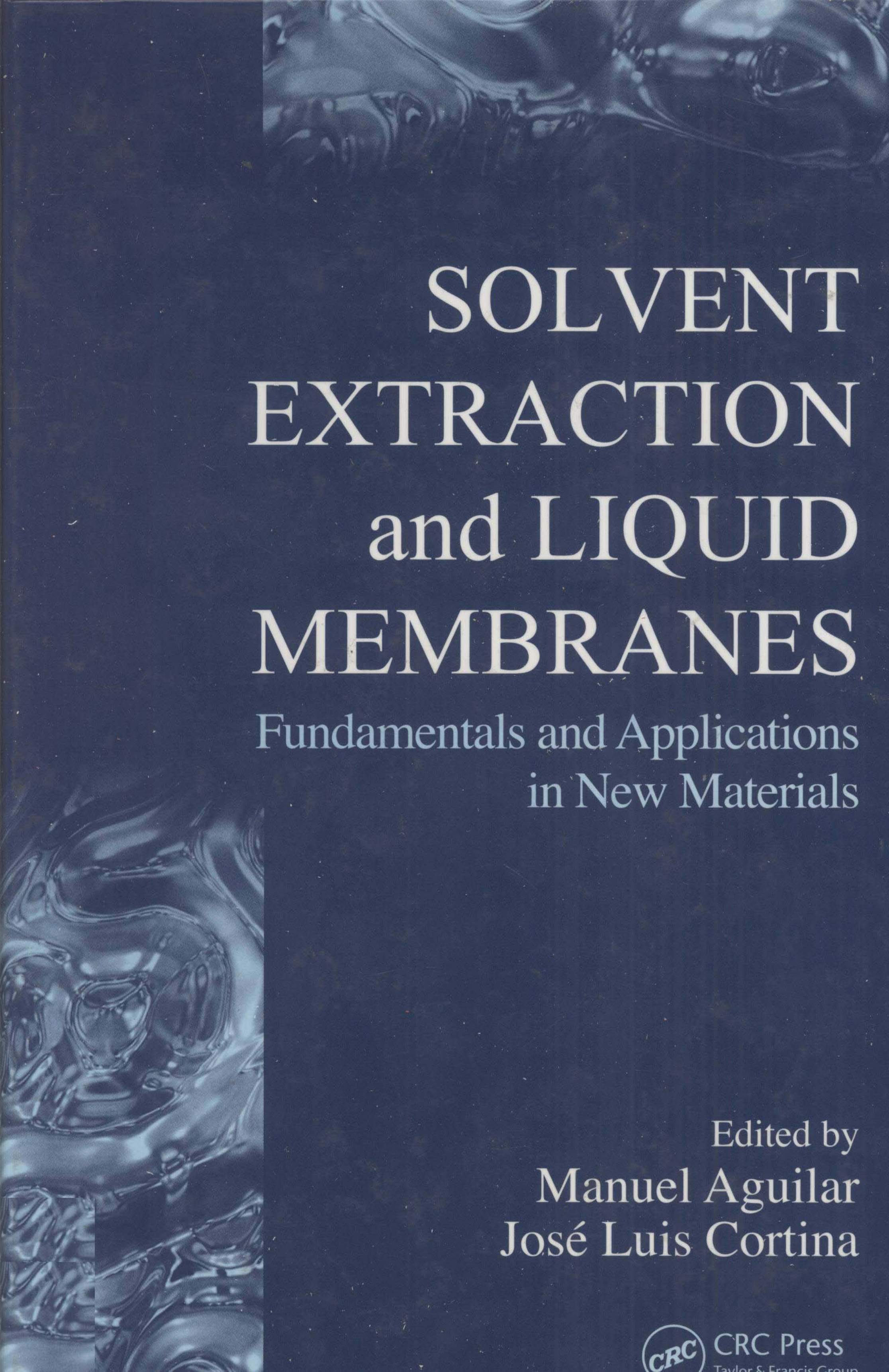

SOLVENT EXTRACTION and LIQUID MEMBRANES

Fundamentals and Applications in New Materials

Edited by
Manuel Aguilar
José Luis Cortina

CRC Press
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Foreword

The International Solvent Extraction Conferences (ISECs) have been held every 3 years since 1971 in various countries around the world. The 1999 conference (ISEC99) was held in Barcelona, Spain. It was organized under the concept of being a "good soup," so the best ingredients were combined both to have a good taste and to provide the best healthy nutrition to grow on solvent extraction fundamentals and applications. Under this concept the Organizing Committee decided to cook ISEC99 with a special ingredient by preceding the conference with a Summer School addressing the principles and applications of solvent extraction for the benefit of students and newcomers to this widely used technique in separation science. Although this idea of providing short courses on topics related to the main conference is an established practice elsewhere, this was the first time such a course was offered as part of an ISEC. The aim of the course organizers was to provide a fairly comprehensive overview of the fundamental and practical applications of solvent extraction, so they contacted a number of internationally recognized experts to talk about their particular fields of interest.

As a result, this publication represents a good recipe to feed the present and future newcomers to the solvent extraction community. Thus, the text presents the perspectives of solvent extraction (SX) in the twenty-first century, a new focus of fundamentals of solvent extraction, renewed topics of calculations on extraction equilibria, liquid membranes, and industrial applications. The book also introduces topics of new materials and solid sorbents for solvent extraction including the improved and developing topic of solvent impregnated resins. The content of this publication, presented with a tutorial focus, will benefit the understanding of solvent extraction for today's practice.

Michael Cox
Manuel Valiente

Preface

Following the activities of the first School in Solvent Extraction in Barcelona in 1986, and coincident with the 1999 International Solvent Extraction Conference (ISEC), the second International Solvent Extraction School (ISES) was held in Bellaterra, Spain. The school gathered senior and young scientists and engineers with the main idea of discussing the fundamentals and practice of solvent extraction (SX) and liquid membranes (LM) and to grow the new ideas and trends to contribute to the best understanding of applications of SX and LM in the future. The lecturers were leading experts in solvent extraction and liquid membranes.

