Book Review

Macromolecules Containing Metal and Metal-Like Elements, Volume 3: Biomedical Applications Edited by Alaa S. Abd-El-Aziz (The University of Winnipeg), Charles E. Carraher, Jr. (Florida State University), Charles U. Pittman, Jr. (Mississippi State University), John E. Sheats (Rider University), and Martel Zelden (Hobart and William Smith Colleges). John Wiley & Sons, Inc.: Hoboken, NJ. 2004. xiv + 218 pp. $125.00. ISBN 0-471-66737-4.

Thomas S. Hughes

J. Am. Chem. Soc., **2005**, 127 (12), 4538-4539• DOI: 10.1021/ja040973p • Publication Date (Web): 03 February 2005

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BOOK REVIEWS

Encyclopedia of Electrochemistry, Volume 8: Organic Electrochemistry. Edited by Hans J. Schäfer (Universität Münster). Series edited by Allen J. Bard and Martin Stratmann. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2004. x + 654 pp. $455.00. ISBN 3-527-30400-2.

One of the main objectives of the *Encyclopedia of Electrochemistry* is to provide an up-to-date source of information for electrochemists and "those in other fields who use electrochemistry". Volume 8, the organic electrochemistry installment, successfully fulfills this goal by providing a detailed and current review of the subject field, with an emphasis on synthetic applications. Many of the authors stress how electrochemical methods provide a convenient means of generating and exploiting the chemistry of reactive organic intermediates such as radicals, radical ions, carbocations, and carbanions. They also point out how electrochemical oxidations and reductions can change the fundamental nature and polarity of a functional group (e.g., nucleophile → electrophile and vice versa) to achieve a desired chemical objective. Readers of this text should get a good sense of what transformations are possible with these methods and why they work. They should also gain a sufficient understanding of the experimental design that will enable them to successfully adopt these methods for their specific interests and applications.

The first two chapters focus on the logistics of organic electrochemistry: methods used to study the mechanisms of electrochemical oxidations and reductions are described as are the practical issues pertaining to preparative-scale electrochemistry, e.g., cell design, electrode materials, solvents, electrolyte, instrumentation, etc. After a very nice chapter by the editor of the volume who candidly discusses the advantages *and* disadvantages of synthetic organic electrochemistry (compared to more common chemical methods for achieving analogous transformations), emphasis is on the major reactions of organic compounds, roughly classified according to functional group.

In Chapters 4−12, electrochemical oxidation and reduction of hydrocarbons and organic compounds containing nitrogen, oxygen, sulfur, and halogen are discussed. There is also a chapter on heterocyclic compounds and another that provides an overview of the field of electrosynthesis. There is some overlap among the chapters that arises because of the nature of the classifications. However, rather than being a problem, this overlap provides the reader with a good perspective that is derived from the different viewpoints. These middle chapters are somewhat variable in the style and depth of their presentations. Some provide little more than a listing of transformations that were accomplished electrochemically, whereas others offer discussions of the reactions in terms of substrate structure (including MO theory), likely reaction mechanism, and synthetic design.

The subsequent chapters (13−15) cover organic electrochemistry in more general terms. One chapter summarizes results for a variety of reactions (many of which were discussed previously) but focuses more on issues of regio-, chemo-, *and* stereoselectivity. Specific examples and the rationale for the observed selectivity are discussed in depth based upon first principles. Other chapters cover electrogenerated acids and bases and mediated electron transfer (indirect electrochemistry). The book concludes with a chapter dealing with conducting polymers.

Although the first chapter is a description of the techniques used to study the mechanisms of electrochemical oxidations and reductions, with the few exceptions of linear and cyclic voltammetry (LSV, CV), the subsequent chapters unfortunately do not build upon this foundation. Also, the book does not provide an exhaustive review of recent advances in mechanistic organic electrochemistry. However, leading references are provided for the reader wishing to pursue these issues further.

