's studies of reversed micelles of single- and double-alkyl tail surfactants. These chapters do not provide extensive introductions to their topics, but they do abstract a portion of the literature that may not be accessible to most readers in the U.S.

Finally, "Study of the Boundary Viscosity of Organic Liquids by the Blow-Off Method," by B. V. Derjaguin and V. V. Karasev, reviews experiments employing a technique that is much more elegant than suggested by its name. The blow-off method measures the distribution of apparent viscosity across a thin liquid film that coats one of two parallel planes separated by vapor-filled channel. Air or nitrogen passes between the planes and blows the film down the channel. Under certain conditions, the pressure drop over a given length of channel is proportional to the mean shear stress exerted by the gas on the film. Interferometry or ellipsometry measures the local thickness of the film; scanning the length of the film or following the time variation of thickness at a fixed point provides the film thickness profile. The liquid velocity profile can be calculated from the kinematics of the deformation. Mean shear stress, divided by the local velocity gradient, yields the local viscosity.

The difference between the liquid's "boundary" viscosity and its bulk viscosity reflects surface-induced structure in the liquid. Although the theoretical section of the chapter that produces boundary viscosity profiles is difficult to follow, the authors present mostly thickness profile data that clearly manifest surface structure. The chapter reviews extensive results for oligomeric and polymeric liquids including polydimethylesiloxanes, polyisobutene, organo-silane oligomers, hexadecane, and various oils. Researchers with interests in lubrication, tribology, and liquid polymer-solid interfaces may find relevant information in this chapter.

Overall, Volume 15 in the *Surface and Colloid Science* series provides a comprehensive view of emerging developments in micellization and solubiliza-

tion utilizing block copolymers and surfactants in nonaqueous solvents. The volume should find a place in all university and industrial research libraries. Three chapters introduce block copolymer micelles, reversed micelles, and hydrotropes in a manner suitable for newcomers to these areas. Specialists in reversed micelles, microemulsions, and molecular tribology will find valuable reviews of less-accessible bodies of literature.

Harry J. Ploehn
Dept. of Chemical Engineering
Texas A&M University
College Station, TX 77843

Protein Purification Process Engineering

Edited by R. G. Harrison, Marcel Dekker, New York, 1993, $155.

Protein separation operations are expensive. The expanding research and development resources committed to the rational design of protein purification trains by biotech companies reflect the need to minimize manufacturing costs as production scales increase and market pressures mount. Product discovery efforts often result in the development of a small-scale isolation procedure and associated physicochemical property databases for the target protein and major contaminating species. However, the direct scaling of bench isolation biochemistry to production levels won't cut it. The low-cost producer will have a purification process development team with expertise in bioseparation unit operations, comprising an understanding of the design and performance of large-scale protein separation techniques in relation to the properties of the product and impurities. *Protein Purification Process Engineering* should be among the resources consulted by those looking to develop or expand such an expertise.

In this book, Harrison assembled a team of experts, largely from the biotech industry, who discuss current design and scaleup issues for the major unit operations of bioseparations. Each chapter is devoted to a separate unit operation and is self-contained. The operations addressed include cell disruption, membrane filtration, liquid-liquid extraction, precipitation, conventional and affinity chromatography, and lyophilization, as well as associated analytical methods development and validation. The treatment level is introductory and the style is practical. The physical bases for the various techniques and the impact of key process parameters on performance are described qualitatively; detailed quantitative developments are eschewed. Several chapters are rich with examples of industrial applications. Those interested in delving deeper will find that the exhaustive referencing provides multiple entrees into the research literature for each of the operations discussed.

Clear standouts are the chapters on analytical considerations, membrane filtration, precipitation, and conventional chromatography. The chapter on analytical considerations gives a detailed listing of the various assay techniques for purity and bioactivity and describe how assay procedures are integrated with a process. Particularly useful is a discussion of the types of impurities typically encountered during downstream processing and how analytical methods may be tailored to follow their fate throughout a process. It also discusses transforming growth factor beta and recombinant tissue plasminogen activator case studies, as well as the need for assay validation; however, the actual mechanics of validation is vaguely treated just like the FDA has been. This chapter should be required reading for anyone contemplating the development of a commercial protein purification process.

On membrane filtration filtrate flux and solute rejection are discussed concisely with respect to concentration polarization and fouling phenomena as well as operating conditions. Numerous examples are focused on the various applications of microfiltration, from cell harvesting to virus removal. Affinity membrane systems are introduced briefly as an alternative to chromatographic separations.

The chapter on fractional precipitation describes the protein physical properties governing protein solubility and current colloidal solubility theories against an extensive background of the forces governing protein-protein interactions. It includes an encyclopedic catalog of who has precipitated what protein with what reagent. In this regard, the chapter can be overwhelming since so many examples and counterexamples of protein solubility behavior are provided that one is lead, rightly, to question solubility paradigms. General principles of precipitate formation in terms of nucleation, growth and aging phenomena and their relation to the design of precipitation equipment are treated pragmatically with several process flow diagrams. A must-read for protein precipitation operations.

An eminently practical guide to conventional chromatographic separations clearly explains various modes of chromatography, including the powerful, yet oft-neglected displacement mode. Simplified design equations are presented with key procedural and physical details such as column packing, clean-in-place, sterilization, depyrogenation, and inclusion of air traps. These considerations are usually absent from background descriptions of chromatography. Procedures for the identification of the rate-controlling mass-transfer step in a given chromatographic separation are discussed, with which process optimization efforts may be aimed in fruitful directions.

I had a mixed reaction to the chapters on cell breakage, liquid-liquid extraction and lyophilization. The discussion of cell disruption was largely anecdotal and circular in nature. Although important operating parameters for high-pressure homogenizers and bead mills are outlined, little information was given to aid a first-pass design. I would have welcomed a discussion of the close coupling between cell disruption and subsequent centrifugation or microfiltration operations for debris removal. The chapter on liquid-liquid extraction introduces practical process considerations within the context of several case studies, leading to a somewhat scattered presentation. However, in the hepatitis B surface antigen PEG/dextran extraction used as the primary example, key process information such as the temperature, pH and ionic strength were omitted. No discussion of available aqueous two-phase systems and diagrams was given, nor the theory of aqueous two-phase partitioning, the extensive efforts of Blanch's group at Berkeley and Hall's group at N.C. State. Although the author suggests that liquid-liquid extraction should find wider application in industry, it's not clear that this chapter is enabling. The topic of lyophilization is usually and unaccountably omitted from most books on protein separations. This book, however, discusses qualitative freezing, primary and secondary drying processes illustrated with phase diagrams and representative differential scanning calorimetry thermograms of the product. However, the apparently conscious avoidance of even simple mass and heat flux equations made the description of transport phenomena governing this process awkward. No reference at all