One of the conclusions from the International Solvent Extraction Committee was to recommend to the authors of this book and the chairs of the ISES to produce a reference book by converting the lectures into written material.

The different uses of liquid–liquid extraction, liquid membranes, and solvent impregnated materials make the subject important for university students of chemistry, metallurgy, hydrometallurgy, and chemical and mineral processing technology. Some universities offer special courses on separation processes in which those techniques are minor topics in more comprehensive courses. Laboratory experiments on liquid–liquid and liquid membranes are common in chemical and mineral processing engineering curricula. Because of the breadth of the subject, the treatment in such courses is often scarce, and more comprehensive text is difficult to find in a form suitable for use directly with students.

To meet this demand, and to answer the request of the ISEC, we initiated this project to develop a simple text suitable not only for students but also for scientists and engineers in the field. However, no single scientist or engineer can be an expert in all parts of the field. Therefore, it seemed that the best idea was to develop this book as a joint project among many expert authors, each of whom has in many cases years of experience in research, teaching, or industrial development. The result is an international book at a high scientific and technical level.

In this context, we would like to point out that this book represents the effort to bring together the key important topics dealing with thermodynamics, kinetics, interfacial behavior, process and plant applications, including chemical and engineering aspects of new extraction systems based on synthetic materials by the leading experts at the school. The book is directed toward third- to fourth-year undergraduate and postgraduate chemistry and chemical engineering students as well as toward researchers and developers in the chemical industry, the mining and mineral processing industry, and the waste treatment industry. The book is also intended for chemical, metallurgical, mineral processing, and waste treatment engineers who already use this technique but have a desire to understand better or to solve existing process problems. Furthermore, the book should be useful for researchers in solvent extraction who wish to learn about its applications in areas other than their own.

