

ION EXCHANGE AND SOLVENT EXTRACTION

edited by JACOB A. MARINSKY
and YIZHAK MARCUS

Volume **10**

ION EXCHANGE AND SOLVENT EXTRACTION

A SERIES OF ADVANCES

Volume 10

EDITED BY

Jacob A. Marinsky

Department of Chemistry
State University of
New York at Buffalo
Buffalo, New York

Yizhak Marcus

Department of Inorganic Chemistry
The Hebrew University
Jerusalem, Israel

MARCEL DEKKER, INC.

New York and Basel

The Library of Congress has cataloged this work as follows:

Ion exchange and solvent extraction. v. 3- 1973-
New York, M. Dekker.

v. illus. 24 cm.

Editors: 1973- J. A. Marinsky and Y. Marcus.
Formed by the union of: Solvent extraction reviews, ISSN
0038-125X, and: Ion exchange, ISSN 0075-0328, and continues
the vol. numbering of the latter.
ISSN 0092-0193 = Ion exchange and solvent extraction.

1. Ion exchange--Collected works. 2. Solvent extraction--
Collected works. I. Marinsky, Jacob A., ed. II. Marcus,
Yizhak, ed.

[DNLM: W1 I01125]

QD561.I58 541'.3723

73-645531
MARC-S

Library of Congress 73[8602r85]rev

COPYRIGHT © 1988 by MARCEL DEKKER, INC.

ALL RIGHTS RESERVED

Neither this book nor any part may be reproduced or transmitted in
any form or by any means, electronic or mechanical, including
photocopying, microfilming, and recording, or by any information
storage and retrieval system, without permission in writing from
the publisher.

MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

ION EXCHANGE AND SOLVENT EXTRACTION

Preface

Solvent extraction is involved in many industrial, scientific, and technological fields, including analytical chemistry, coordination chemistry, hydrometallurgy, processing chemistry, purification and recovery of organic chemicals and biochemicals, radiochemistry, and waste treatment. Appropriately, International Solvent Extraction Conferences (ISEC) devoted to the science and technology of solvent extraction take place every three years or so. Since Volume 8 in the Ion Exchange and Solvent Extraction series devoted to solvent extraction was published, the ISEC '83 in Denver, Colorado and ISEC '86 in Munich, Federal Republic of Germany have taken place, and ISEC '88 is announced for Moscow, USSR. This international activity is good evidence for the viability of the subject, as it is for the desirability of periodic authoritative reviews of its contents and philosophy. The present volume is a contribution to this, within the scope of the series.

The method of selection of the subjects for review and the authors best suited for reviewing them was essentially the same as that used previously. Areas of continued importance were identified, and viewpoints from different schools of investigation were solicited. Chapters on five subjects resulted from this process, but readers interested mainly in an aspect covered in a certain chapter will

benefit from also perusing the other chapters, since cross-fertilization from different areas has always been one of the most important sources of new ideas.

Much of the solvent extraction literature and industrial practice in the past has evolved around the recovery and separation of metals from aqueous solutions. However, in recent years the recovery and separation of organic compounds have gained increasing importance. The chapter by King and Senetar addresses the developments in this field, both from the standpoint of the recovery of valuable materials and from that of the purification of wastewaters. (One aspect of the solvent extraction of organic compounds, namely the extraction of ion pairs of pharmaceutical significance, was reviewed by Schill in Volume 6 of this series.)

Two of the newer areas in solvent extraction are the application of liquid membranes and of liquefied gases under very high pressures. The chapter by Noble, Way, and Bunge deals with liquid membranes, both those supported in solid matrices and those that are constituents of double emulsions. An aspect not heretofore dealt with in this series is the separation of gases by means of solvent extraction, and supported liquid membranes are shown in this chapter as a possible means to this end. The application of liquefied gases under pressure to extraction is a well-known and widely applied process in the food industry (decaffeination of coffee by means of condensed carbon dioxide), but its wider applicability to many other systems has not caught the attention of investigators so far. The chapter by Brunner rectifies this oversight and presents the range of possible applications as well as the scientific and technological premises required for them.

