ION EXCHANGE & SOLVENT EXTRACTION

ION EXCHANGE AND SOLVENT EXTRACTION

A SERIES OF ADVANCES

Volume 11

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ION EXCHANGE AND SOLVENT EXTRACTION

Preface

This volume of *Ion Exchange and Solvent Extraction* presents four important paths developed for the consideration and interpretation of the ion-exchange phenomenon. It was felt that their educated and sophisticated presentation in one volume would provide the interested reader an excellent opportunity for examination, evaluation, and comparison of state-of-the-art ion-exchange theory. For this reason, meaningful demonstration of the advantages of an approach, wherever possible, and extension of the boundaries of its application for this purpose were sought from the authors.

Chapter 1, by Steven A. Grant and Philip Fletcher, presents an overview of the chemical thermodynamics of cation-exchange reactions, highlighting recent developments in theory and practice. Particular importance is placed on liquid-phase- and solid-phase-activity coefficient models. The major liquid-phase-activity coefficient models are reviewed emphasizing their application to mixed electrolyte aqueous solutions. Because the development of excess Gibbs-energy-based solid-phase-activity coefficient models is in a much more rudimentary

stage, their review is restricted to appropriate mathematical forms, a survey of the mathematical models by which they may be evaluated, and the statistical techniques employed to optimize the design of cation-exchange experiments.

The simple, three-parameter model, used with so much success for the correlation of ion-exchange phenomena, is reviewed in Chapter 2 by Erik Högfeldt, who introduced it. The model, based on the Guggenheim zeroth approximation, provides an acceptable fit to all kinds of ion-exchange data through the use of a few parameters with simple physical meaning. Its only drawback is the absence of any predictive properties.

In Chapter 3, Wolfgang H. Höll, Matthias Franzreb, Jürgen Horst, and Siegfried H. Eberle provide an excellent description of the development and application of surface complexation theory to the ion-exchange phenomenon. The equilibria of representative organic ion-exchange resins described with the surface complexation model are shown to compare favorably with the experimental results.

Further insight with respect to the surface complexation model is provided by Garrison Sposito in Chapter 4. His description of metal-natural colloid surface reactions and their consideration by surface complexation modeling complements Chapter 3.

The Gibbs-Donnan-based analysis of ion exchange and related phenomena is presented by Jacob A. Marinsky in Chapter 5. It is claimed that with the Gibbs-Donnan approach a much more realistic picture of the physical aspects of ion-exchange phenomena is forthcoming. Insights inaccessible to the other models are inherent in the Gibbs-Donnan model.

Chapter 6, which considers the influence of humic substances on the uptake of metal ions by naturally occurring materials, is authored by James H. Ephraim and Bert Allard. Their development of this topic compares the applicability of both the Gibbs-Donnan and surface complexation model in their attempts to analyze the various observations made.

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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 Högfeldt*

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 EXCHANGERS *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 CROSSLINKING AND IONIC FORM *Zoya I. Sosinovich, Larissa V. Novitskaya, Vladmir 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

Volume 10

SOLVENT EXTRACTION OF INDUSTRIAL ORGANIC SUBSTANCES FROM AQUEOUS STREAMS *C. Judson King and John J. Senetar*

LIQUID MEMBRANES *Richard D. Noble, J. Douglas Way, and Annett L. Bunge*

MIXED SOLVENTS IN GAS EXTRACTION AND RELATED PROCESSES
Gerd Brunner

INTERFACIAL PHENOMENA IN SOLVENT EXTRACTION
Valery V. Tarasov and Gennady A. Yagodin

SYNERGIC EXTRACTIONS OF ZIRCONIUM (IV) AND HAFNIUM (IV)
Jiri Hala

Contents

Preface iii
Contributors to Volume 11 v
Contents of Other Volumes xi

Chapter 1 Chemical Thermodynamics of Cation Exchange Reactions: Theoretical and Practical Considerations *Steven A. Grant and Philip Fletcher*

I. Introduction 1
II. Chemical Thermodynamics of Cation-Exchange Reaction 2
III. Chemical Thermodynamics of Electrolyte Solutions 18
IV. Excess Gibbs Energy Models 52
V. Methods to Evaluate Excess Gibbs Energy Models 60
VI. Design of Ion-Exchange Experiments 65
VII. Appendix 1. Derivation of Equations for Solid-Phase Activity Coefficients 90
VIII. Appendix 2. Adjusting Exchange-Equilibrium-Constant Values for Different Choices of Ionic-Solute Activity 93
List of Symbols 97
References 104

Chapter 2 A Three-Parameter Model for Summarizing Data in Ion Exchange *Erik Högfeldt*

