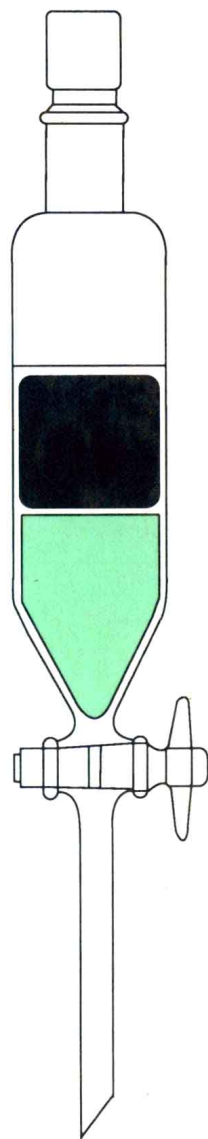


Principles and Practices of Solvent Extraction



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Preface

The partition of a solute between two immiscible solvents is a major technique in separation both in the laboratory and in industry. This technique has been designated *liquid-liquid distribution* by the International Union of Pure and Applied Chemistry (IUPAC), but it is more commonly called *solvent extraction*, the term we use. Solvent extraction has been developed in a broad field of applications: (1) for studying inorganic and organic complex equilibria, either for fundamental understanding or for developing selective separation schemes; (2) for separations in analytical chemistry; (3) for large scale industrial separation processes in the inorganic, organic, pharmaceutical, and biochemical industries; (4) for industrial waste treatment. It also serves as a base for other analytical techniques, such as liquid partition chromatography and ion selective electrodes.

The many uses of solvent extraction make the subject important for university students of chemistry. Some universities offer special courses in solvent extraction, whereas others include it as a topic in more comprehensive courses. Pilot-scale experiments on solvent extraction are common in chemical engineering curricula. However, because of the breadth of the subject, the treatment is often scanty, and a satisfactory advanced discussion is difficult to find in a form suitable for use directly with students.

Although solvent extraction has a certain scientific and engineering integrity, no one scientist or engineer can be an expert in all parts of the field.

Therefore, it seemed best to develop a book as a joint project among many expert authors, each of whom has decades of experience in research, teaching, or industrial development. The product is a truly international book at a high scientific and technical level. The task of making it homogeneous, consistent, and pedagogical has been undertaken by the editors.

The book is directed to third- to fourth-year undergraduate and postgraduate chemistry and chemical engineering students, as well as to researchers and developers in the chemical industry. The book is also intended for chemical engineers in industry who either have not kept up with modern developments or who are considering use of this technique, as well as engineers who already are using this technique, but desire to understand it better. Furthermore, the book should be useful to researchers in solvent extraction who wish to learn about its applications in areas other than their own.

We want to express our gratitude to the coauthors, who made this book possible through their helpful suggestions and extensive efforts to produce a useful textbook. Prof. Bert Allard, Prof. Eckhart Blass, Prof. Michael Cox, Dr. Pier Danesi, the late Prof. Steven Kertes, Dr. Philip Lloyd, Prof. Yizhak Marcus, Dr. Gordon Ritcey, Prof. Tatsuya Sekine, Prof. Gabriella Schmuckler, Dr. Wallace Schulz, Prof. Ronald Wennersten, and Dr. Martin Zangen have worked hard and successfully on their own chapters and have given us much valuable guidance.

We regret the death of Steven Kertes during the writing of this book, as he was an admired colleague and a good friend whose continued advice would have been helpful in making this a better text.

One of the editors (J.R.) wants to express his special gratitude to M. Pages for inviting him to stay at the Institut Curie in Paris while beginning this book.

Jan Rydberg, Claude Musikas, and Gregory R. Choppin

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1

Introduction to Solvent Extraction

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1.1 PRESENTATION OF THE SUBJECT

*Solvent extraction** involves the distribution of a solute between two immiscible liquid phases in contact with each other. Scientists and engineers are concerned with the extent and dynamics of the distribution and its use scientifically and industrially for separation of solute mixtures.