A subject of great importance in solvent extraction, that bears strongly on the rate of extraction, is surface phenomena. A previous review of electrical phenomena (by Scibona, Danesi, and Fabiani in Volume 8 of this series) touched on this subject, but the present paper by Tarasov and Yagodin deals with it in a comprehensive manner, examining alternative views and various conditions that contribute

to the variety of surface phenomena in solvent extraction, hence to the rate of mass transfer.

Finally, in the tradition of previous volumes, there is the chapter by Hala describing the solvent extraction of a group of metal ions, namely the refractory zirconium and hafnium. Their extraction and separation from aqueous solutions is an important radiochemical problem, and one of the means of enhancing the separability of these very similar metal ions is by synergism applied judiciously to appropriate extraction systems. The last chapter thus concentrates on the problem of synergism, as applied to the separation of the Zr(IV) and Hf(IV) ions.

It is hoped that the readers will find in these chapters stimulating information and ideas that will help them to make their own contributions to this expanding field of solvent extraction.

Yizhak Marcus

Contributors to Volume 10

Gerd Brunner Arbeitsbereich Verfahrenstechnik II, Technische Universität Hamburg-Harburg, Hamburg, Federal Republic of Germany

Annette L. Bunge Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado

Jiri Hala Department of Inorganic Chemistry, J. E. Purkyne University, Brno, Czechoslovakia

C. Judson King Department of Chemical Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, California

Richard D. Noble Center for Chemical Engineering 773.1, National Bureau of Standards, Boulder, Colorado

*John J. Senetar** Department of Chemical Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, California

Valery V. Tarasov D. I. Mendeleev Institute of Chemical Technology, Moscow, USSR

J. Douglas Way⁺ Center for Chemical Engineering 773.1, National Bureau of Standards, Boulder, Colorado

Gennady A. Yagodin D. I. Mendeleev Institute of Chemical Technology, Moscow, USSR

* *Current affiliation:* Amoco Oil Company, Amoco Research Center, Naperville, Illinois

⁺ *Current affiliation:* Chemical Engineering Laboratory, SRI International, Menlo Park, California

Contents of Other Volumes

Volume 1

TRANSPORT PROCESSES IN MEMBRANES *S. Roy Caplan and Donald C. Mikulecky*

ION-EXCHANGE KINETICS *F. Helfferich*

ION-EXCHANGE STUDIES OF COMPLEX FORMATION *Y. Marcus*

LIQUID ION EXCHANGERS *Erik Högfeltd*

PRECISE STUDIES OF ION-EXCHANGE SYSTEMS USING MICROSCOPY
David H. Freeman

HETEROGENEITY AND THE PHYSICAL CHEMICAL PROPERTIES OF ION-EXCHANGE
RESINS *Lionel S. Goldring*

ION-EXCHANGE SELECTIVITY *D. Reichenberg*

RESIN SELECTIVITY IN DILUTE TO CONCENTRATED AQUEOUS SOLUTIONS
R. M. Diamond

INTERPRETATION OF ION-EXCHANGE PHENOMENA *Jacob A. Marinsky*

Volume 2

ION EXCHANGE IN GLASSES *Robert H. Doremus*

ION EXCHANGE IN MOLTEN SYSTEMS *E. C. Freiling and M. H. Rowell*

THE ION-EXCHANGE PROPERTIES OF ZEOLITES *Howard S. Sherry*

INTERACTIONS BETWEEN ORGANIC IONS AND ION-EXCHANGE RESINS
Jehuda Feitelson

PARTITION CHROMATOGRAPHY OF SUGARS, SUGAR ALCOHOLS, AND SUGAR
DERIVATIVES *Olof Samuelson*

SYNTHESIS OF ION-EXCHANGE RESINS *R. M. Wheaton and M. J. Hatch*

Volume 3

EXTRACTION OF METALS BY CARBOXYLIC ACIDS *D. S. Flett*

SOLVENT EXTRACTION WITH SULFONIC ACIDS *G. Y. Markovits and G. R. Choppin*

NUCLEAR MAGNETIC RESONANCE STUDIES OF ORGANOPHOSPHORUS EXTRACTANTS
W. E. Stewart and T. H. Siddall III

EXPERIENCE WITH THE AKUFVE SOLVENT EXTRACTION EQUIPMENT *J. Rydberg, H. Reinhardt, and J. O. Liljenzin*