There are only a few typos and misspellings, and these do not detract from the overall high quality of the volume. This book is presumably targeted toward synthetic organic chemists who might be interested in using electrochemistry to achieve a desired transformation. In this regard, my only criticisms are that the authors missed an opportunity to clear up some of the confusion that such a novice might experience, e.g., the definitions of and differences between oxidation and reduction potentials, half-wave potentials, and peak potentials—terms that are used in various chapters. Also, each chapter reports potentials relative to different reference electrodes; a table containing the approximate relation between these standards, presented early, would have been helpful. Overall, though, these are relatively minor issues that are overshadowed by the high quality and content of the volume as a whole.

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JA040998O

10.1021/ja040998o

Macromolecules Containing Metal and Metal-Like Elements, Volume 3: Biomedical Applications. Edited by Alaa S. Abd-El-Aziz (The University of Winnipeg), Charles E. Carraher, Jr. (Florida State University), Charles U. Pittman, Jr. (Mississippi State University), John E. Sheats (Rider University), and Martel Zelden (Hobart and William Smith Colleges). John Wiley & Sons, Inc.: Hoboken, NJ. 2004. xiv + 218 pp. $125.00. ISBN 0-471-66737-4.

This book is the third volume in a series dealing with organometallic and metalloid-containing polymers and covers three types of biomedical applications of these materials. It is the first volume in the series that reviews a series of applications; the others appear to be organized around the metals contained in the polymer.

After a first chapter that gives a historical orientation to the topic of bioactive organometallic compounds, the second and third chapters describe metal-containing DNA analogues. The

10.1021/ja040998o CCC: $30.25

bulk of the book, four chapters, deals with tin-, iron-, and platinum-containing anticancer and antiviral oligomers and polymers, and the final chapter is a discussion of inorganic−organic acid materials with dental applications.

The section on DNA covers derivatives containing pendant organometallic groups, such as ferrocene, and others with unnatural base pairs that associate by metal chelation rather than hydrogen bonding. There is a useful and timely discussion of the issue of electron transfer in DNA within the context of the electrochemistry of surface-bound ferrocene derivatives. The references in these two well-written chapters are very current, and the figures are instructive and clear. These chapters should be of general interest to many in the chemical community, as well as those with macromolecular or biomedical interests.

The next and largest section of the book contains a useful historical discussion of monomeric organometallic pharmaceuticals, and there are general discussions of the benefits and design parameters of polymeric and oligomeric drug delivery in several of the chapters. The medicinal examples in these chapters mostly consist of structural representations of anticancer or antiviral polymeric drugs (sometimes sloppily drawn) followed by a brief description of an assay or clinical result. A good variety of polymeric drugs is covered, and the modes of action are discussed for several, although not in as much detail as might be hoped. The lack of mechanistic detail in these discussions is probably attributable to what contributors Carraher and Siegmann-Louda refer to as the "gulf between chemist[s] and medical researcher[s]". As such, the middle and largest section of the book is most likely to be of interest to those in medicinal fields.

The stated theme is covered fairly well in this book, from sequence-specific DNA sensors, to polymers as drug delivery systems, to biomaterials. However, the specific topic of applications of biomaterials could have been treated in greater detail. As the editors themselves point out in the preface, the use of polysiloxanes in medical implants is a significant area of research; thus, at least one chapter covering this topic would have been welcome. The thematic approach taken in this volume challenged the editors to choose a series of topics that would represent biomedical applications of organometallic polymers in great enough depth and breadth. Because of the wide variety of applications covered, it might be difficult to identify a broad community that would find equal interest in all three sections of this book. However, each section covers its topic well, and the book as a whole does succeed in providing a good representative treatment of current biological and medicinal applications of organometallic polymers.

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JA040973P

10.1021/ja040973p

Ion Exchange and Solvent Extraction, Volume 17. Edited by Yizhak Marcus (The Hebrew University of Jerusalem) and Arup K. SenGupta (Lehigh University). Marcel Dekker, Inc.: New York, Basel. 2004. xx + 390 pp. $185.00. ISBN 0-8247-5492-1.

The current volume provides panoptic reviews of the many aspects of complexation chemistry applied to the science of separations, with the complexation of ionic and molecular species from aqueous solutions using the principles of solvent extraction being the common thread through its six chapters. A reader need not be involved solely with solvent extraction to gain important information from this book; due to the variety of complexants discussed in the different chapters, it should also be of interest to scientists whose research encompasses coordination chemistry.