The principle is illustrated in Fig. 1.1. The vessel (a, separatory funnel) contains two layers of liquids, one that is generally water (S_{aq}) and the other, generally, an organic solvent (S_{org}). In the example shown the organic solvent has a lower density than water, but the opposite situation is also possible. A solute A, which initially is dissolved in only one of the two liquids, eventually distributes between the two phases. When this distribution reaches equilibrium, the solute is at concentration $[A]_{\text{aq}}$ in the aqueous layer and at concentration $[A]_{\text{org}}$ in the organic layer. The *distribution ratio* of the solute

$$D = [A]_{\text{org}}/[A]_{\text{aq}} \quad (1.1)$$

*The International Union of Pure and Applied Chemistry recommends the use of the term *liquid-liquid distribution*. However, more traditionally, the term *solvent extraction* (sometimes abbreviated SX) is used in this book.

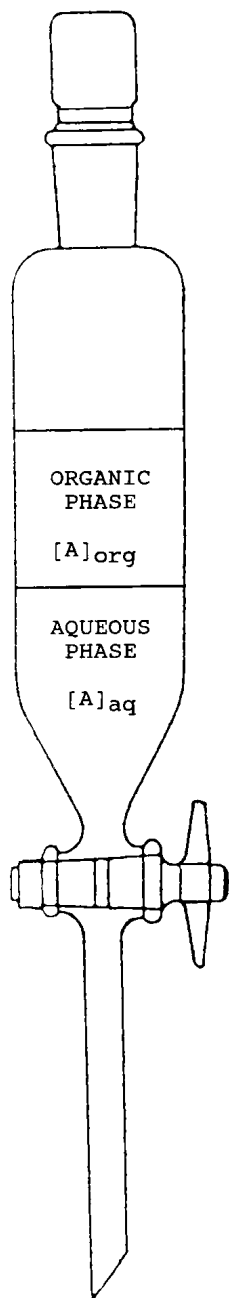


Fig. 1.1 A schematic representation of solvent extraction (liquid–liquid distribution). A solute A is distributed between the upper layer, an organic solvent (S_{org}), and the lower layer, an aqueous phase (S_{aq}).

is defined as “the total analytical concentration of the substance in the organic phase to its total analytical concentration in the aqueous phase, usually measured at equilibrium” (IUPAC 87b), irrespective of whether the organic phase is the lighter or heavier one. If a second solute, B, is present, the distribution ratios for the various solutes are indicated by D_A , D_B , and so on. If D_B is different from D_A , A and B can be separated from each other by (single or multistage) solvent extraction. D is also called the *distribution coefficient* or the *extraction coefficient*.

Solvent extraction is used in numerous chemical industries to produce pure chemical compounds, ranging from pharmaceuticals and biomedical to heavy organics and metals, in analytical chemistry, in environmental waste purification, as well as in research. Unfortunately, most university training provides only elementary knowledge about this field, which is unfortunate for both industrial development and the advancement of data on solution chemistry and metal ion complexation (e.g., for environmental systems). Because solvent extraction is an intersection of organic, inorganic, and physical chemistry, and of chemical engineering, theoretical as well as practical, no one can be an expert in all its aspects. This book, therefore, is written by chemists from various disciplines of chemistry and by chemical engineers.

The text covers the fundamental chemistry of the solvent extraction process, the techniques for its use in industry, and a large number of applications. In this introductory chapter we consider solvent extraction in its chemical context, review its historical development, and project possible future trends.

1.2 SOLVENT EXTRACTION: A FUNDAMENTAL SEPARATION PROCESS

Under normal conditions, matter can appear in three forms of aggregation: solid, liquid, and gas. These forms, or *physical states*, are consequences of various interactions between the atomic or molecular species. The interactions are governed by *internal chemical properties* (various types of bonding) and *external physical properties* (temperature and pressure). Most small molecules can be transformed between these states (e.g., H_2O into ice, water, and steam) by moderate change of temperature or pressure. Between these physical states—or *phases*—there is a sharp boundary (*phase boundary*), which makes it possible to separate the phases (e.g., ice may be removed from water by filtration). The most fundamental of chemical properties is the ability to undergo such phase transformations. This allows the isolation of pure compounds from natural materials.

