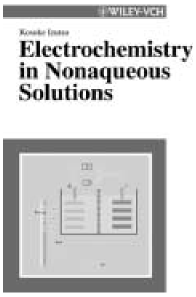
Current Events

Electrochemistry in Nonaqueous Solutions. By *Kosuke Izutsu*. Wiley-VCH, Weinheim 2002. 346 pp., hardcover € 129.00.—ISBN 3-527-30516-5

Since the mid-1960s and the groundbreaking developments of that period, which included new types of potentiostats based on electronic circuits, the refinement of electroanalytical methods based on polarography, and the introduction of computer-controlled instruments, there has been a growing trend towards measurements in nonaqueous media, mainly organic solvents, for characterizing the redox properties of molecules. The advantages that this can offer include improved solubility, especially for nonpolar substrates, and the fact that in such solvents the intermediates involved in electron-transfer-induced reactions are often sufficiently long-lived to be observed on an experimentally achievable time-scale. These advantages outweigh the possible difficulties due to low conductivity, toxicity, or volatility associated with many organic solvents. As a result of these considerations, "molecular electrochemistry" has now become almost a synonym for "nonaqueous electrochemistry".



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Many modern textbooks and monographs on electrochemistry now also deal with nonaqueous electrolytes, though usually from an electrochemical point of view. In this book Kosuke Izutsu adopts a different approach, by taking a balanced view of both aspects, the electrochemistry and the nonaqueous media. His monograph is very clearly structured. In the four chapters making up the first part of the book he begins by classifying nonaqueous solvents according to their physical, chemical, toxicological, and other properties, then discusses the solvation of ions and the behavior of electrolytes, including complex formation, both in equilibrium and from a dynamic standpoint. Acid–base and redox reactions in nonaqueous media are then discussed in detail.

This leads naturally into the second part of the book, which deals with the experimental aspects of nonaqueous electrochemistry. It begins with a detailed description of the most important electroanalytical methods. Of course, these can be found in other books, but they are needed here as an essential part of a book that can stand alone as complete within itself. Next potentiometric methods are considered in detail (i.e., measurement of potentials, usually under equilibrium conditions), followed by conductometric methods (recording conductivity), then polarographic or voltammetric methods (methods measuring current). Experimental techniques (both old and new) which do not fall within the above classical categories are also described, including spectroelectrochemistry, measurements using an electrochemical quartz microbalance, scanning electrochemical microscopy (SECM), etc. This experimental part ends by discussing the preparation and purification of solvents, including methods for testing purity, and describing in detail how to choose and prepare supporting electrolytes for measurements in nonaqueous media.

The last chapter describes technological applications of electrochemistry in organic solvents, such as lithium ion accumulators (e.g., using propylene carbonate), modern electrolytic capacitors (using γ-butyrolactone), conducting polymers (formed, e.g., in acetonitrile), reductive electrochemical fixing of atmospheric CO_2 (using dimethylformamide), electrochemical refinement of copper (with acetonitrile), and deposition of metals (e.g., with dimethylformamide or tetrahydrofuran). Other topics discussed here are the use of supercritical liquids and of ionic compounds that are liquid at room temperature. Such processes with potential for environmentally friendly benefits are examples of the possibilities for "green chemistry" which the author already mentions in his introduction to the book.

Although a number of monographs on electrochemical methods have appeared recently, including some that are very up-to-date and topical, the book reviewed here is outstanding in that Kosuke Izutsu has explored some new aspects of the subject. The close relationship between the two fields of study mentioned in the title is emphasized again and again throughout. Difficulties are not avoided, but are discussed thoroughly from both practical and theoretical standpoints. I mention here just a few of these problem areas: 1. the effects of diffusion potentials (liquid junction potentials) that may be present; 2. the problem of reference electrodes and of how to report electrode potentials, including a discussion of the relevant IUPAC recommendations (which unfortunately are still often not followed in the literature); 3. double-layer effects; 4. solvent dynamics; 5. the nuisance of the IR potential drop and ways of avoiding it or compensating for it.

The text is carefully written and is easy to read. The literature coverage extends to very recent publications. The figures are of excellent quality throughout. The

  1433-7851/02/4118-3501 $ 20.00+.50/0

chapters include many tables listing numerical data for various solvent and electrolyte properties. There is a good subject index affording detailed access to the contents of the book.

Thus, Kosuke Izutsu has produced here an excellent monograph and reference source, which will be a valuable aid in the daily work of every electrochemist engaged in experimental studies with nonaqueous solvents. Also, as the author writes in the introduction, the book will be helpful to non-electrochemists who need to use electrochemical methods. Those readers will perhaps find that there is not as much discussion about interpreting results as they would wish, but nevertheless the book will provide them with some sound background knowledge which is essential for the analysis of electrochemical experiments in nonaqueous systems.

