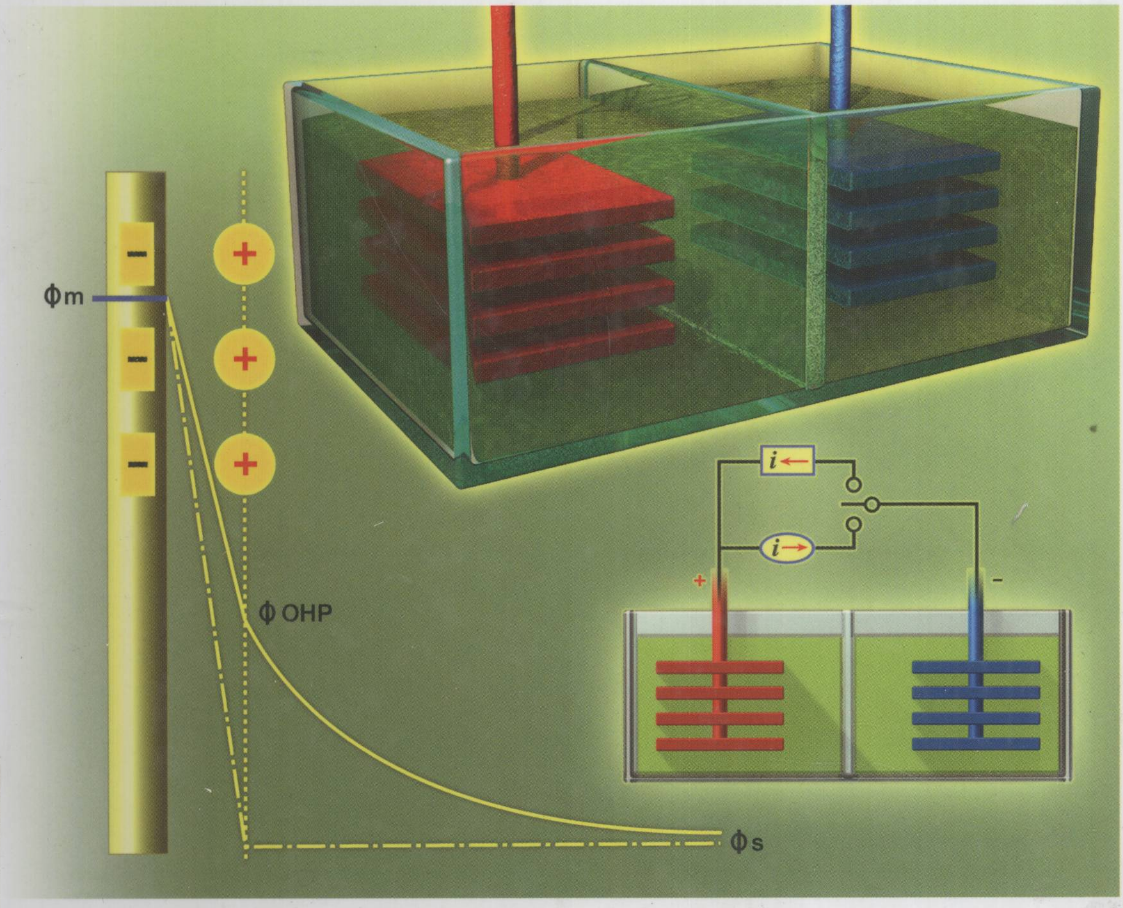
Kosuke Izutsu

WILEY-VCH

Electrochemistry in Nonaqueous Solutions

Second, Revised and Enlarged Edition



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Preface to the First Edition

A majority of chemical reactions are carried out in solution. The use of a solvent as reaction medium makes it easy to control reaction conditions such as temperature, pressure, pH, rate of mass transfer and concentration of reactant. Water is the most popular solvent. However, by using appropriate nonaqueous solvents, substances that are insoluble in water can be dissolved, substances that are unstable in water remain stable and chemical reactions that are impossible in water become possible. The reaction environments are markedly wider in nonaqueous solvents than in water.

The widespread use of nonaqueous solvents, especially dipolar aprotic solvents, began in the 1950s in various fields of pure and applied chemistry and has contributed greatly to advances in chemical sciences and technologies. From the very beginning, electrochemistry in nonaqueous solutions has played an important role in exploring new chemical possibilities as well as in providing the methods to evaluate static solvent effects on various chemical processes. Moreover, many new electrochemical technologies have been developed using nonaqueous solvents. Recently, electrochemistry in nonaqueous solutions has made enormous progress: the dynamic solvent effects on electrochemical processes have been greatly elucidated and solvent effects are now understood much better than before. On the other hand, however, it is also true that some useful solvents have properties that are problematic to human health and the environment. Today, efforts are being made, under the framework of 'green chemistry', to find environmentally benign media for chemical processes, including harmless nonaqueous solvents, immobilized solvents, ionic liquids, supercritical fluids, aqueous systems and even solventless reaction systems. For electrochemical purposes, replacing hazardous solvents with harmless solvents, ionic liquids and supercritical fluids appears to be promising.