The first chapter is thematically different from the others in that it centers on molecular separations of interest to the pharmaceutical industry. The remaining five chapters are reviews of ionic separations via solvent extraction (ionic separations with polymeric extractants have been reviewed in earlier volumes). Chapter 2 gives an overview of solvent extraction, Chapters 3, 4, and 5 cover specific extractants (alkylenediphosphonates, sulfoxides, and bis(dicarbollide)s, respectively), and Chapter 6 complements Chapter 5 by concentrating on the physical chemistry of ion-pair extraction with bulky anions. Thus, the first chapter is a review of biochemically relevant molecular separations, with the remaining chapters complementing each other by covering the state-of-the-art in the solvent extraction of metal ions.

In Chapter 1, "Applications of Supercritical Fluid Solvents in the Pharmaceutical Industry" by Perrut, carbon dioxide is shown to be a versatile solvent used in supercritical fluid extraction (the most developed application), supercritical fluid fractionation, and supercritical fluid chromatography. There is also discussion of two interesting applications in the area of drug delivery, wherein a supercritical antisolvent is used to prepare nano- or microparticles of poorly water-soluble drugs (e.g., insulin particles used for inhalation delivery), and a compound, such as insulin, is impregnated into polymer beads swollen by a supercritical fluid for controlled delivery.

Bart and Stevens, the authors of Chapter 2, "Reactive Solvent Extraction", discuss processes in which chemical interactions are used to accomplish a separation. The interaction can range from van der Waals forces to covalent or ionic binding as occurs when using an organic phase of mixtures of liquid anion or cation exchangers (or neutral complexants). The physical chemistry of mass transfer, solution theory, and equations relevant to equilibria, such as the Gibbs−Duhem equation, are discussed, as are the equipment used for solvent extraction and the mass transfer associated with it.

In Chapter 3, "Symmetrical *P*,*P*′-Disubstituted Esters of Alkylenediphosphonic Acids as Reagents for Metal Solvent Extraction", Chiarizia and Herlinger focus on diphosphonates as solvent extractants for ionic separations and thoroughly review their synthesis and spectroscopic characterization within the context of their coordination chemistry. Metal ion extraction by the diphosphonates in water-immiscible diluents is interpreted through the basicity of the phosphoryl oxygen, cooperative bonding by both phosphonate groups, size of the chelate ring, and the effect of aggregation. The authors also give numerous log D vs log(acid concentration) correlations for alkaline earth cations and Am(III) and discuss the reasons behind the correlations.

The succeeding chapter, "Sulfoxide Extractants and Synergists" by Kolarik, updates a review published in 1976. Distribution data and thermodynamic parameters are tabulated, and the effect of variables, including the structure of the groups on the

sulfoxides, the organic phase, and salt concentrations in the aqueous phase are discussed. The author focuses on actinides and, to a lesser extent, lanthanides and transition metal ions. Selectivity sequences are presented, and there is an extensive section on synergistic combinations of sulfoxides.

In Chapter 5, "Extraction with Metal Bis(dicarbollide) Anions: Metal Bis(dicarbollide) Extractants and Their Applications in Separation Chemistry", Rais and Grüner focus on the collaboration that developed bis(dicarbollide)s as extractants for nuclear applications by researchers at the Nuclear Research Institute and the Institute of Inorganic Chemistry of the Czech Academy of Sciences in Rez, Czech Republic. The first part of the review details the synthesis and properties of metal bis(dicarbollide)s wherein the emphasis is on cobalt bis(dicarbollide)s due to their applicability to separations of nuclear waste. The second part of the review analyzes extraction studies of the cobalt bis(dicarbollide)s, including studies in the presence of synergists.

The final chapter, authored by Rais, is entitled "Principles of Extraction of Electrolytes". The electrolytes discussed here are ion pairs: the cation is extracted with a neutral ligand, and the anion is co-extracted due to electroneutrality. The physical chemistry of the transfer of inorganic cations accompanied by bulky anions from an aqueous phase into a polar organic phase is explored in order to understand the mechanism of the extraction. General considerations of extraction equilibria are presented along with a discussion of the standard molar Gibbs energy of transfer.