Bernd Speiser
Institut für Organische Chemie
Universität Tübingen (Germany)

Electroanalytical Methods. Guide to Experiments and Applications. Edited by *Fritz Scholz*. Springer Verlag, Heidelberg 2002. 331 pp., hardcover € 49.95.—ISBN 3-540-42229-3

Electrochemical methods for qualitative, and especially quantitative, analysis, are unrivalled in their sensitivity and limits of detectability for many applications. They also have the advantages that the instruments are relatively cheap and the operating costs are modest. Analytical methods in which electrochemistry has only a supporting role (such as titrations using conductometric or potentiometric indicators) also have significant advantages. However, outside the circle of committed electrochemists, the capabilities of electrochemical methods do not always seem to be as fully appreciated as they deserve. Therefore, one welcomes a book which aims to overcome such reservations, to explain the proper and most effective use of these methods, and to give the potential user helpful advice that goes beyond the instrument manufacturer's handbook and operating instructions. For a single author to try to cover this broad field, which embraces such a wide variety of methods and principles, would be a bold and risky undertaking (although the book *Analytical Electrochemistry* by J. Wang, published by VCH in 1994, deserves a favorable mention here). The book reviewed here has been edited by an expert in this area, who has co-authored several of the chapters. All the other chapters have also been written by scientists who are leading experts on the particular methods that they describe. However, the choice of the word "Electroanalytical" in the title of the book is questionable. The reader expecting a book devoted to analytical methods in the original sense of that word may be rather disappointed. It rather overstretches the meaning of the word when methods for investigating the localization or the mechanism of complicated electrode reactions are included. However, as the word "analytical" appears in the titles of many journals, where it is given a meaning exactly like that in this book, it would be pointless to argue about their names. But that does not alter one's wish for a meaningful and appropriate book title.

The book begins with a chapter by Z. Stojek on the electrical double layer and its structure. The broadly worded title of this chapter might lead one to expect a textbook-style introduction to the topic, but that idea is soon dispelled on seeing that it consists of only six pages. On closer examination one is impressed at the start by the equivalent circuit diagram of an electrochemical cell. This is followed by a rather eclectic collection of discussions linking double-layer phenomena (specific adsorption, charging current) with electrochemical topics such as catalysis, peaks in voltammetry, and zero charge potential. A survey of theoretical models of the double layer is followed by a short section on the thickness of the double layer, but the reader is unlikely to be able to gain much from this. Although it ends with some indications of modern trends and new developments, that did not prevent me from wondering what was the purpose of this chapter. Also there is the closely related problem that applies to any multi-author work which includes practical aspects, namely that any editor finds it extremely difficult to impose a consistent pattern of structure, choice of content, and presentation. That problem applies especially to introductory chapters, which often do not draw specifically on the author's knowledge of his or her own speciality. As the book has obviously not been written for complete beginners in electrochemistry (since otherwise it would have had to begin with a well-structured survey of the various methods), it can be confidently assumed that the reader already has some knowledge about the electrical double layer.

In the following chapter on the thermodynamics of electrochemical reactions, F. Scholz gives a clear explanation of how observable electrochemical quantities, in particular electrode potentials and cell voltages, are related to thermodynamic parameters. Special attention is given to characteristic values measured when using electrochemical methods, such as half-wave potentials. The author answers some questions that many users will certainly have asked. His way of introducing the subject by describing a cyclic voltammogram may seem rather surprising, as it is hardly a typical approach in a discussion about thermodynamics, but it serves the author's intention very well. The next chapter, by G. Inzelt, is devoted to the kinetics of electrode reactions. After giving the derivation of the Butler–Volmer equation, which is no doubt already well known to many readers, the chapter goes on to discuss the effects of material transport and—with refreshing clarity—the concept of reversibility in electrochemical kinetics.

The following part of the book consists of nine chapters dealing with particular electrochemical methods or families of methods. By this stage the reader will have discovered that this is not a handbook of electrochemical analysis, so it will hardly come as a surprise that cyclic voltammetry is a dominant theme occupying much of the space, covered by F. Marken, A. Neudeck, and A. M. Bond. A short historical survey is followed by a description of an impressive example of the linking of chemical and electrochemical processes, in which cyclic voltammetry made a vital contribution to elucidating the mechanism. However, in aiming to link together the text, figures, and equations in a systematic way, the authors have gone a little too far: on page 52 there is a reference to

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