This book was written to provide readers with some knowledge of electrochemistry in nonaqueous solutions, from its fundamentals to the latest developments, including the current situation concerning hazardous solvents. The book is divided into two parts. Part I (Chapters 1–4) contains a discussion of solvent properties and then deals with solvent effects on chemical processes such as ion solvation, ion complexation, electrolyte dissociation, acid–base reactions and redox reactions. Such

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solvent effects are of fundamental importance in understanding chemistry in nonaqueous solutions; furthermore, their quantitative evaluations are often carried out by means of electrochemical techniques. Part II (Chapters 5–12) mainly deals with the use of electrochemical techniques in nonaqueous solutions. In Chapter 5, the fundamentals of various electrochemical techniques are outlined in preparation for the following chapters. In Chapters 6–9, the applications of potentiometry, conductimetry, polarography, voltammetry and other new electrochemical techniques in nonaqueous solutions are discussed by focusing on the chemical information they provide. Chapters 10 and 11 examine methods of selecting and purifying the solvents and electrolytes of electrochemical importance. Finally, in Chapter 12, some practical applications of nonaqueous solvents in modern electrochemical technologies are discussed. These include their use in batteries, capacitors and display devices, and such processes as electrolytic refining, plating, synthesis and polymerization. The applicability of ionic liquids and supercritical fluids as environmentally benign media for electrochemical technology is also dealt with.

Most chemists are familiar with chemistry in aqueous solutions. However, the common sense in aqueous solutions is not always valid in nonaqueous solutions. This is also true for electrochemical measurements. Thus, in this book, special emphasis is placed on showing which aspects of chemistry in nonaqueous solutions are different from chemistry in aqueous solutions. Emphasis is also placed on showing the differences between electrochemical measurements in nonaqueous systems and those in aqueous systems. The importance of electrochemistry in nonaqueous solutions is now widely recognized by nonelectrochemical scientists – for example, organic and inorganic chemists often use cyclic voltammetry in aprotic solvents to determine redox properties, electronic states and reactivities of electroactive species, including unstable intermediates. This book will therefore also be of use to such nonelectrochemical scientists.

I obtained most of the information included in this book from the publications of many scientists in this field. I would like to express my sincere thanks to all of them. I also would like to thank my coworkers for their cooperation, the editorial and production staff of Wiley-VCH for their help and support and my wife for her assistance and patience.

Matsumoto
December 2001

Kosuke Izutsu

Preface to the Second Edition

The second edition consists of three parts: Part I (Chapters 1–4) is for electrochemical aspects of the fundamentals of chemistry in nonaqueous solutions, Part II (Chapters 5–12) deals with the electrochemical techniques and their applications in nonaqueous solutions and Part III (Chapters 13 and 14) is concerned with the electrochemistry in new solvent systems. Chapter 13 is on the electrochemistry in clean solvents and special emphasis is placed on supercritical fluids and (room-temperature) ionic liquids. Chapter 14 is on the electrochemistry at the liquid–liquid interfaces and, in addition to charge transfers at the interface between water and organic solvents, those at the interface between water and ionic liquid are also discussed. Since the publication of the first edition, considerable efforts have been made in pursuing green solvents that are benign to human health and the environment. Especially, the movement in the field of ionic liquids has been remarkable and the rapid progress is still continuing. Most of the ionic liquids are nonvolatile, nonflammable, less toxic, chemically and thermally stable and good solvents for both organic and inorganic materials. Due to their aprotic properties, many ionic liquids can replace aprotic organic solvents, particularly for use in electrochemistry. Moreover, the immiscibility of ionic liquids with water makes possible their applications to the water/ionic liquid interfaces in various ways, including electrochemical uses.

Besides the addition of the two new chapters, each of the Chapters 1–12 has been updated and revised. Especially, the revision in Chapter 12 is considerable because the use of nonaqueous solutions in modern electrochemical technologies is steadily increasing.

Although some nonaqueous solvents that are hazardous to human health and the environment cannot be used or should be used with great care, the needs for the electrochemical use of less hazardous solvents, including supercritical fluids and ionic liquids, are increasing. Thus, the knowledge of electrochemistry in nonaqueous solutions is also increasing its importance.

Finally, I wish to thank the editorial and production staff at Wiley-VCH Verlag GmbH, for their help and support in making this edition.

Musashino, Tokyo
August 2009

Kosuke Izutsu

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