In a gas mixture, such as the earth's atmosphere, the ratio of oxygen to nitrogen decreases slightly with atmospheric height because of the greater gravitational attraction of oxygen. However, the gravitational field of the earth is not enough for efficient separation of these gases, which, however, can be separated by ultracentrifugation and by diffusion techniques. In crushed iron ore, it is possible to separate the magnetite crystals, Fe_3O_4 , from the silicate gang material by physical selection under a microscope or by a magnetic field. In chemical engineering, such separation techniques are referred to as *nonequilibrium processes*. Other common nonequilibrium processes are electrolysis, electrophoresis, and filtration.

In contrast with these, we have the *equilibrium processes* of sublimation, absorption, dissolution, precipitation, evaporation, and condensation, through which the physical states of solid, liquid, and gas are connected. For example, the common crystallization of salts from seawater involves all three phases. Distillation, which is essential for producing organic solvents, is a two-step evaporation (liquid \rightarrow gas) condensation (gas \rightarrow liquid) process.

The importance of phase transformations is shown in Fig. 1.2, which illustrates the physical processes used in separation of mixtures of chemical compounds. However, the figure has been drawn asymmetrically in that *two liquids* (I and II) are indicated. Most people are familiar with several

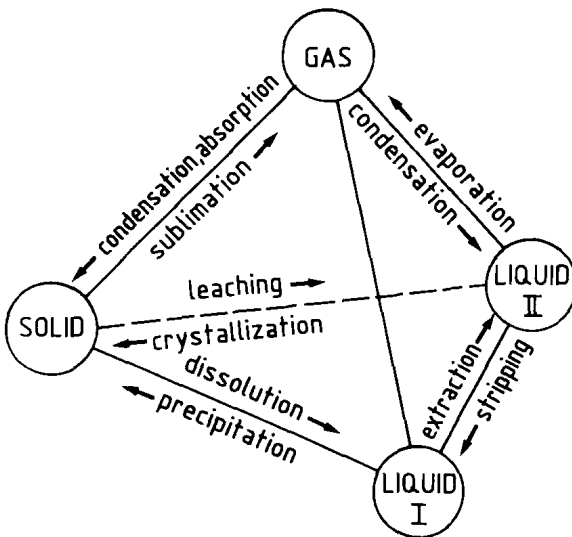


Fig. 1.2 Model of a four-phase system consisting of two liquid phases (e.g., an aqueous and an organic) in equilibrium with a gas phase and a solid phase.

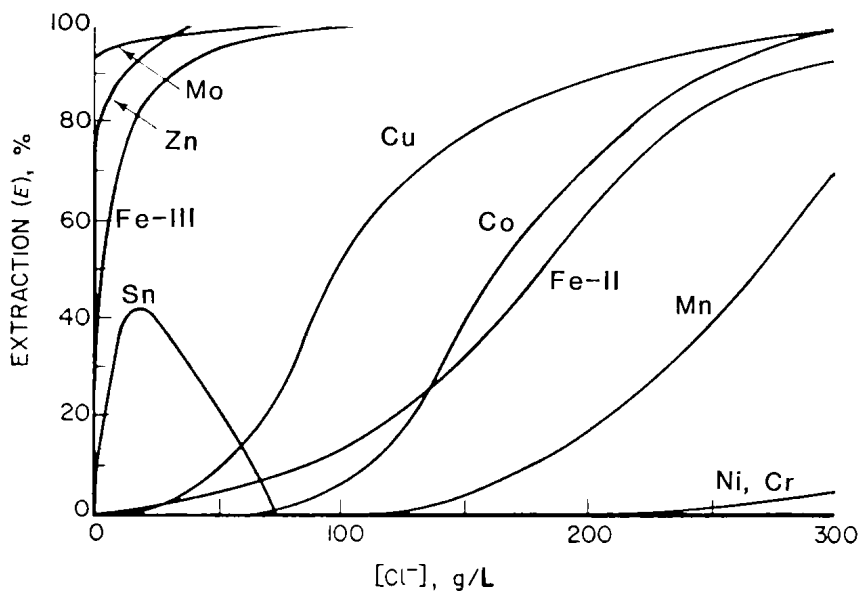


Fig. 1.3 Percentage of extraction of various metals from a solution of dissolved stainless steel scrap. The organic phase is 25% tertiary amine, 15% dodecanol, and 60% kerosene. The aqueous phase is a CaCl_2 solution at pH 2.