Volume 4

ION EXCHANGE IN NONAQUEOUS AND MIXED SOLVENTS *Yizhak Marcus*

LIGAND EXCHANGE CHROMATOGRAPHY *Harold F. Walton*

LIQUID ION EXCHANGE TECHNOLOGY *Robert Kunin*

ELECTRONIC AND IONIC EXCHANGE PROPERTIES, CONDUCTIVITY, AND PERMSELECTIVITY OF ORGANIC SEMICONDUCTORS AND REDOX EXCHANGERS
René Buvet, Michel Guillou, and Liang-Tsé Yu

EQUATIONS FOR THE EVALUATION OF FORMATION CONSTANTS OF COMPLEXED ION SPECIES IN CROSSLINKED AND LINEAR POLYELECTROLYTE SYSTEMS
Jacob A. Marinsky

Volume 5

NEW INORGANIC ION EXCHANGES *A. Clearfield, G. H. Nancollas, and R. H. Blessing*

APPLICATION OF ION EXCHANGE TO ELEMENT SEPARATION AND ANALYSIS
F. W. E. Strelow

PELLICULAR ION EXCHANGE RESINS IN CHROMATOGRAPHY *Csaba Horvath*

Volume 6

ISOLATION OF DRUGS AND RELATED ORGANIC COMPOUNDS BY ION-PAIR EXTRACTION *Göran Schill*

THE DYNAMICS OF LIQUID-LIQUID EXTRACTION PROCESSES *G. G. Pollock and A. I. Johnson*

APPLICATION OF THE SOLUBILITY CONCEPT IN LIQUID-LIQUID EXTRACTION
H. M. N. H. Irving

SOLVENT EXTRACTION IN THE SEPARATION OF RARE EARTHS AND TRIVALENT ACTINIDES *Boyd Weaver*

Volume 7

INTERPHASE MASS TRANSFER RATES OF CHEMICAL REACTIONS WITH CROSSLINKED POLYSTYRENE *Gabriella Schmuckler and Shimon Goldstein*

INFLUENCE OF POLYMERIC MATRIX STRUCTURE ON PERFORMANCE OF ION-EXCHANGE RESINS *V. A. Davankov, S. V. Rogozhin, and M. P. Tsyurupa*

SPECTROSCOPIC STUDIES OF ION EXCHANGERS *Carla Heitner-Wirguin*
ION-EXCHANGE MATERIALS IN NATURAL WATER SYSTEMS *Michael M. Reddy*
THE THERMAL REGENERATION OF ION-EXCHANGE RESINS *B. A. Bolto and D. E. Weiss*

Volume 8

METAL EXTRACTION WITH HYDROXYOXIMES *Richard J. Whewell and Carl Hanson*
ELECTRICAL PHENOMENA IN SOLVENT EXTRACTION *Giancarlo Scibona, Pier Roberto Danesi, and Claudio Fabiani*
EXTRACTION WITH SOLVENT-IMPREGNATED RESINS *Abraham Warshawsky*
SOLVENT EXTRACTION OF ELEMENTS OF THE PLATINUM GROUP *Lev M. Gindin*
SOLVENT EXTRACTION FROM AQUEOUS-ORGANIC MEDIA *Jiri Hala*

Volume 9

ION-EXCHANGE PROCESSES USED IN THE PRODUCTION OF ULTRAPURE WATER REQUIRED IN FOSSIL FUEL POWER PLANTS *Calvin Calmon*
A SYSTEMATIC APPROACH TO REACTIVE ION EXCHANGE *Gilbert E. Janauer, Robert E. Gibbons, Jr., and William E. Bernier*
ION-EXCHANGE KINETICS IN SELECTIVE SYSTEMS *Lorenzo Liberti and Roberto Passino*
SORPTION AND CHROMATOGRAPHY OF ORGANIC IONS *G. V. Samsonov and G. E. Elkin*
THERMODYNAMICS OF WATER SORPTION OF DOWEX 1 OF DIFFERENT CROSS LINKING AND IONIC FORM *Zoya I. Sosinovich, Larissa V. Novitskaya, Vladimir S. Soldatov, and Erik Högfeldt*
DOUBLE-LAYER IONIC ADSORPTION AND EXCHANGE ON POROUS POLYMERS *Frederick F. Cantwell*
HUMIC-TRACE METAL ION EQUILIBRIA IN NATURAL WATERS *Donald S. Gamble, Jacob A. Marinsky, and Cooper H. Langford*