So, after an introduction to SX and LM in the perspective of the twenty-first century (Chapter 1), the following two chapters (Chapters 2 and 3) present the physical principles (thermodynamics and kinetics) in SX processes and the tools for computation of the equilibrium and kinetic parameters. They are followed by three chapters of various industrial applications and process experience on SX and LM (Chapters 4 through 6), including optimization and modeling tools. The three final chapters (Chapters 7 through 9) focus on new materials in SX and LM science and technology, including functionalized organic and inorganic solid sorbents and solid impregnated sorbents, indicating the research frontiers and future developments in new materials.

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We the editors want to express our gratitude to the contributors, who made this book possible through their helpful suggestions and extensive efforts. Professor Michael Cox, Professor Josef Havel, Dr. Karel Jeřábek, Professor Vadim Korovin, Dr. Anil Kumar Pabby, Professor Immaculada Ortiz Uribe, Professor Angel Irabien, Dr. Jun S. Lee, Dr. Sergio Gomez Salazar, Professor Ana María Sastre, Dr. Yuri Shestak, Dr. Kathryn C. Sole, Professor Lawrence L. Tavlarides, Professor Hitoshi Watarai, Dr. Yuri Pogorelov, and Professor Abraham Warshawsky worked hard and successfully on their chapters and provided us much valuable help. The success of this book belongs to our distinguished authors.

We thank Nita Lekhwani and David Russell on the initial editorial staff at Marcel Dekker and to David Fausel and Barbara Glunn and the new staff at Taylor & Francis for their invaluable editorial assistance.

About the Editors

Manuel Aguilar, Ph.D., was born in Spain in 1943. He achieved his licentiate studies in chemistry at the University of La Laguna in Tenerife, Spain with a main focus in analytical chemistry. From 1965 to 1969 he was assistant lecturer at the University de Los Andes in Venezuela. From 1970 through 1976 he was research assistant at the Royal Institute of Technology in Stockholm, Sweden, where he completed his Ph.D. studies under the supervision of Professor E. Hogfeldt. In 1976 he returned to Spain and was assistant professor of inorganic and analytical chemistry at the Universidad Autonoma in Barcelona. Since 1977, he has been professor of chemistry in the Department of Chemical Engineering at the Universitat Politécnica de Catalunya. Dr. Aguilar has been active in chemical research for many years, with a main interest in the field of ionic equilibrium and solvent extraction, and he has published more than 100 papers in this field. He has also been involved in the field of education, in which he has published different books and compendia on ionic equilibrium and has directed two international solvent extraction schools and diverse postgraduate courses in Spain and South America. Dr. Aguilar has been active in equilibrium analysis and computers, participating in the production of various programs for treatment of hydrochemical systems and in the program of virtual laboratory for experimental laboratory teaching for basic chemistry courses.

José Luis Cortina, Ph.D., was born in Ligüerrre de Cinca, Spain, in 1964. He has been professor of chemical engineering at the Universitat Politécnica de Catalunya in Barcelona, Spain, since 2001 and project research technical director at the Water Technology Center (CETaqua) since 2007. Dr. Cortina received B.Sc., D.Sc., and Ph.D. degrees from the University of Barcelona in Spain. He has been a visiting scientist at the Polymer Chemistry Department at the Weizmann Institute of Science in Rehovot, Israel, and at the Center for Process Analytical Chemistry at the University of Washington in Seattle at the Fiber Optical Chemical Laboratory. Dr. Cortina has been active in chemical technology research for many years, with a main interest in the field of treatment and separation processes for industrial and environmental applications using solvent extraction and ion exchange, and he has published more than 70 papers in this field. During the last several years his research has been centered on the treatment technologies for soil and groundwater remediation. He has been a member of the International Committee on Ion Exchange since 2004.

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1 Liquid–Liquid Extraction and Liquid Membranes in the Perspective of the Twenty-First Century

Michael Cox

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1.1 LIQUID–LIQUID EXTRACTION

Liquid–liquid extraction is now very well established, featuring extensively as a selective separation process. Liquid membranes are a more recent development, which as yet have not featured significantly in industrial applications. This chapter focuses on the current and future prospects of these techniques largely in the context of metal extraction, as that is the area in which I have spent most of my time.

