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Determination of Acidity Constants of ARS and Stability Constants of Calcon with Al^{3+} at Aqueous and Nonaqueous solutions

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بهمن‌ماه ۱۳۸۴

IN THE NAME OF GOD

DETERMINATION OF THERMODYNAMIC PARAMETERS OF ALIZARIN RED S IN NONAQUEOUS MIXED SOLUTION: ACID_ BASE CONSTANT AND DETERMINATION OF STABILITY CONSTANTS OF CALCON WITH AL^{3+}

BY

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THESIS

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To

My parents

&

My husband

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Abstract

Part I

The effect of different organic-water mixtures on the acidity constants of alizarine red s were determined at 25°C and an ionic strength of 0.1 M are studied by a multiwavelength spectrophotometric method. Two pK_a values for the –OH derivatives were determined. The organic solvents used were the amphiprotic (ethanol) and dipolar aprotic (dimetylsulfoxide). To evaluate the pH-absorbance data, a resolution method based on the combination of soft- and hard-modeling is applied. The acidity constants of all related equilibria are estimated using the whole spectral fitting of the collected data to an established factor analysis model. Data analysis (DATAN) program applied for determination of acidity constants. Generally, the pK_a values increase with an increase in the content of the organic solvent. This behavior can be accounted for in terms of the high stabilization of both the non-protonated and ionic forms of this compound by dispersion forces rather than by hydrogen bonding. There are linear relationship between acidity constants and the mole fraction of different solvents in the mixtures. The effect of solvent properties on acid-base behavior is discussed.

Part II

The stability constant of different Al-Calcon complexes were determined by a multiwavelength spectrophotometric method. SQUAD (Stability QUotients from Absorbance Data) is a computer program used for evaluation of the best set of stability constants from absorbance data measurements. The electronic absorption spectra of solutions of different calcon:Al ratios at various pH values at 400-650 nm intervals were determined and recorded. Outputs of SQUAD are the values of stability constants of different complexes which may be produced in the solution with their standard deviations (SD), titration spectra of each ligand:metal ratio solution with H^+, pure spectra of individual species in each ligand:metal ratio and distribution diagrams of species as the pH of the solution change. The log β values of different Al-calcon complexes were investigated spectrophotometrically in four different ligand:metal ratios of 1:0, 1:1, 2:1 and 4:1 at 25 °C. As the extent of ligand in ligand:metal ratio increased, the absorption of complexes which has two ligands in their structure (ML_2 and ML_2H) increased and the absorption of complexes which has one ligands in their structure (MLH and MLH_2) decreased. According to distribution diagrams it may conclude that the spectra at pH lower than 3.5 assigned to LH_2 form in calcon solution and MLH_2 form in different calcon:Al ratios, because this form is dominated at this range. In pH 3.5-6.5 the LH^- form in calcon solution and MLH form in different calcon:Al ratios are the dominated forms. And at pH > 6.5, L^{2-} form in calcon solution and ML_2H form in different calcon:Al ratios are the dominated forms.

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1. Introduction

1.1. General Introduction

The young scientific discipline "chemometrics" has rapidly developed in the past two decades. This enormous increase was initiated by advances in intelligent instruments and laboratory automation as well as by the possibility of using powerful computers and user-friendly software. So, chemometrics become a tool in all parts of quantitative and qualitative chemistry. Nowadays, the analyst is increasingly faced with the need to use mathematical and statistical methods in his daily work [1].

The roots of chemometrics go back to 1969 when Jurs, Kowalski and Isenhour published a series of paper in Analytical Chemistry [2-4] on the application of linear learning machine to classify low-resolution mass spectra. These papers introduced an innovative way of thinking to transform large amount of analytical data into meaningful information.

The young Swedish scientist Svante Wold first coined the name chemometrics was in the early 1970s. His cooperation with Kowalski, who at the time was working on methods for pattern recognition in chemistry, resulted in the foundation of the International Chemometrics Society (ICS) in 1974s.

Several definitions for chemometrics are presented, that frequently employed in the analytical text is: chemometrics is a chemical discipline that uses mathematics, statistics and formal logic (a) to design or select optimal experimental procedures; (b) to provide maximum relevant chemical information by analyzing chemical data; and (c) to obtain knowledge about chemical systems [5].

ICS-definition for chemometrics is presented, that chemometrics is mathematical, statistical, graphical or symbolic methods to improve the understanding of chemical information. Useful at any point in an analysis, from the first conception of an experiment until the data is discarded.