I. Introduction 109
II. The Model 109
III. Application to Ion Exchange 111
IV. Applications 118
V. Concluding Remarks 148
References 149

Chapter 3 Description of Ion-Exchange Equilibria by Means of the Surface Complexation Theory *Wolfgang H. Höll, Matthias Franzreb, Jürgen Horst, and Siegfried H. Eberle*

I. Introduction 151
II. Theory 153
III. Derivation of Resin-Specific Equilibrium Parameters 166
IV. Evaluation of Equilibrium Data 176
V. Comparison of Experimental and Predicted Equilibria 191
VI. Conclusions 203
VII. Appendix 205
References 206

Chapter 4 Surface Complexation of Metals by Natural Colloids *Garrison Sposito*

I. Introduction 211
II. Surface Complexes of Cu(II) on Smectites 214
III. Detection and Quantitation of Surface Complexes 223
IV. Modeling Surface Complexation 226
References 234

Chapter 5 A Gibbs-Donnan-Based Analysis of Ion-Exchange and Related Phenomena *Jacob A. Marinsky*

I. Introduction 237
II. The Gibbs-Donnan Model 241
III. Documentation of the Gibbs-Donnan-Based Approach 244
IV. Conclusions 325
References 331

Chapter 6 Influence of Humic Substances on the Uptake of Metal Ions by Naturally Occurring Materials *James H. Ephraim and Bert Allard*

I. Introduction 335
II. Acid-Base Properties of Humic Substances 336

III. Conceptualization of Humic Substances 339
IV. Metal-Humate Interactions—A Review of Experimental Techniques 340
V. Steps of the Approach 342
VI. Adsorption of Metal Ions onto Natural Solids 352
VII. Effects of Ligands on Metal Adsorption 354
VIII. Humic Substances as Ligands 354
IX. Modeling of Metal Uptake by Natural Solids 356
X. Interpretation of Zinc and Cadmium Adsorption on Alumina 361
XI. Interpretation of Mercury Adsorption on Alumina 361
XII. Summary 362
References 363

Index 369

1

Chemical Thermodynamics of Cation Exchange Reactions: Theoretical and Practical Considerations

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I. INTRODUCTION

The ion-exchange reaction consists of the replacement of an electrostatically sorbed ion by a like-charged ion from solution. The exchangeable ions may be either positively or negatively charged; the ion exchanger may be solid or liquid; and the equilibrating solution may be aqueous or a mixture of solvents. Given the many chemical environments in which the ion-exchange reaction occurs, it is difficult to write clearly about "general" ion-exchange-reaction thermodynamics. With some loss of generality, this chapter will be restricted to cation-exchange reactions on solid cation exchangers bathed by aqueous electrolyte solutions. This chapter will not neglect consideration of the commonly observed sorption by the cation exchanger of water and neutral salts. It is hoped that the reader will be able to adopt directly any useful ideas found here to his or her particular research problem.

The measurement and chemical-thermodynamic characterization of cation-exchange reactions is commonly employed to understand the process or the environment in which the process occurs. The objective of any formulation of the chemical thermodynamics of

cation-exchange reactions is to calculate from experimentally measured cation-exchange data values of thermodynamic functions (typically exchange equilibrium constants and solid-phase activity coefficients) which characterize the distribution of [exchanging ions] between the solid and liquid phases. It is essential to distinguish between ion-exchange models, such as those for predicting behavior using molecular or empirical assumptions, and chemical-thermodynamic formulations designed to *quantify* experimental measurements.

This chapter does not attempt to repeat what has been presented in the several excellent reviews of chemical thermodynamics of cation-exchange reactions [1,2]. Most of this chapter concentrates on liquid-phase and solid-phase activity coefficients and the models which have been developed to estimate their values. The two sections following this introduction describe the chemical-thermodynamic treatment only, considering the alternative conventions and techniques that have been used for dealing with both solid and liquid phases. The chemical thermodynamics of concentrated electrolyte solutions is described in order to facilitate the use of chemical-thermodynamic data to predict or characterize equilibria of multispecies cation-exchange reactions.

Later sections consider the compact description of measured chemical-thermodynamic properties of solid cation exchangers with so-called excess Gibbs energy models. Emphasis is placed on experimental design and the statistical techniques necessary to choose suitable models and estimate model parameters. This chapter is concerned only with the properties of solid cation exchange materials. However, ligand exchange and the properties of liquid cation exchangers are equally accessible to chemical-thermodynamic characterization.

II. CHEMICAL THERMODYNAMICS OF CATION-EXCHANGE REACTIONS

A chemical-thermodynamic treatment of cation-exchange reactions requires the unambiguous definition of *reaction stoichiometries* as well as *standard states*, *reference states*, and *reference functions*