Contents

Preface	iii
Contributors to Volume 10	vii
Contents of Other Volumes	xi
Chapter 1 SOLVENT EXTRACTION OF INDUSTRIAL ORGANIC SUBSTANCES FROM AQUEOUS STREAMS	1
<i>C. Judson King and John J. Senetar</i>	
I. Introduction	1
II. General Considerations	6
III. Recovery of Specific Substances	27
IV. Removal of Contaminants from Aqueous Streams	40
References	54
Chapter 2 LIQUID MEMBRANES	63
<i>Richard D. Noble, J. Douglas Way, and</i> <i>Annette L. Bunge</i>	
I. Introduction	63
II. Experimental Methods	70
III. Modeling	74
IV. Applications	84
V. Industrial Applications of Liquid Membrane Technology	92
VI. Conclusions	94
References	95
Chapter 3 MIXED SOLVENTS IN GAS EXTRACTION AND RELATED PROCESSES	105
<i>Gerd Brunner</i>	
I. Introduction	105
II. Gas Extraction with Pure Solvents	107

III.	Gas Extraction with Solvent Mixtures	114
	References	139
Chapter 4	INTERFACIAL PHENOMENA IN SOLVENT EXTRACTION	141
	<i>Valery V. Tarasov and Gennady A. Yagodin</i>	
I.	Introduction	141
II.	Fundamentals of Extraction Kinetics	142
III.	Methods of Studying Extraction Kinetics	168
IV.	Methods for Studying the Interface Properties	172
V.	Identification of Interfacial Processes	173
VI.	Results of the Studies of Interfacial Processes	192
VII.	Conclusion	227
	List of Symbols	231
	References	233
Chapter 5	SYNERGIC EXTRACTIONS OF ZIRCONIUM (IV) AND HAFNIUM (IV)	239
	<i>Jiri Hala</i>	
I.	Introduction	239
II.	Neutral Organophosphorus Synergists	240
III.	Nitrogenous Bases as Synergists	247
IV.	Acidic Synergists	251
V.	Extractions with Two Similar Extractants	252
VI.	Synergisms in Micellar Systems	258
VII.	Extraction from Mixed Electrolyte Solutions	259
	List of Acronyms and Symbols	264
	References	265
Index		271

Solvent Extraction of Industrial Organic Substances from Aqueous Streams

C. JUDSON KING and JOHN J. SENETAR^{*} Department of Chemical Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, California

I. INTRODUCTION

The purpose of this paper is to review the current uses and the potential of solvent extraction for recovery of organic substances from aqueous streams. The place of extraction in the overall scheme of separation processes for such systems is explored first. A number of general factors are next considered. These include prediction and manipulation of phase equilibria, the difference in capabilities and characteristics between ordinary ("physical") solvents and chemical solvents or extractants, process equipment and configuration alternatives, and methods of solvent regeneration and of recovery of residual dissolved solvent. Some specific cases of current industrial importance are next considered in some detail. These include recovery of acetic acid, phenols, and certain polyfunctional organic solutes. Means of fractionating selectively among solutes are then

^{*} *Current affiliation:* Amoco Oil Company, Amoco Research Center, Naperville, Illinois

described. The final section covers processes and opportunities for removal and recovery of organics from aqueous condensate and effluent streams by solvent extraction.

A. Uses of Solvent Extraction

Solvent extraction is used widely and on very large scales for a number of industrial applications, most notably hydrometallurgical processing (see, e.g., [1]). It also sees extensive use on an analytical scale for separations of organics from aqueous solution, and as a method for preconcentration before other analytical techniques, such as combined gas chromatography/mass spectrometry. There are also several specific instances where solvent extraction has found large-scale use for separations involving organic substances -- for example, processes for separating aromatics from paraffins and naphthenes (UDEX, Sulfolane, etc.), fractionation of coal-tar chemicals, and recovery of isobutylene from mixed butanes and butenes. The industrial uses of solvent extraction are covered in the *Handbook of Solvent Extraction* [2].