1.2. Multicomponent Analysis

The term multicomponent analysis is used for procedures in which several components in a sample are determined simultaneously. Over the years, we have observed the inclusion of experiments involving analysis of two-component mixtures in undergraduate instrumental analysis laboratory manuals [6,7].

In spectroscopic experiments, the concentrations of the components are determined by employing simultaneous equations after obtaining the absorptivity coefficients of the components at two wavelengths. Another approach uses a multiwavelengths linear regression analysis, [8] which is more effective in resolving heavily overlapped signals. Applications of the above techniques become limited when systems with three or more components are involved.

The availability of scanning instruments and spread sheets capable of performing advanced mathematics had led to parallel development in multicomponent analysis techniques, which are collectively called multivariate techniques [9,10].

With respect to the overlapped signals, chemometrics methods have provided very good results in the resolution of the mixtures of several components. Where these techniques are successful, they offer an advantage in simplicity over well-established separation techniques such as gas or liquid chromatography.

1.3. Multivariate Curve Resolution

All the resolution methods were born as a tool to analyze multivariate experimental data coming from multi-component dynamic or static system [11-18]. The common goal for all these methods is to mathematically decompose the global instrumental response into the pure contributions due to each of the components in the system. The use of such methods has become valuable when obtaining individual signals experimentally is not possible or when this process is too complex or too time-consuming.

The multivariate output of an experiment monitoring a dynamic or equilibrium process is organized in matrix **D** containing mixed information about the evolution of all the components present in the successive stages of the chemical process. The ultimate goal of the curve resolution (CR) methods is the decomposition of the initial mixture data matrix **D** into the product of two data

matrices **C** and **S**, each of them including the pure response profiles of the n mixture components associated with one of the directions of the initial data matrix (Figure 1.1).

In matrix notation, Eq. 1.1 gives the general expression valid for all CR procedures;

$$\mathbf{D}=\mathbf{C}\mathbf{S}^{T}+\mathbf{E} \qquad (1.1)$$

where **D** (r×c) is the original data matrix, **C** (r×n) and $\mathbf{S}^T$ (n×c) are the matrix containing the pure response profiles related to the data variation in the row direction and in the column direction respectively, and **E** (r×c) is the error matrix, i.e. the residual variation of the data set that is not related to any chemical contribution. n is the number of chemical components in matrix **D**.

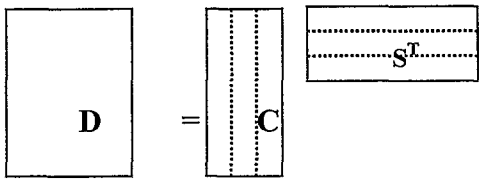

Fig. 1.1. Graphical view of the decomposition of a multi-component data matrix

Taking as an example a pH-dependent process monitored spectrometrically, the **C** matrix would contain the pure concentration profiles of all the absorbing species and the $\mathbf{S}^T$ matrix would be formed by their related pure spectra.

1.4. Spectrophotometric Method for Determination of Acidity Constants

Acid dissociation constants (pK_a) are useful physico-chemical values describing the extent of ionization of functional group of acids with respect to pH. These parameters are very important in most research areas such as acid-base titration, solvent extraction, complex formation, and ion transportation. Much of the theoretical foundation of modern organic chemistry is based on the observation of the effects on acid-base equilibrium of changing molecular structures [19,20]. It has been shown that the pK_a values affect the toxicity, chromatographic retention behavior, and pharmaceutical properties of organic acids and bases [21]. But in order to determine acidity constants of organic reagents we are faced with several barriers, such as low solubility in aqueous solutions and the low values of acidity constants. For passing through these barriers we forced to use mixed solvents. Mixed solvents are interesting, because two solvents mixed together produce a solvent with quite different properties, both, physically (dielectric, density and viscosity) and chemically (acid-base and donor-acceptor properties). As far as the acid-base properties are concerned, an important feature is that the nature of the solvent is crucial for the strength of acids and bases. In particular, important is the proton affinity, in other words, the proton-donating and proton-accepting properties of solvent, as well as its polarity [22-25]. In addition, the ionization degree of solute depends on the dielectric constant of solvent. Media of high dielectric constants are strongly ionizing, whereas those of low dielectric constants ionize to a lesser extent [26].

By mixing solvents of different polarity in proper ratios, dielectric constant of the medium can be varied and controlled and, at the same time, the values of acidity constants and solubilising efficiency of dissolved acids and bases [27].

The spectroscopic instrumentation used today, however, are most invariably has the capacity to collect data in a full spectral range. Using a single or a few wavelengths discard most of information in the collected spectra and requires both the presence and knowledge of such suitable wavelengths. However, in many cases, the spectral responses of components overlap and analysis is no longer possible [28,29].

