Spectrophotometric Investigation of Complexes with Organic Reagents for the Optimization of Spectrophotometric Determinations (uv + vis) of Inorganic Analytes*

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Summary. The knowledge of complex equilibria of elements with organic analytical reagents in solutions and that of thermodynamic and optical parameters of complexes and their distribution in the system is of considerable importance for the selection of optimal conditions for an exact spectrophotometric determination (uv + vis) of an element. All necessary parameters are available by means of a detailed graphical and numerical interpretation of spectrophotometric data. This approach is shown by example of some chromogenic reactions of 4-(2-pyridylazo)resorcin, 2-(2-thiazolylazo)-4-methoxyphenol and 2-(2-pyridylazo)-1-naphthol-4-sulfonic acid.

Introduction

The selected topic simultaneously touches three questions: a) are organic reagents still of immediate interest in analytical practice? b) how to get sufficient information on complex equilibria in solutions most effectively? c) which is the optimal way to develop, optimize and characterize particular spectrophotometric procedures?

With respect to these questions our opinion and results of some longtime studies are given in this paper, discussing as examples some N-heterocyclic azo dyes, which had many years ago been found to be especially suitable reagents.

Present State of Organic Analytical Reagents

Nowadays the significance of organic analytical reagents in inorganic analysis is considered to decrease because of intense development of instrumental methods especially in routine and trace analysis. In spite of this development methods based on chemical equilibria are still significant in analytical routine laboratories, e.g. because of increased interest in continuous techniques. Moreover, the use of organic complexing agents especially concerns among others molecular absorption spectrophotometry (uv + vis), but they will also play an important role in the analytical exploitation of physical properties of their complex species and in the combination with highly efficient separation proce-
dures and pre-concentration of element traces \([1−12, 114,115]\). An immense quantity of sometimes controversial information on the behaviour and reactivity of organic analytical reagents is available in literature today. On the other hand, several hundreds or organic reagents were described but some dozens only are practically used in inorganic analysis. This makes their rational classification, evaluation and selection highly topical. Thus, it is the main goal to select the most suitable organic reagents from many others for the particular analyte, either in an experimental way or by theoretical prognosis. Finally, the selected reactions for the proper analyte are optimized with respect to basic parameters such as precision, accuracy, sensitivity, determination limit and from the point of matrix composition which correlates with the selectivity of the method.

Various different approaches were developed to explain the reactivity or coordination selectivity of organic reagents for prognostic purposes. Nevertheless, the prognosis of the adequate structure of the most suitable reagent for the particular analyte is a not fulfilled challenge.

The early preparative search for suitable functional groups of donor atoms in the organic molecule \([13, 14]\) was replaced by systematic studies or reaction equilibria of organic analytical reagents in solutions to find correlations between reactivity of the reagent as well as thermodynamic, optical and other properties of reagent complexes, and the electronic structure of the metal ion, the type, number and steric arrangement of donor atoms, the type and position of substituents, the size and number of chelating rings, the nature of analyte-donor atom bondings, the overall structure of the reagent and its complex species. It is tried to extrapolate in this way some general postulates for the particular reactivity of the reagent \([15−22]\).

The HSAB concept of Pearson \([23]\) enables one to foresee the reactivity and optical properties of an organic reagent and its analyte complex by comparing the strength of the functional atomic group and the chromophoric resonance system of the reagent with the strength of the particular analyte \([24, 25]\).

More or less rigorous quantum chemical interpretations of electronic structures and optical properties of dye reagents and their complexes were carried out using MO, LCAO, SCF(PPP) or EHT procedures \([26−29]\). They establish the \(n\)-electron density distribution for the ground and excited states of the organic reagent and its various chelates. The probable absorption maxima for electron transitions between particular energy levels can be calculated from the energy level differences of the molecule in the ground and excited states. Tautomeric forms of the reagent are discovered in solution as well as the most probable acidobasic scheme, the nature of metal-donor atom bond and the whole bonding arrangement in chelates of various kinds of metal ions, if results of quantum chemical calculations for various probable reagent structures are compared with experimental data. Moreover the changes in values of coulombic integrals at selected donor atoms of the reagent enable one to simulate effects of various \(\pi\)-donor or \(\pi\)-acceptor substituents in various positions of the molecule against the reagent chromophore or key donor atom group. In this way the reactivity and optical properties of various reagent structures and their complexes can be predicted. Unfortunately, results of current quantum chemical treatments are still limited by the agreement and disagreement between calculated and experimental data, or some correlation between properties of the system and studied parameters. Such semiempirical procedures give approximate results for complicated molecules which can be even ambiguous or questionable or depend on the kind of quantum-chemical approximation used. Such procedures are sensitive against the proper selection of input parameter values such as molecular geometry, bond length, values of coulombic, bonding and overlapping integrals. In addition, the electron transitions between calculated ground and excited levels in the reagent or its metal complex often are compared with experimental absorption spectra under conditions where the particular complex equilibria or the number and stoichiometry of complexes are unknown or have not been proved before. Thus, a partial disagreement between various kind of interpretation or experimental experience can be understood for 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)resorcin and their metal chelates \([27, 29, 92, 112]\).

A full conformation analysis was also used to predict or explain the effect of various functional groups of donor atoms and substituents on the properties of the reagent and its analyte complexes. Comprehensive data are available for arsenazo III and its analogues and other analytically interesting azodyes \([30−34]\).

**Spectrophotometric Investigation of Complex Equilibria in Solutions**

Since many complex of organic reagents strongly absorb radiation in u.v. or visual, spectrophotometry enables one to study even complicated complex equilibria and to evaluate, a) the true reaction equilibria and complex speciations in solution under broad experimental conditions and particular ionic strength, b) the number, stoichiometry and distribution of complex species with appropriate equilibrium and stability constants and optical parameters, c) various competition equilibria of buffers, during hydrolysis or protonation,