Each chapter includes an extensive list of references, many of which are relatively current, i.e., one-third to one-half of the references in each chapter refer to literature published after 1994. In conclusion, it is a pleasure to recommend this volume to colleagues interested in coordination chemistry and both the chemical and engineering aspects of separations science.

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JA0409762

10.1021/ja0409762

Spin Crossover in Transition Metal Compounds III. Topics in Current Chemistry, 235. Edited by Philipp Gütlich (Johannes Gutenberg-Universität, Mainz) and Harold A. Goodwin (University of New South Wales). Springer-Verlag: Berlin, Heidelberg. 2004. xiv + 268 pp. $259.00. ISBN 3-540-40395-7.

The advent 50−60 years ago of the use of crystal and ligand field theory to understand the electronic properties of transition metal coordination complexes led to a renaissance in coordination chemistry as well as in solid state and inorganic chemistry. Indeed, crystal field theory provided the first rational explanation of why some iron(II) complexes were paramagnetic with substantial effective magnetic moments and why other, seemingly similar, iron(II) complexes were essentially diamagnetic. The key to this puzzle, the strength of the ligand crystal field and the resulting weak-field high-spin or strong-field low-spin iron(II) complexes, soon led to the realization that in the presence of the appropriate crystal field, the iron(II) complex might be induced to undergo a spin-state change from one state to the other—the change that is now referred to as either a spin-state crossover or a spin-state transition. The same crystal field approach could also be applied, rather beautifully, to understand the unusual magnetic properties of some iron(III) dithiocarbamate complexes that had been discovered in the 1930s by Cambi as well as the properties of many related d^4 to d^7 complexes. This volume, and its two companion volumes, is a result of this renaissance, and references to the use of crystal and/or ligand field theory may be found on almost every page.

The editors of the three volumes are leaders in their respective fields of research, and as would be expected from such world authorities on the spin-state crossover, the three volumes taken together present a full and balanced overview of the subject. However, the reader who is seeking an introduction to the crystal field and the consequent spin-state crossover should start with the first volume, which provides the basic background on the topic. In contrast, the third volume, with one exception, contains chapters that deal more with special topics in the field, such as the spin-crossover at high applied pressures or in large applied fields, elastic interactions, and vibrational changes in the complexes at the crossover, or with special investigative techniques, such as studies of heat capacities and, finally, nuclear inelastic scattering with synchrotron radiation—studies that depend on the iron-57 Mössbauer effect. The one exception is the last chapter, which deals with the future applications of spin-crossover compounds in so-called "molecular memory" devices, switches, and displays. The progress to date is exciting, but clearly such real applications are still far in the future. A specialist in the field will learn much from these chapters on special topics, most of which cover the literature up to and in some cases through 2002 and into early 2003.

This is the third volume in a series of three that were all apparently published in 2004. As is always the case with Springer-Verlag, the volumes are well-produced, well-illustrated, and durable, but this reviewer does wonder why three, rather small, separate volumes were required when two would surely have been adequate. Also, some of the chapters would have benefited from more careful editing, both to remove annoying typographical errors and, in some chapters, to improve the standard of the English.

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JA041006H

10.1021/ja041006h

Chromatography: Fundamentals and Applications of Chromatography and Related Differential Migration Methods, Part A: Fundamentals and Techniques, 6th ed. Journal of Chromatography Library, Volume 69A. Edited by Erich Heftmann (Orinda, CA). Elsevier B. V.: Amsterdam. 2004. xl + 544 pp. $245.00. ISBN 0-444-51107-5.

Attempting to address a topic as large as the fundamentals and techniques of chromatography and related separation methods within the space of 518 pages is an ambitious undertaking. The book is composed of a series of chapters authored by leading scientists working in chemical and biochemical separations. This edition has been completely rewritten since its predecessor in 1992. It has chapters on column liquid, affinity, ion, size exclusion, planar, electroki-

netic, and gas chromatography, as well as chapters on the theory behind separations, capillary zone electrophoresis, combined techniques, microfabricated analytical devices, and instrumentation.

