NEW BOOKS

Yu. A. Bankovskii

THE CHEMISTRY OF INNER-COMPLEX COMPOUNDS OF 8-MERCAPTOQUINOLINE AND ITS DERIVATIVES*

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The widespread use of organic reagents in analytical chemistry and the purposeful synthesis of reagents with more valuable analytical properties are impossible without a detailed, systematic investigation of the compounds already existing and in use. Such investigations have been carried out and evaluated for dithizone, hydroxyquinoline, oximes, phthalexone, phenylfluorones, pyrazolone derivatives, and others. However, there is only a monograph by G. Ivanchev, Dithizone, published in 1961, on sulfur-containing reagents. Yu. A. Bankovskii and his students, starting from the theoretical prerequisites developed by Prof. V. I. Kuznetsov, have thoroughly cultivated this interesting field of chemistry. In the monograph, all of the most important questions of complex formation between metal ions and 8-mercaptoquinoline and its derivatives are discussed. Considerable attention is given to consideration of the properties of the inner-complex compounds formed. The book contains eight chapters. In Chapter I, methods of synthesis are described and the general characteristics of 8-mercaptoquinoline and its derivatives are given. Improved syntheses of many compounds are presented, including syntheses of chelated sorbents containing the mercaptoquinoline grouping. Some physical properties of more than 200 derivatives of 8-mercaptoquinoline and its salts are given. Much attention is given to purification of the compounds, which is particularly important for their subsequent use as analytical reagents. In Chapter II, the electronic and vibrational spectra are discussed together with intramolecular hydrogen bonding and the dipole moments of 8-mercaptoquinoline and its derivatives. The spectral characteristics of the ionized, protonated, zwitterionic, and thiol forms are given. The tautomeric equilibrium in solutions of 8-mercaptoquinoline is discussed and the effects on it of the nature of the solvent and of other factors as well. The characteristic frequencies in the 3800-400 cm^{-1} region are assigned for the vibrational spectra of 8-mercaptoquinoline and its derivatives. The existence of intramolecular hydrogen bonding is characteristic for this class of compounds and so the author has studied the effect of the nature of the substituents and of the solvent properties on it.

Chapter III is devoted to the ionization constants of 8-mercaptoquinoline and its derivatives, which are amphoteric compounds. The partition of the reagents between the aqueous phase and an organic solvent is studied by the partition method. Values of the two-phase ionization constants and distribution constants in inert solvents are given for halogen-, methyl-, S-methyl-, and other substituted mercaptoquinolines. Considerable attention is given to the zwitterionic form of 8-mercaptoquinoline (Ch. IV), the form in which the reagents exist in aqueous solution at the isoelectric point and which form in polar solvents.

The greater part of Chapter V is devoted to the interaction of 8-mercaptoquinoline and its derivatives with ions of the elements and to the properties of the resultant, inner-complex compounds (ICC). An interesting inclusion in Chapter V is a comparison of 8-mercaptoquinoline with its oxygen and selenium analogs. For an understanding of the properties of the reagents and their chelates with metals, a comparison of the properties of ligands in which the bonding atom of the salt-forming group is replaced by another atom of the same group of the periodic system is of great importance. It is stressed that a study of 8-mercaptoquinoline, the sulfur analog of 8-hydroxyquinoline, is necessary for the successful solution of problems in the chemistry of coordination compounds and for the creation of a theoretical base for the reaction of metal ions with organic reagents, especially reagents with the same structure but different donor atoms. In spite of great structural similarity

*Zinatne, Riga (1978).

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between the two reagents, one finds a great difference in their physicochemical properties and analytical possibilities. Coordination compounds of 8-mercaptoquinoline and its derivatives, unlike 8-hydroxyquinoline, are used for group concentration. In all chapters of the monograph, the appropriate information needed to compare hydroxyquinoline and its derivatives with the reagents being described is given.

Chapter VI deals with the stability constants of inner-complex compounds. In Chapter VII, the nature of the chemical bond, the structure of ICC, the absorption spectra and electronic structure of ICC of elements with complete and incomplete d subshells, and the effect of the medium and the degree of dissociation on the structure of ICC are considered. Chapter VIII is devoted to examples of the application of 8-mercaptoquinoline and its derivatives in analytical chemistry. They are more selective and their ICC are more stable in two-phase systems to the action of hydrogen ions than the hydroxyquinolinates of the corresponding metals. Results of a systematic study of the physicochemical characteristics of these reagents have served as the basis for the creation of new, valuable analytical methods. The application of the reagents for the concentration, separation, and determination of ions is described. The high sensitivity and selectivity distinguish them from extraction-photometric, luminescence, and radiochemical methods. There is great interest in the application of 8-mercaptoquinoline and its derivatives in amperometric analysis. Summary tables exhaustively illustrate the analytical possibilities of the reagents described. Regrettably, only one of the eight chapters in the book is devoted to practical applications. The literature cited contains 849 papers by domestic and foreign authors (an additional list has 66 names) and shows the major contribution of Soviet scientists (principally Yu. A. Bankovskii and his students) to the chemistry of 8-mercaptoquinoline and its derivatives and to the development of analytical methods based on them.

Among the virtues of the monograph under review must be counted the fact that the position of the author on each question is supported by numerous data obtained with the help of contemporary research methods. In the monograph, changes in the properties of "hydroxyquinoline—mercaptoquinoline—selenoquinoline"; regularities in the change of properties of halo-, methyl-, methoxy-, and sulfo-derivatives of mercaptoquinoline; and the effect of reagent structure on the properties of their ICC are considered in turn. In this sense, this monograph has no analog in the analytical literature. The thoroughness of the treatment of the literature substantially increases the value of the book, which can serve as a good handbook. It is furnished not only with a detailed table of contents but also with a thorough index which allows one to rapidly find the necessary information about a specific question.

The inexact use of scientific terminology must be accounted a deficiency. For example, the author sometimes calls 8-mercaptoquinoline a complex former. The period between the writing and publication of the monograph was too long, with the result that not a few, interesting publications have appeared. It has thus become necessary to list the additional literature, which is doubtless satisfactory but does not settle the question.

New ideas will occur to the readers of Yu. A. Bankovskii's monograph, not only for research in the field of 8-mercaptoquinoline and its derivatives, but in allied fields as well. For many readers it will become a useful aid in their daily work.