organic liquids, like kerosene, ether, benzene, and others) that are only partially miscible with water. This lack of miscibility allows an equilibrium between two liquids that are separated from each other by a common phase boundary. Thus, the conventional physical system of three phases (gas, liquid, and solid, counting all solid phases as one), which ordinarily are available to all chemists, is expanded to four phases, when two immiscible liquids are involved. This can be of great advantage, as will be seen when reading this book.

Solutes have differing solubilities in different liquids owing to variations in the strength of the interaction of solute molecules with those of the solvent. Thus, in a system of two immiscible or only partially miscible solvents, different solutes become unevenly distributed between the two solvent phases. This is the basis for the *solvent extraction* technique. In this context “solvent” almost invariably means *organic solvent*. This uneven distribution is illustrated in Fig. 1.3, which shows the extractability into a kerosene solution of the different metals, which appear when stainless steel is dissolved in aqueous acid chloride solution. The metals Mo, Zn, and Fe(III) are easily extracted at low chloride ion concentration, and Cu, Co, Fe(II), and Mn at intermediate concentration, whereas, even at the highest

chloride concentration in the system, Ni and Cr are not extracted. This is used industrially for separating the metals in superalloy scrap to recover the most valuable ones; this system is further discussed in Chapter 10.

The explanation of the limited solubilities for solvent mixtures and solutes, as well as rules for solute distribution, are described in the first part of this book (Chaps. 2–6), whereas the second part (Chaps. 7–13) covers industrial solvent extraction technique and numerous uses of solvent extraction in separation science.

The three main separation processes between solid, gas, and liquid have long been known, whereas solvent extraction is a relatively new technique, as is described in the brief historical review in next two sections. Nevertheless, because all solutes (organic as well as inorganic) can be made more or less soluble in aqueous and organic phases, the number of applications of solvent extraction is almost limitless. Since large-scale solvent extraction is a continuous process (in contrast with batch processes) and can be made more selective than the conventional gas–liquid–solid separation techniques, it offers numerous industrial possibilities to achieve desired separation efficiently and economically.

1.3 EARLY STEPS TOWARD USE OF SOLVENT EXTRACTION

The Greek philosophers, about 500 B.C., recognized four elements: earth, water, phlogiston (~air), and fire. This view harmonizes with the present concept of three physical states of aggregation and of heat. Aristotle (~350 B.C.) emphasized that these “elements” were not eternal, but could be changed into each other. Five thousand years before, man had already found that when certain green minerals were heated in a coal fire, metallic copper was obtained. At Aristotle’s time it was known how to produce metals such as copper, gold, tin, lead, silver, iron, mercury, and arsenic. Furthermore, by transmuting certain earths with fire, ceramics and glasses were made. These arts were probably developed by the Egyptians, the first true chemists. *Alchemy* is derived from Arabic and Greek and is supposed to mean “art of transmutations as practiced by the Egyptians.” Fruit juices were fermented; oils and fats were squeezed out of vegetables and animal parts, and purified by digestion with earths, bones, and such. Crucibles, retorts, and even distillation equipment seem to have been in use (Fig. 1.4). We must think of these early alchemists as endlessly mixing, heating, boiling, digesting, cooling, and such, everything they could collect from nature. The purpose of these transmutations varied: for lamps, weapons, pigments, perfumes, and poisons; for cosmetics and medicines to prevent aging and to prolong life (*elixir vitae*); for tanning chemicals, soap, anesthet-