There are many new chapters and new emphases within chapters in the sixth edition. With the exception of two chapters, the authors of the individual chapters are also new to this edition. I was sorry to see that some chapters in the previous edition did not survive to be included in this one, for example, those on countercurrent chromatography, supercritical fluid chromatography, field-flow-fractionation, and electrophoresis. However, the new chapters on electrokinetic chromatography, capillary zone electrophoresis, combined techniques, microfabricated analytical devices, and instrumentation are welcome additions. The focus of the chapter on ion-exchange chromatography in the fifth edition was redirected in this edition to the important subfield of ion chromatography. In general, the editor made a good effort in this edition to emphasize the most relevant current topics in the field of separations.

With such a large scope and a page allowance of just over 500 pages of text, the treatment in each chapter is usually brief by necessity. Each of the chapters could easily be the sole topic for an entire book. This volume is, however, generally well indexed and contains plenty of references; thus, it can serve as a starting point for learning more about a specific topic.

I was eager to determine if this book might work as a textbook for a graduate-level course on chemical separations. In this regard I do not think the book would be suitable (I do not believe it was ever intended to be a textbook). In most instances, the book assumes a fairly high level of pre-existing knowledge about chemical separations. For that reason, this book is better suited to be a handy and concise reference for inclusion in institutional libraries and the personal libraries of practicing separations chemists.

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JA040972X

10.1021/ja040972x

Orotidine Monophosphate Decarboxylase: A Mechanistic Dialogue. Topics in Current Chemistry, 238. Edited by Jeehiun K. Lee (Rutgers University) and Dean J. Tantillo (University of California, Davis). Springer-Verlag: Berlin, Heidelberg, New York. 2004. x + 152 pp. $139.00. ISBN 3-540-20566-7.

If you find enzymes interesting, you have probably heard or read something about the power of orotidine phosphate decarboxylase (ODCase) as a catalyst. As first pointed out by Beak and Siegel, the reaction catalyzed by this enzyme seems chemically improbable, and in 1995, it was determined that the rate of product formation by the yeast enzyme exceeds the extrapolated rate constant of the nonenzymatic reaction by 17 orders of magnitude. Two other groups of enzymes have been shown to produce even larger rate enhancements, but each of those requires the presence of a metal or other added cofactor that has catalytic properties of its own. ODCase, on the other hand, retains the distinction of functioning as a purely protein catalyst. During the past 10 years, mechanistic enzymologists, molecular biologists, crystallographers, and computational chemists have left few stones unturned in attempting to understand this enzyme, but the riddle of its mechanism of action remains unsolved. The present volume contains six review articles that summarize many of the experimental findings and convey a vivid sense of the dialogue that is now taking place between theory and experiment. At last count, no fewer than six catalytic mechanisms had been proposed for the ODCase reaction, their multiplicity reflecting the fact that the many crystal structures of this enzyme show remarkably few strong interactions with the pyrimidine ring where the action takes place. A leitmotif that emerges is the mysterious role of the proton. Four of the proposed mechanisms involve protonation of the substrate's pyrimidine ring at *O*-2, *O*-4, *C*-6, or *C*-5. The results of quantum mechanical simulations, described in this book, seem to imply that none of these processes, by itself, is likely to account for the observed rate enhancement. This addition to the *Topics in Current Chemistry* series serves as a welcome introduction to this particular enzyme and its challenges to our understanding of the catalytic power of enzymes in general.

Brian P. Callahan and Richard Wolfenden, *University of North Carolina*

JA040982Y

10.1021/ja040982y

Electronic Noses and Sensors for the Detection of Explosives. Edited by Julian W. Gardner (University of Warwick) and Jehuda Yinon (University of Central Florida). Kluwer Academic Publishers: Dordrecht, The Netherlands. 2004. xviii + 308 pp. $132.00. ISBN 1-4020-2317-0.

This book was developed from material presented at a NATO Advanced Research Workshop on the topic in Warwick, England, in 2003. In it, the application of electronic nose technology and the development of chemical sensors to detect explosives, such as land mines, are examined. There are chapters on the principles behind electronic nose technology, polymer-based sensors, metal oxide semiconducting resistive sensors, electrochemical sensors, the improvement of chemical sensors using pattern recognition techniques, use of biological systems as a model for chemical sensors, new types of electronic noses, the importance of sampling technologies, the design of microfluidic systems, and the future of trace explosive detection systems. The book concludes with a summary of the workshop and a subject index.

