Solvent Extraction Chemistry

Fundamentals and Applications

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To Professors David Dyrssen,
the late Lars Gunnar Sillén,
and Nobufusa Saito

Solvent extraction is becoming more and more important in inorganic and analytical chemistry, and the number of chemists who are employing this simple but excellent experimental technique in their work today is enormous. Since a variety of liquid-liquid systems have been developed, it should be possible to find, among the solvent extraction methods that been reported, one which meets the requirements of almost any chemical problem; and the extraction can be carried out successfully if the operations are properly conducted according to the recommended procedure in the literature.

However, since the details of each chemical problem are different, it may be difficult for a student who has not had much experience with solvent extraction to find the best way to handle a given problem. A reported method, in many cases, deals with a special problem under given conditions, or else the description of the method is given in a very general way. Thus, to find the most suitable procedure for a particular problem, systematized information on the chemical form of the materials and their distribution equilibria in liquid-liquid systems is always the first thing necessary.

The present book has been written, first of all, as an introduction to the chemical facts involved in solvent extraction systems from a rather fundamental standpoint. At the same time, the book is intended as a handbook for those who want to apply solvent extraction methods to chemical processes. Furthermore, it is the authors' hope that analytical chemists and inorganic chemists who have already been using solvent extraction in their work will also find the book worthy of reading, for they may obtain additional basic information on the chemical equilibria in solvent extraction systems and also some helpful suggestions to improve their experimental procedures.

This book is mainly based on the authors' research work in their laboratory, and also on their experience in teaching university seniors and graduate students. During the course of teaching, the authors have very often found that these students, who have already studied physical, organic, inorganic, and analytical chemistry but have not been especially trained in each of these

fields, cannot connect their basic knowledge with actual chemical problems. For example, they know some inorganic substances can be treated by solvent extraction, but they cannot relate the extraction equilibria involved in the system with Berthelot's partition law. They use various chemical terms such as "salting-out effect," "polar solvents," "organophilic nature," and so on, but they cannot explain what these terms actually mean in the chemical systems they encounter in the laboratory.

For this reason, a brief description of the chemical phenomena in both aqueous and organic solutions is given in Chapter 2. The authors have tried to summarize this very wide and deep field of solution chemistry in such a way as to provide the reader who is not informed on this subject with at least a basic understanding of it.

Chapter 3 deals with the statistical treatment of liquid-liquid distribution equilibria indispensable for quantitative descriptions of solvent extraction phenomena from the thermodynamic standpoint.

Chapter 4 describes the presently known solvent extraction systems. It contains information on how the distribution of materials in solvent extraction systems is affected by various equilibria from both the statistical and chemical standpoints. Naturally, it is difficult to express in a simple and easily understandable way an equilibrium in a given solvent extraction system, and a very general expression of it is sometimes quite confusing for a beginner. Therefore, an effort has been made to analyze actual systems statistically showing typical examples whenever possible. The examples are often given in the form of a graph because such an expression gives a clearer picture of the extraction system. The authors have taken many of these examples from their own research, although undoubtedly the many excellent studies of the same kind reported by other workers could also have provided suitable examples.

The distribution data in some kinds of solvent extraction systems can be quantitatively analyzed from the standpoint of the chemical equilibria involved in the system. Actually, the change in the distribution ratio of a material in some systems can be expressed by an equation that contains several terms for the equilibrium constants and concentrations of materials in the system. Such statistical treatment of solvent extraction data has been applied to many systems by many workers. However, sometimes the authors have used oversimplified assumptions, and, consequently, their conclusions cannot always be accepted without question. This situation seems to arise mainly for two reasons. One is that a solvent extraction system usually involves various minor equilibria in addition to the dominant one governing the distribution behavior of the material under consideration. When the system involves such minor equilibria and if they are overlooked in the statistical analysis, an erroneous conclusion may be reached. The authors have tried in this book to point out the effect of these minor equilibria on the extraction,

as in the case of, for example, the effect of complex formation of metal ions with a chelating extractant in the aqueous phase. If the extraction is carefully carried out, the effect of this formation can be observed in many systems, although it is very often overlooked in consideration of the data.

The other reason for the misunderstanding of solvent extraction equilibria is an underestimation of the change in the activity coefficients of the materials involved when the concentration of one or more components in the system is greatly changed. The proper estimation of this change is a very difficult problem because the behavior of the activity coefficients in electrolyte solutions, especially those containing a large amount of electrolyte as are very often found in the aqueous phases of solvent extraction systems, is exceedingly complicated; and in organic solvents, almost nothing is known about the activities of ions. At present, the control of the activity coefficient of each species in electrolyte solutions at high concentrations does not seem to be quite satisfactory when a large fraction of one ion is replaced by another. Furthermore, any attempt to make a theoretical correction for the change in an activity coefficient of an ion in concentrated electrolyte solution has not been very successful.

For these reasons, any discussion of chemical equilibria in solvent extraction systems where the electrolyte concentration in the aqueous phase is greatly changed and/or dissociation of the extracted species in the organic phase occurs may contain some uncertainties; and the conclusions with respect to the equilibria in such systems should be regarded as more or less tentative. In such cases, although the authors are cognizant of this situation, descriptions of important solvent extraction systems of this kind do appear in this book, without any special comment.

