ELECTRONIC STRUCTURE EFFECTS IN EXTRACTIONS. I

L. N. Mazalov

Liquid extraction has been widely used as a method of separating mixtures and isolating individual chemical compounds in pure form. A description of the types of extractable compounds and extraction processes and mechanisms requires data on the structure and composition of these compounds. This review presents results from studies of extractants and extraction products using ultrasoft X-ray emission spectroscopy, X-ray absorption (EXAFS and XANES spectroscopy), and X-ray photoelectron spectroscopy.

Key words: X-ray spectroscopy, X-ray photoelectron spectroscopy, EXAFS, XANES, electronic structure, extractants, extraction constants, correlation dependences in extractions, extraction complexes.

CONTENTS

Introduction
1. Extraction Constants. Correlations Dependences in Extractions
   1.1. Extraction Constants and Their Relationship with the Electronic Structure of Interacting Molecules
   1.2. Extraction Constant–Electronic Structure Correlations
   1.3. X-Ray and X-Ray Photoelectron Measurements of Atomic Charges in Extractant Molecules and Extraction Ability–Charge Correlations
2. Electronic Interactions in Extraction Complexes
   2.1. Interactions in Solvatocomplexes. Frontier Orbitals
   2.2. Electronic Interactions in Extraction Complexes
   2.3. HOMO and LUMO Structure of Main Extraction Reagents and Their Interactions During Extraction

INTRODUCTION

Separation of mixtures and isolation of pure individual compounds are problems of fundamental importance in modern chemistry. Interest in these problems has developed enormously in view of the demands of nonferrous and rare metal metallurgy as well as semiconductor technology and atomic industry. The development of separation and purification procedures has also been stimulated by the demands of the oil, chemical, and pharmaceutical industries. Liquid extraction is a promising method of separation.

The major advantages of this technique are high selectivity and purity of separation, the possibility of handling both high and low concentrations of substances, the absence of product contamination, a simple and continuous technological process, and high productivity. The importance of extraction methods in nonferrous and
trace element technologies has been steadily growing in connection with their applications to the processing of lean raw materials. Another important application of extractions consists in the processing of secondary raw material, particularly in nonmetallurgical industries. Extraction is the key method of processing raw materials in the atomic industry. “Inorganic extraction chemistry is extremely rich and variegated. This is due to the use of a wide range of nonaqueous media (diluents) and differently operating extractants (coordination, ion-exchange, and synergistic extractants), as dictated by the chemical state of metals in aqueous solutions. On the other hand, the behavior of metals in condensed media can be understood in terms of a coherent treatment of the electronic structure of reagents and reaction products as well as their interactions with solvents” [1].

A broad spectrum of problems underlying the basic principles of modern extraction theory have been formulated and solved by the research team headed by Academician A. V. Nikolaev (Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences).

Extraction is generally understood as a selective separation of substances. In the course of extraction, a solute is transferred from one liquid phase into another, not miscible with the former on contact. This transfer results from the tendency of the system toward a physicochemical phase equilibrium. It is characterized by an equilibrium distribution of the substance in the phases and depends on the reaction conditions and on the rate at which the system approaches the equilibrium [2–5].

Liquid extraction is dominated by the chemical nature of the substances constituting the phases. Extraction can lead to new compounds, which, under definite conditions, decompose into the starting compounds (re-extraction). Two mutually insoluble liquids and the extracted component distributed between them form an extraction system. The distributed (extracted) components can be organic or inorganic substances, or complex compounds. Thus, extraction involves two liquid phases: the reactant and the starting solution.

As noted in [6], extractable metal compounds are chiefly coordination compounds, which have a central atom and ligands directly linked to the central atom and forming the nearest coordination sphere. From this viewpoint, extraction can be regarded as synthesis of coordination compounds under conditions of an extraction system; many aspects of extraction research parallel those of coordination chemistry as concerns implementation and methods of investigation. At all stages of development of extraction theory, as well as in coordination chemistry, much attention has been paid to issues related to extraction efficiency, properties of the central atom, and the structure of extractants and solvents.

Classifications of extraction systems, processes, and extractants exist in great numbers [9–13]. Thus, Nikolaev proposed a specific classification system of extractions according to the nature of the so-called “extraction beam” [14]. To classify extraction processes, one can use different criteria: the nature and properties of extractants, the type of compound to be transferred to the organic phase, and the extraction mechanism [15]. A convenient classification is the one that takes into account the type of compound in whose composition an extractable element is transferred to the organic phase [16]. In this case, all compounds can be classified into two large categories: nonionized compounds and ionic associates [13, 15]. These compounds differ not only in chemical composition but also in the mechanism of their formation and transfer to the organic layer. Some of them exist beforehand or preferentially form in aqueous solution and are therefore extracted using pure diluents. Others are formed in the course of extraction by interaction between the reagent dissolved in the organic phase and the metal cations contained in the aqueous solution. The compounds belonging to either of the two categories, in turn, differ in structure, in the nature of chemical bonding, and in the character of their interactions with extractants. Extraction involves simultaneous processes of formation of extractable compounds, their distribution between aqueous and organic phases, and reactions in the organic phase. All classification systems employ concepts of electronic interactions between compounds involved in extraction. The electronic interactions between molecules and complexes during extraction are currently analyzed using qualitative models expressed in the form of stoichiometric equations defining extraction.

The group of nonionized compounds includes neutral compounds with an unsolvated coordination sphere [15] and molecular substances with predominantly covalent bonds. These compounds do not undergo appreciable hydration or solvation; they are insoluble in water but are readily soluble in various organic solvents. Extraction of these compounds occurs by means of van der Waals or weak donor–acceptor interactions and obeys distribution laws. As extractants one uses solvents of various nature, for example, benzene, carbon tetrachloride, hexane, etc. Extraction does not change the chemical formula of extractable compounds.

The class of nonionized compounds found in the organic phase includes intracomplex compounds (ICC s) or chelates — one of the most widespread classes of extractable compounds. These are grouped into coordinatively saturated ICCs, in which the inner coordination sphere of the metal ion is fully occupied by organic ligand molecules,