JA041014Y

10.1021/ja041014y

Environmental Instrumentation and Analysis Handbook. Edited by Randy D. Down (Forensic Analysis & Engineering Corp., Raleigh, NC) and Jay H. Lehr (The Heartland Institute, Chicago, IL and Bennett and Williams, Inc., Columbus, OH). John Wiley and Sons, Inc.: Hoboken, NJ. 2005. x + 1068 pp. $150.00. ISBN 0-471-46354-X.

More than three dozen professionals in environmental instrumentation and analysis were charged "to catalog nearly all

the equipment and techniques that are available to modern scientists, engineers, and technicians" for this book. Each chapter gives a detailed description of the instrument and methodology at hand, which is supported by valuable case studies and enriched by discussions of common pitfalls and how to avoid them. The chapters are organized into the following categories: Instrumentation Methodologies; Water Quality Parameters; Ground Water Monitoring; Air Monitoring; and Flow Monitoring. A detailed subject index (53 pages) concludes the book.

JA041011L

10.1021/ja041011l

Spectroscopy of Emerging Materials. Edited by Eric C. Faulques (Institut des Matériaux Jean Rouxel, Nantes), Dale L. Perry (University of California, Berkeley), and Andrei V. Yeremenko (Verkin Institute of Low Temperature Physics and Engineering, Kharkov, Ukraine). Kluwer Academic Publishers: Dordrecht, The Netherlands. 2004. xii + 414 pp. $165.00. ISBN 1-4020-2394-4.

This book was developed from the NATO Advanced Research Workshop "Frontiers in Spectroscopy of Emergent Materials: Recent Advances toward New Technologies" held in Sudak, Crimea, Ukraine, in September, 2003. Its focus is on modern spectroscopic investigations (optical, electronic, and magnetic) of emerging materials, which are defined in the preface as "(a) absolutely novel, recently synthesized compounds and new forms (ultrathin, nanostructured, etc.) of known materials, and (b) well-known materials with recently discovered exciting properties." There are 34 chapters, an author index, and a list of contributors.

JA0410136

10.1021/ja0410136

Carbocation Chemistry. Edited by George A. Olah and G. K. Surya Prakash (Loker Hydrocarbon Research Institute, University of Southern California). John Wiley and Sons, Inc.: Hoboken, NJ. 2004. x + 394 pp. $99.95. ISBN 0-471-28490-4.

This book was developed from a Kimbrough Research Symposium sponsored by the Loker Hydrocarbon Research Institute in January, 2001, to commemorate "100 Years of Carbocations". It features selected papers from the symposium chosen "to give a representative and broad view of the field, including its history, preparative aspects, characterization techniques, empirical and theoretical treatments, and applications in synthesis", to quote from the preface. A detailed index completes the book.

JA041009U

10.1021/ja041009u

CRC Handbook of Chemistry and Physics: A Ready-Reference of Chemical and Physical Data, 85th ed. Edited by David R. Lide (National Institute of Standards and Technology). CRC Press LLC: Boca Raton, FL. 2004. 2712 pp. $139.99. ISBN 0-8493-0485-7.

This famous handbook continues to provide current, critically evaluated chemical and physical data in a one-volume format. A goldmine of information, this reference work has grown over the years from 113 pages in the first edition, published in 1913, to the 2712 pages in the current edition, which includes a foreword by the well-known neurologist Oliver Sacks. The 85th edition features a new table on Azeotropic Data for Binary Mixtures as well as tables on Index of Refraction of Inorganic Crystals and Critical Solution Temperatures of Polymer Solutions. Several tables have been updated and expanded, such as Aqueous Solubility of Organic Compounds, Thermal Conductivity of Liquids, and Table of the Isotopes. In response to user requests, the topics Coefficient of Friction and Miscibility of Organic Solvents have been restored to the handbook. This volume also includes the latest recommended values of the Fundamental Physical Contants, which were released in 2003, and a revision of the Appendix on Mathematical Tables.

JA041017A

10.1021/ja041017a