Chapter 5 introduces the kinetics of solvent extraction, a field that seems to have remained practically unexplored until the early 1960s but is now making rapid progress. Study of these kinetics is very important in order to carry out extractions, especially of some metals with chelating extractants.

The last two chapters describe the applications of solvent extraction to solution chemistry, analytical chemistry, and preparative chemistry. Chapter 6 explains how the liquid-liquid distribution method can be applied to the determination of various equilibrium constants and rate constants in solutions. Thus it shows how to obtain quantitative information on metallic and nonmetallic materials dissolved in either an aqueous or an organic solution. Chapter 7 describes the application of solvent extraction to analytical and preparative chemistry. After a brief consideration of separation by solvent extraction, commonly employed extractants are summarized from the standpoint of their practical use. Then, in Section III of Chapter 7, a survey is presented of a very large number of reports treating the solvent extraction of individual elements. It is almost impossible to compile a

complete survey of all the reports in such a limited space, and the authors
regret that the solvent extraction of each individual element can be only
rather sparsely treated. To present a detailed description of solvent
extraction of all the elements under various conditions by using a variety of
reagents would require at least another volume of the size of this book. It
is, however, hoped that the reader can find various useful suggestions for
solving his particular extraction problem from the description in this chap-
ter, and that he can also find useful leads for obtaining further detailed
information from the original sources.

The English text was revised by Professor Harold F. Walton of the
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LIST OF SYMBOLS AND ABBREVIATIONS

(org)	Chemical species in the organic phase. No notation denotes those in the aqueous phase.
$K_{(org)}$, $\beta_{n(org)}$, etc.	Equilibrium constant for a reaction in which all the chemical species taking part exist in the organic phase.
K_d	Distribution constant for materials containing no metal.
K_{dm}	Distribution constant for materials containing metal.
K_{ex}	Extraction constant; the equilibrium constant for a reaction in which a material exists in both phases.
K_a	Dissociation constant of acid.
K_{diss}	Dissociation constant.
K_{dim}	Dimerization constant.
K_n	Stepwise stability constant for the "nth" complex. β_1 is equal to K_1.
β_n	Overall stability constant for the "nth" complex.
$\beta_{a,b}$	Stability constant for polynuclear complex. The subscripts a and b denote the number of metal ions and of ligands, respectively.
K^T, β_n^T, etc.	Thermodynamic equilibrium constant; the concentrations are given by thermodynamic activities.
γ	Activity coefficient.
{ }	Concentration given by thermodynamic activities.
[ ]	Concentration given by stoichiometric molar units.
$C_{HA(org)}$, C_{OH^-}, etc.	Concentration in the initial state; the initial concentration of an acid in the organic phase, that of hydroxide in the aqueous phase, etc.

D	Distribution ratio of a material; ratio of the total concentrations of the material in the organic and aqueous phases.
L^{i-}	Complex-forming ligand having a minus l charge.
E	Neutral extractant.
HA	Acid and acidic extractant.
TTA	2-Thenoyltrifluoroacetone.
oxine	8-Hydroxyquinoline.
MIBK	Methylisobutyl ketone, that is, 4-methyl-2-pentanone.
TBP	Tributylphosphate.
TOPO	Trioctylphosphine oxide.
DEHP	Di(2-ethylhexyl)phosphoric acid.
PAN	1-(2-Pyridylazo)-2-Naphthol.

Some other reagents are also abbreviated; but, in such cases, the full name
is given when the abbreviation first appears in that section.

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CONTENTS

PART I

FUNDAMENTALS

CHAPTER 1

INTRODUCTION

Transport of materials from one phase to another is the most fundamental procedure for the separation of a chemical species from the medium or from other coexisting components. Thus distillation and condensation (liquid phase to gas phase and vice versa), dissolution and crystallization or precipitation (solid phase to liquid phase and vice versa), and sublimation (solid phase to gas phase and vice versa) have been employed in various experiments since the early days of chemistry. Solvent extraction is also a kind of interphase transport process; and from this point of view, it should be regarded as essentially the same kind of experimental technique as these classical methods. Solvent extraction, however, usually permits much simpler and cleaner separation of materials at both macro and tracer concentrations. The procedure can be carried out by using only a simple apparatus and merely shaking the sample for a few minutes by hand, and yet the contamination from other components is less than that in these other methods.

The differences in the liquid-liquid distribution behavior among various organic substances was recognized by many early chemists, and solvent extraction has been a fundamental technique of organic chemistry for a very long time [1]. Actually, a separatory funnel has always been a basic tool in every organic chemistry laboratory, just like distillation apparatus and many other common items of glassware. The solvent extraction of some inorganic compounds was known in the nineteenth century. The first of such examples was the extraction of uranyl nitrate into diethylether reported in 1842 by Peligot [2]. The second example worthy of note was the extraction of iron in hydrochloric acid with diethylether reported in 1892 by Rothe [3] and by Hanroit [4]. This method was then applied to the separation of this element from many other metal ions [5]. A quantitative understanding of

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