It first addresses the subject of liquid–liquid extraction, dealing in turn with extractants, systems, and, lastly, equipment.

1.1.1 EXTRACTANTS

Because metals generally exist in aqueous solution as hydrated ions before the metal can be extracted into a nonpolar organic phase, the water molecules must be replaced and any ionic charge reduced or removed. This can be achieved in different ways by using three types of extractants: acidic, basic, and solvating, which extract metals according to the following equilibrium reactions:

$$\text{Acidic: } M^{z+}_{(aq)} + z\,HA_{(aq,\text{ or }org)} \Leftrightarrow MA_{z\,(org)} + z\,H^{+}_{(aq)} \tag{1.1}$$

$$\text{Basic: } (n\text{-}z)R_4N^{+}_{(aq\text{ or }org)} + MX_n^{(n\text{-}z)\text{-}}{}_{(aq)} \Leftrightarrow (n\text{-}z)R_4N^{+}MX_n^{(n\text{-}z)-}{}_{(org)} \tag{1.2}$$

$$\text{Solvating: } MX_{z\,(aq)} + mS_{(org)} \Leftrightarrow MX_zS_{m\,(org)} + mH_2O \tag{1.3}$$

Acidic extractants include simple reagents such as carboxylic acids and organophosphorus acids, as well as chelating acids. The latter are often derived from analytical reagents, such as β-diketones, 8-hydroxyquinoline, and hydroxyoximes. Extraction occurs by a change of the acidity in solution; thus, increasing the pH of solution increases extraction, and decreasing the pH promotes stripping or back-extraction. Therefore, by changing the acidity of the system the metal can be cycled to and from the organic phase.

The extent of extraction also depends on the magnitude of the metal-extractant formation constant and concentration of extractant. These factors can be combined with the distribution coefficient in the following equation derived from Equation 1.1 and the law of mass action:

$$\text{Log } D = \log K_f + z\log[HA] + z\text{pH} \tag{1.4}$$

This equation allows the stoichiometry of Equation 1.1 to be confirmed by constructing linear plots of log D versus pH and log D versus log[HA]. Note in situations where the extractant cannot satisfy both the coordination number and ionic charge of the metal ion, then additional nonionized extractant molecules can be added to the complex (Equation 1.5). In this case the linear log D versus log[HA] plot will have a slope of (z + s).

$$M^{z+}_{(aq)} + (z + s)HA_{(aq,\ or\ org)} \Leftrightarrow MA_z\,(HA)_{s(org)} + z\,H^+_{\ (aq)} \qquad (1.5)$$

As noted already, the extent of extraction depends on the relevant formation constant of the metal or extractant (K_f). For metals in the first transition series this will generally follow the Irving-Williams series: that is, for divalent metals, V < Cr < Mn < Fe < Co < Ni < Cu > Zn. Thus, unless other factors are involved copper will be extracted at lower pH values than the other elements. In addition it is found that $M^{4+} > M^{3+} > M^{2+} > M^+$, so that thorium(IV) will be extracted before iron(III) in turn before copper(II) before sodium.

Although the majority of acidic extractants is based on oxygen donor groups, some commercial compounds include a sulfur donor atom. These, of course, would be favored when the extraction of a soft metal is required. These generally consist of elements in low oxidation states or the heavier elements in any group in the Periodic Table.

In certain cases, the separation of metals is a result of kinetic rather than thermodynamic considerations, such as extraction of copper at a lower pH than iron(III) by a commercial 8-hydroxyquinoline derivative, Kelex 100 (Cognis, Inc., Tucson, Arizona, formerly Witco Corporation). If contact is restricted to about 5 minutes then copper extraction is preferred, but when the reaction is allowed to progress to equilibrium then the iron is extracted. This is in contrast to the separation of copper and iron(III) with β–hydroxyoximes, such as LIX860 (Cognis, Inc., formerly Henkel Corporation) or M5640 (Avecia, formerly Zeneca Specialties), which is thermodynamically controlled.