Solvent extraction is also used industrially for recovering certain organic substances from predominantly aqueous streams. Prominent examples include the Phenosolvan and Chem-Pro processes for recovery of phenols and cresylic acids, processes for recovery of acetic acid from aqueous solution, and a number of different applications in the manufacture of pharmaceuticals.

For a number of reasons, the large-scale uses of solvent extraction for recovery of organic solutes from water will become greater and more diverse in the years immediately ahead. The principal factors leading to increased use of solvent extraction will be the needs to avoid thermal degradation, to gain selectivity among solutes, and to increase energy efficiency.

One prominent factor is the anticipated growth of biosynthetic processing techniques, or "commercial biotechnology" [3]. Solvent extraction provides a way of avoiding thermal stress and recovering nonvolatile reaction products, using chemical specificity where

needed. Contamination of a biological medium by residual dissolved solvent can be a problem, but can be avoided by utilizing any of several separation techniques that immobilize the solvent and are close relatives of extraction. These include the use of functionalized adsorbents or absorbents, and solid-supported (polymer) or emulsion liquid membranes.

Growing environmental regulations and economic considerations will lead to greater use of solvent extraction for recovery of organic chemicals from effluent streams or even for replacing biological or incineration degradation processes. Still another growth area for solvent extraction should be separation of relatively dilute and low-volatility organic products from aqueous streams in which they are made by oxidation processes or other conventional means. Distillation or evaporation of water from such mixtures is expensive and will become more so as costs of energy continue to increase. Finally there are cases of product inhibition where extraction affords a means to remove the product continuously from a reactor and thereby increase yields and/or conversion rates. Two examples are manufacture of ethanol by fermentation [4,5] and manufacture of furfural from pentosan-containing substances [6].

B. The Role of Solvent Extraction

For recovery and/or removal of organics from water, solvent extraction is usually most attractive over a middle range of feed solute concentrations.

The residual solubility of the solvent in water can necessitate an additional separation process for reclaiming solvent from the exit water stream. Some alternatives for this are described later. At very low feed solute concentrations, tendencies for loss of solvent to the aqueous phase -- through solubility, entrainment, and/or formation of micelles -- may be essentially unavoidable and can become very important. For a very dilute solute and/or an expensive solvent, the cost of lost solvent can place a large economic burden on the process in comparison with the value of the recovered solute.

On the low-concentration end, solvent extraction competes with adsorption. For a given feed flow rate, costs of adsorption processes tend to increase directly with increasing feed solute concentration, because of the need for larger adsorbent beds and/or more frequent regeneration or replacement of the adsorbent. Extraction processes, on the other hand, have costs that are roughly proportional to the required solvent-circulation rates, which in turn vary inversely with the equilibrium distribution coefficient of the solute from water into the solvent phase. If the equilibrium distribution coefficient is independent of solute concentration or varies only slightly, then the cost of an extraction process will change rather little with changes in feed concentration. Therefore costs of extraction become more favorable in comparison with costs of adsorption as feed solute concentration increases.

In the present states of development of adsorption and extraction, extraction offers more opportunity for changing chemical factors to gain selectivity among solutes, but can suffer from solvent losses or contamination of the aqueous phase caused by the solubility of the solvent in water. Regeneration is often more economical for extraction processes than for adsorption processes, because of incomplete regeneration and/or strong sites in the case of adsorption.

For solutes less volatile than water, the energy cost for distillation increases in proportion to the amount of water that must be taken overhead, and thus is greater for more dilute feed streams. On the other hand, the solvent-to-water flow ratios required for extraction often become greater at high solute concentrations, because of saturation of the solvent by the solute. Hence costs for distillation usually become more favorable in comparison with those for extraction as the feed solute concentration increases. Solvent extraction can serve as a preconcentration process for more dilute feeds, before distillation. Extraction can also be favored for