BOOK REVIEWS

Electrochemical Process Engineering: A Guide to the Design of Electrolytic Plant

By F. Goodridge and K. Scott, Plenum Press, 1995, 312 pp., $59.50.

If you needed to start from scratch to design a reactor for electrosynthesis of an organic compound, this book could help you through the steps. It offers a few of the basics of electrochemical systems, such as thermodynamics and mass transfer, although it does not provide a critical knowledge of any subtle points. It also brings in nonelectrochemical subjects by relating the design problem to conventional (stirred-tank and plug-flow) reactors, to associated heat exchange and downstream separations, and to cost estimation for capital and operating costs. As a result, you may be able to produce a preliminary reactor design and some rough cost estimates. This 300-page book is modest in its goals.

You, however, will not come away with any in-depth view of how electrochemical reactors work, and there is a lack of historical perspective. References are generally restricted and come from the secondary literature (either reviews or later work). To my astonishment, the essence of my MS thesis was reproduced in Chapter 5 without a proper citation.

The book is mainly about electroorganic syntheses, although there is passing mention of inorganic syntheses (including metal winning and refining) and effluent treatment. Deliberately neglected are fuel cells and batteries.

We should like to be able to decide whether a chemical conversion can be performed electrochemically in an economical manner, in competition with purely chemical routes. An objective of this book is to lay out the elements needed for this decision. A secondary impact is to concentrate on electrochemical reactor models simple enough to be integrated into more or less standardized methods or software packages for the design of other components of the plant. In this way, one can create an approach to the design of the overall plant.

Design examples indicate how certain variables do or do not interact strongly with associated nonelectrochemical equipment. I learned something useful here about the principles of optimization of subsystems within a process. Thus, it is better to design for a specified conversion unless the cost of subsequent separation is included. On the other hand, optimization over the average current density is generally safer (although some interaction with heat-transfer equipment may occur).

John Newman
Dept. of Chemical Engineering
University of California
Berkeley, CA 94720

Innovations in Supercritical Fluids: Science and Technology

Edited by K. W. Hutchenson and N. R. Foster, ACS Symp. Ser. 608, American Chemical Society, 1995, 408 pp., $125.95.

Until quite recently, supercritical fluids were often described as a solution looking for a problem. During the last decade, however, a number of novel environmental, pharmaceutical and materials processing applications have given the field vitality and a renewed sense of purpose. This is true not just for technology-driven research: improved fundamental understanding is now seen as key to the commercialization of processes that exploit the properties of supercritical mixtures over wide ranges of temperature and pressure. In their informative introductory chapter to this selection of papers presented at the Symposium on Supercritical Fluid Science and Technology held at the 1994 AIChE meeting, the editors illustrate this point convincingly. They show that our ability to measure and predict solubility falls far short of what is needed for reliable scale-up of processes involving even the simplest of supercritical mixtures. The limitations of commonly-used equations of state in the vicinity of the critical point, and the discrepancies that exist in the published literature on the solubility of biological molecules in carbon dioxide, are well-chosen reminders of the gaps in basic knowledge that exist and of their technical consequences.

The editors have organized the contents into four sections: Molecular Interactions and Phase Behavior (eight chapters), Chemical Reactions in Supercritical Fluids (seven chapters), Special Topics and Applications (nine chapters), and Supercritical Fluids in the Forest Products Industry (five chapters). They are preceded by a truly excellent introductory chapter, a critical discussion of the technical and commercial impact of current limitations in modeling and measurement of solubilities, followed by a review of recent developments in chemistry and catalysis in supercritical fluids, in oxidative destruction of organic wastes in supercritical water, and in particle formation techniques utilizing supercritical fluids.

The section on Molecular Interactions and Phase Behavior includes three interesting computational studies of hydrogen bonding and solvation in supercritical water. Mizan et al. explore hydrogen-bond cluster statistics; Cummings and coworkers investigate ion pairing between Na^+ and Cl^- in supercritical water; and Johnston, Rossky and coworkers contrast the solvation of electrolytes and nonelectrolytes in water, from ambient to slightly subcritical conditions, using molecular dynamics and fluorescence spectroscopy. These studies illustrate the valuable insights into solvation and solution structure in supercritical water than can be obtained by computer simulation. An important unresolved question here is the discrepancy between neutron diffraction and simulation data on hydrogen bonding in supercritical water, as well as the unambiguous interpretation of the neutron data (Postorino et al., *Nature*, **366**, p. 668, 1993). Another interesting study in this section is due to Zhang and Fulton, who report on the different behavior upon pressurization of normal (oil-in-water) and reverse (water-in-oil) microemulsions formed in supercritical solvents. The large changes in conductivity and viscosity in the latter type of complex fluid are particularly noteworthy.

The section on reactions includes an interesting chapter by Brennecke and coworkers on the use of pulse radiolysis

to study ionic reactivity and intermolecular interactions in supercritical solvents. Buelow and coworkers report on the hydrothermal destruction of organic wastes from the production of nuclear materials. Chapters by Tester and coworkers and by Savage and coworkers also deal with the treatment of organic wastes in supercritical water, while Ding et al. report encouraging results on the use of heterogeneous catalysts in supercritical water oxidation of aromatic hydrocarbons, and Subramanian and Jooma discuss the benefits of operation at supercritical conditions on the mitigation of catalyst deactivation during the isomerization of 1-hexene.

