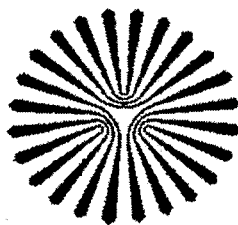


بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



**Payame Noor
University**

School of Science

Department of Chemistry

**Investigation of Non-Aqueous Solvents
Effect on The Acidity Constants of ARS
And
Dimerization Reaction of a Dye in Water at
Different Ionic Strengths By Chemometrics Method**

Submitted in Partial fulfillment of the
Requirements for the Degree of M.S.
in Analytical Chemistry

By

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And

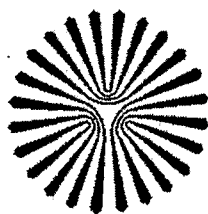
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IN THE NAME OF GOD

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BY
SHAHRAM LOTFI


THESIS


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Dedicated to
My parents

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Abstract

Part One

The accurate determination of acidity constant values is often required in various chemical and biochemical areas. The acidity constants of organic reagents play very fundamental role in many analytical procedures such as acid-base titration, solvent extraction complex formation and ion transport. The acidity constants of alizarin R S (ARS) in binary mixtures of methanol-water and acetonitrile - water at 25° C have been determined spectrophotometrically. 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. As percent of methanol and acetonitrile increases in their mixtures the pKa constants also increased or acidity constants decreased. There is a linear relationship between acidity constants and the mole fraction of methanol and acetonitrile in their mixtures. Effect of solvent composition on acidity constants and pure spectrum of each species are also discussed.

Part Two

The monomer-dimer equilibrium of a dye has been investigated by means of UV-Visible spectroscopy. The dimerization constants of methylene green (MG) have been determined by studying the dependence of their absorption spectra on the temperature in the range 20–90 °C at different total concentrations of methylene green (9.85×10^{-5} to 2.98×10^{-4} M) and different

concentrations of NaCl as supporting electrolyte. The equilibrium parameters of the dimerization of methylene green have been determined by chemometrics refinement of the absorption spectra obtained from thermometric titrations which performed at different ionic strengths. The dimerization constants are varied by changing the ionic strength and the degree of dimerization are increased by increasing of the ionic strengths of the medium. The enthalpy and entropy of the dimerization reactions were determined from the dependence of the equilibrium constants on the temperature (van't Hoff equation).

Investigation of Non-Aqueous Solvents
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And

Dimerization Reaction of a Dye in
Water and Water-Non Aqueous Solvents
Mixture By Chemometrics Methods

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Chapter One

Introduction

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 instrument and laboratory automation as well as by the possibility of using powerful computer and user-friendly software. So, chemometrics become a tool in all parts of quantitative chemistry, but partially in the field of analytical chemistry. Now a days, 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 papers 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 system" [5].

ICS-definition for chemometrics is presented, "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 [6].

The data flood generated by modern analytical instrumentation is one reason that analytical chemists in particular have developed the applications of chemometrics methods. Chemometrics in analytical chemistry is a discipline that uses mathematical, statistical methods to obtain relevant information on material system [7].

1.2.Spectrophotometric Multicomponent Analysis

The term multicomponent analysis is used for procedures that 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 [8,9]. Since Spectrophotometry is a rapid, sensitive and inexpensive analytical tool, during the last decade there has been resurgence in the use of absorption spectroscopy for quantitative analysis of multicomponent system. This change has to our increased ability to handle the required matrix transformation on computers and to fact that many spectrophotometers, both infrared and UV-visible, have been interfaced to computer or microprocessor, which can perform the matrix transformation almost instantaneously.

In spectroscopic experiments, the concentration of the components is determined by employing simultaneous equations after obtaining the absorptivity coefficients of the components at two wavelengths. Another approach uses a multiwavelength linear regression analysis[10], which is more effective in resolving heavily overlapped signals. Application of the above techniques become limited when system with three or more components are involved.

The availability of scanning instruments and spectra sheets capable of performing advanced mathematics has led to parallel development in multicomponent analysis techniques, which are collectively called multivariate calibration techniques [11,12]. With respect to the overlapped signals, chemometrics methods such as multivariate calibration and different kinds of derivative methods have provided very good results in the resolution of mixture 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. Nonlinear Iterative Partial Least Squares (NIPAS)

Nonlinear Iterative Partial Least Squares (NIPAS) is an algorithm designed to extract eigenvalues and eigenvector directly from the data without requiring pre-multiplication of the matrix by its transpose. Pairs of eigenvector (row and columns) are stripped out one at a time, from the largest to the smallest eigenvalues. Data reproduction can quickly be checked during the decomposition and the process can be determined at any desirable point without requiring extraction of all eigenvalues.

To demonstrate the underlying principles of NIPALS, using singular value decomposition (SVD) [13] notation. SVD is another important mathematical technique for decomposing a matrix into eigenvectors. In SVD notation the data matrix is expressed as:

$$D = USV^T \quad (1.1)$$

Where U and V are orthogonal matrix such that $U^T U = I_r$ and $V^T V = I_c$ where I_r and I_c represented identity matrices. S is diagonal elements, called singular values, are equal to the square roots of the respective eigenvalues.

Therefore, NIPAS is an efficient iterative algorithm, which extracts the full- spectrum loading vectors (eigenvectors) from the spectra in the order of their contribution to the variance in the calibration spectra. After the first loading vector has been determined, it is removed from each calibration spectrum, and the process is repeated until the desired number of loading vector has been calculated [14].

1.4.Spectrophptometric Method for Determination of Acidity Constants

The accurate determination of acidity constant values is often required chemical and biochemical areas. These are of vital importance in understanding the distribution, transport behavior, binding to receptors and mechanism of action of certain pharmaceutical preparations [15,16]. The acidity constants of organic reagent play very fundamental role in many analytical procedures such as acid-base titration, solvent extraction and complex formation [17].

Determination of equilibrium constants for ionizable compounds has long been a concern in analytical chemistry. Traditionally, pH-metric titration was employed to determine the pK_a 's of ionizable group in aqueous solutions [18]. However, the success of this approach is sometimes hampered by poor aqueous solubility ($< 10^{-4}$).

Spectrophotometric pK_a determination is an attractive alternative provided that the compound is water soluble to the extent of 10^{-6} M and it contains chromophore(s) in proximity to the ionization center(s) such that the protonated and deprotonated forms exhibit sufficient spectral dissimilarities[19,20].

Spectrophotometric methods are in general highly sensitive and are as such suitable for studying chemical equilibria in solution. When the