The predefined model, known as hard-modeling analysis, can not be applied if crucial information is missing. Soft modeling or model free approaches are based on much more general prerequisites, such as positive molar absorbance, positive concentration of all species, unimodality of concentration profiles. Naturally, if the strength of hard-modeling and soft-modeling methodologies are combined, a much more powerful method of data analysis can be expected [30-32]. Kubista et al. have done so and prepared a data analysis program called DATAN [28,33].

In this work, we applied DATAN version 3.1 programs to determine the acidity constants of ARS in pure water and ethanol-water and DMSO-water binary solvent mixtures.

1.5. Spectrophotometric Method for Determination of Stability Constants

The Benesi – Hildebrand method [34] has been extensively used to evaluate the stability constants of different complexes. For the general reaction

$$M + L \leftrightarrow ML \qquad (1.2)$$

where M is any metal ion and L is any ligand, the following equations may be written:

$$C_M = [M] + [ML] \qquad (1.3)$$

$$C_L = [L] + [ML] \qquad (1.4)$$

$$\beta_{101} = [ML] / [M]\,[L] \qquad (1.5)$$

The subscripts for β refer to the number of metal ions, hydroxide or hydrogen ions, and ligand ions, respectively, associated with that stability constant. The studies are most often performed in a nonaqueous, non-donor solvent, in which case the middle subscript is then always zero. Making use of Beer's law:

$$A = \varepsilon_M [M] + \varepsilon_L [L] + \varepsilon_{ML} [ML] \qquad (1.6)$$

it can be shown that

$$\log [(A - A_0)/(A_c - A)] = \log C_L + \log \beta_{101} \qquad (1.7)$$

where A is the absorbance, at a preselected wavelength, of a solution having a known moiarity of ligand, C_L and known moiarity of metal, C_M, A_0 is the absorbance, measured at the same wavelength, of a solution where $C_L = 0$, and A_c is the measured absorbance of a solution for which $C_L >> C_M$ so that the absorbance is

constant with increasing C_L. Thus a plot of the left – hand side of equation (1.7) against log C_L should give a straight line which intersects the abscissa at -log C_L, which will be equal to log β_{101}.

The Benesi – Hildebrand (B–H) method may be generalized to handle equilibrium systems in which the stoichiometry of the complex formed is unknown. In this situation equation (1.5) becomes

$$B_{10n} = [ML_n] / [M][L]^n \qquad (1.8)$$

and equation (1.7) becomes

$$\log [(A - A_0)/(A_c - A)] = \log C_L + \log \beta_{10n} \qquad (1.9)$$

Thus the slope of the straight line in the log – log plot provides the stoichiometric coefficient for the complex.

Inherent in this method is the assumption that only one complex is formed. This situation is not too frequently encountered and when there is more than one complex present the B–H plots of log $[(A - A_0) / (A_c - A)]$ vs. log C_L will shown considerable curvature. It has been argued [35] that the plots may still yield information concerning the stoichiometry and stability constants of the complexes, but except under the most favourable conditions, encountered when complexes of widely differing stability are formed, this claim is not valid.

This method, and many similar approaches, [36] have the common drawback that they are only applicable if one and only one complex exists under the conditions of measurement. However, in general, more than one complex will exist in solution

unless $C_L >> C_M$ or $C_M >> C_L$. Moreover, when several complexes are present, their nature may not be readily determinable from simple continuous variation or molar ratio experiments. Therefore, more sophisticated and rigorous data processing techniques need to be adopted.

Several general computer programs are currently available [37,38] that permit various equilibrium models to be fitted to the experimental data, by change of one or more data files. This type of program is clearly more desirable than one where the program code needs to be rewritten for each new model tested. The majority of programs developed to data require potentiometric data as input, which may either be obtained from measurements of pH vs. volume of base, or of ion – sensing electrode potentials.

Spectrophotometry is a widely used technique for the study and determination of equilibrium constants but only a few programs are available to process the data [37,38]. Spectrophotometric measurements are generally less precise than potentiometric ones, both inherently and because of the need to prepare several separate solutions. A further complication arises from the fact that for fitting an equilibrium model to absorbance measurements, not only are the stability constants to be determined, but the molar absorptivities for each species, at each wavelength, are also to be evaluated. The situation is not as bad as it might seem, since the evaluation of molar absorptivitives and stability constants is done at two levels within most program, patterned after an approach suggested by Sillen [39].