The section on Special Topics and Applications lacks the thematic coherence of the remaining groupings. Sunol and coworkers present an interesting comparison of aerogel catalysts prepared using supercritical drying and a novel supercritical extraction route and find that the latter allows processing at substantially milder conditions. Two instructive chapters, one by Downey et al. and the other by Mitton et al., address the key and still unsolved issue of corrosion in supercritical water oxidation technology. Bourhis et al. show that lower required inlet temperatures and shorter residence times can result from the addition of small amounts of strong oxidizers to the feed of supercritical water oxidation streams. It is not clear why these three chapters were not included in the section on Chemical Reactions.

Finally, the section on Supercritical Fluids in the Forest Products Industry contains a useful and well-written review by Kiran on the potential of supercritical fluids for delignification, waste treatment, chemical conversion of cellulosic wastes, paper recycling, and wood impregnation. Also noteworthy is a chapter by Teja and coworkers on the supercritical extraction of Taxol, a promising therapeutic alkaloid with a broad range of antileukemic and tumor-inhibiting activity.

The state of the art of the fundamentals and applications of supercritical fluids is well documented in this useful book. While some important topics such as polymerizations in supercritical fluids and particle formation are not represented, this volume is an important and welcome addition to the literature on supercritical fluids.

Pablo G. Debenedetti
Dept. of Chemical Engineering
Princeton University
Princeton, NJ 08544

Polymer Surfaces from Physics to Technology

By Fabio Garbassi, Marco Morra, and Ernesto Occhiello, Wiley, New York, 1994, 462 pp., $95.00.

As the authors state in their preface, the science and technology of polymer surfaces have grown rapidly, resulting in a prolific body of literature that is spread over a large number of journals that deal with a number of different fields. Their goal is to present a comprehensive treatise on the subject that starts from a consideration of the fundamental physical principles that dictate polymer surface properties and proceeds to review important aspects of real-world applications. Toward this end, the book is divided into four sections: Introductory Remarks concerning fundamental surface forces and surface dynamics; Characterization Methods; Modification Techniques; and Applications.

The book begins with a chapter on the origin of surface properties that entails a brief review of surface forces. Van der Waals forces and electrostatic interactions are first treated, leading up to an explanation of the DLVO theory of colloid stability. The chapter continues by highlighting the effects of structural interactions at interfaces, such as ordering at short distances due to geometrical constraints and solvation forces, and steric forces between adsorbed polymer layers. The emphasis is clearly taken from the perspective of a colloidal scientist and provides a fairly comprehensive background for readers interested in solution interfaces. There is little emphasis on short-range interactions, including hydrogen bonding and acid-base interactions that are important to problems involving bulk polymer systems, such as polymer-metal adhesion and wetting. Also absent is any attempt to relate these fundamental surface forces to important measurables such as interfacial tension and adhesion strength, although these topics do receive further attention in later chapters devoted to characterization and applications. The second chapter does well to bring attention to the often neglected fact that polymer surface structure and properties may depend strongly on time, temperature, and the environment. Several examples of experimental evidence demonstrate the importance of dynamic processes at interfaces: coalescence of crazes, surface reconstruction of copolymers, aging of plasma-treated surfaces, and reorganization of side chains and functional groups at surfaces.

The second section of the book describes substantively current techniques available for the characterization of polymer surfaces. The principles that underlie each of the methods are described, followed by a brief overview of considerations regarding instrumentation and several examples of experiments that illustrate the nature of information that can be obtained from application of each technique. Chapter 3 on spectroscopic techniques is organized according to the nature of the physical probe employed: ions, for secondary ion mass spectroscopy, Rutherford backscattering and ion scattering spectroscopy; electrons for X-ray photoelectron spectroscopy; and photons for ultraviolet, visible and infrared spectroscopy techniques. An important comparison of the information obtained by these techniques and practical considerations associated with their application is also provided. After a brief review of classical surface thermodynamics, Chapter 4 focuses primarily on characterizing surface energetics of solid polymers through contact angle analysis. The chapter is divided into three sections: methods for contact angle analysis, the origins of contact angle hysteresis, and semiempirical treatments for inferring surface energetics from contact angle data. Chapter 5 describes new and emerging polymer surface characterization techniques, including direct surface force measurements, surface charge measurements, and neutron reflection.

Part 3 of the book describes techniques available for the modification of polymer surfaces and is organized according to the nature of the method: physical, chemical or bulk modification. A chapter on physical methods provides short overviews of surface modification by bombardment with high-energy species (e.g., flame, corona, plasma, electrons, and ions) and by coating thin films (sputtering and metallization). Methods involving direct chemical surface reactions receive a more substantive discussion. Topics covered include wet chemical treatments, such as etching, oxidation, hydrolysis and surface functionalization reactions, and methods to promote surface grafting reactions. A discussion of bulk modification centers on the design of surface composition in multicomponent polymeric systems. The qualitative aspects of surface segregation phenomena are covered for polymer blends and block copolymers.

Part 4 discusses applications in which surface modification is an essential element in performance. This is the most effective and successful section of the