Stripping of the metal from the loaded organic phase is just as important as extraction, and here this process is achieved quite simply by a change in acidity of the system. However, it should be remembered that extractants that extract metals at low pH values will require more concentrated acid for stripping. Thus, it is not always a good idea to use the extractant that extracts too well. Also it is important to realize that extraction and separation is only one process in a hydrometallurgical flow sheet, and it is necessary to choose the extractant that will most easily interface with the operations both upstream and downstream.

Basic extractants normally consist of alkylammonium species, although for analytical applications organophosphonium or organoarsonium compounds may be used. Quaternary ammonium species as shown in Equation 1.2 or uncharged alkylammonium compounds may be used as extractants. In the latter case the presence of excess anions in the system allows the formation of charged species as, for example, Equation 1.6:

$$R_3N + HX \Leftrightarrow R_3NH^+X^- \qquad (1.6)$$

In the case of alkylammonium extractants it has been observed that the magnitude of extraction follows the order $R_4N^+ > R_3NH^+ > R_2NH_2^+ > RNH_3^+$ with the size of the alkyl group R generally between 8 and 10 carbon atoms. The structure of the alkyl groups is important, and by using straight or branched chain substituents different properties can be found. In commercial practice the trialkylammonium compounds are generally more commonly used in spite of their inferior extraction properties because they are cheaper than the quaternary extractants.

These extractants require the presence of stable anionic metal complexes to form the extractable ion pair complexes, so that only metals that produce such species can be extracted with these compounds. The ease of metal extraction follows the magnitude of the formation coefficient of the anionic complex. Thus, in halide solution, gold (III) > iron (III) > zinc > cobalt > copper >>> nickel.

Stripping of the metal from the loaded organic phase can be achieved by causing the breakdown of either the anionic metal complex with, for example, water, or the cationic extractant by treatment with a base. The latter will, of course, not work in the case of the quaternary tetraalkylammonium ions, R_4N^+.

Solvating extractants operate by replacing the solvating water molecules around the aqueous metal complex, making the resulting species more lipophilic. Such extractants must possess lone pairs of electrons that can be donated to the metal ion, and the most common donor atoms are oxygen and sulfur. Nitrogen and phosphorus can also feature as donors but, for a number of reasons, are not generally used. The types of organic compounds used include those based on carbon—that is, alcohols, ethers, esters, and ketones with compounds such as dibutylcarbitol, nonyl phenol, and iso-butylmethylketone (MIBK). Amides, $RCONR_2$, have also been proposed for specialized applications such as the extraction of actinides and precious metals. However, the most commonly used oxygen-donating solvating extractants are based on the organophosphorus compounds: alkylphosphates, $(RO)_3PO$; alkylphosphonates, $(RO)_2RPO$; alkylphosphinates, $(RO)R_2PO$; and alkylphosphine oxides, R_3PO. The donor properties of the oxygen atom follow the aforementioned trend with the greater the number of C-P bonds, the better the donor; however, for economic reasons trialkylphosphates are the chosen extractants for commercial use, with tri-n-butylphosphate probably the most widely used extractant worldwide.

Sulfur donor extractants are less common, although dialkylsulfides have been used in precious metal extraction, and a trialkylphosphine sulfide, R_3PS (Cyanex 471X, Cytec Inc., New Jersey), is available commercially. Such sulfur donating extractants will need to be considered when extracting and separating soft metals, such as second- and third-row transition metals (e.g., cadmium, mercury, and palladium).

Stripping can be achieved by contact with water (Equation 1.3) or by raising the temperature of the system.

1.1.2 SYNERGISTIC EXTRACTION

On occasion, mixtures of two different extractants will enhance the extraction of a metal above that expected from the summation of the performance of the two reagents separately. This gives rise to the synergistic factor (SF), defined as follows:

$$SF = D_{AB}/(D_A + D_B) \tag{1.7}$$

A large number of examples of synergism can be found in the literature, although very few of these have actually been commercialized. The main reason for the lack of industrial interest is probably the difficulty in maintaining the optimum ratio of extractants in the organic phase to provide synergism. Different extractant losses