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Determination of Dissociation Constant of the Acid Alizarin Violet N Using UV/Vis Spectroscopy

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ABSTRACT

In the present paper, a sensitive, fast and suitable method for calculating dissociation constant (pKa) value of acid alizarin violet N (AVN) is proposed. The study was performed in the absorption spectra at 190–700 nm intervals were recorded. The dissociation constant of AVN at pH range 1.50–10.00 and at constant ionic strength 0.1 mol L^{-1} and 25ºC were determined using DATa Analysis (DATAN) program using spectrophotometric titration data. The calculated pKa of AVN in water was 6.25.

Keywords: Acid alizarin violet N, UV/Vis spectroscopy, Absorption spectra**,** Acidity constant

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INTRODUCTION

The accurate measurement of acidity constant values is usually required in miscellaneous biochemical and chemical areas. These are of basic importance in understating the absorption, distribution, metabolism, transport behavior, linking to receptors and mechanism of action of certain pharmaceutical preparation [1, 2]. The acidity constants of organic compounds play a very fundamental role in many analytical methods, such as solvent extractions, acid–base titrations, and complex formation and ion transport [3]. It has been shown that acid–base properties affect the pharmaceutical properties, chromatography's retention behavior and toxicity of organic acids and bases.

Spectrophotometric methods are in general highly sensitive and as such are suitable for studying chemical equilibrium in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and to determine the equilibrium constant is trivial. Several spectrophotometric methods have been developed to determine the equilibrium constants of chemical processes. Occasionally, problems arise because of strong overlapping of chemical components involved in equilibrium and some doubts from using some complex mathematical algorithms, to solve such problems [4-6]. However, much more information can be extracted if multivariate spectroscopic data are analyzed by a proper multivariate data analysis method. The most relevant reports are on SPECFIT [7], SQUAD [8] and HYPERQUAD [9]. All these computational approaches are based on a first proposal of a chemical equilibrium model defining species stoichiometries and based on mass-action law and mass balance equations (hard-modeling methods) and also involve least-squares curve-fitting procedures. The starting point of using soft-modeling was in 1971 that Lawton and Sylvestre [10] introduced Chemometrics based method for spectral analysis. These approaches are free from restricting the mass-action law and do not need an initial model of species to be set up.

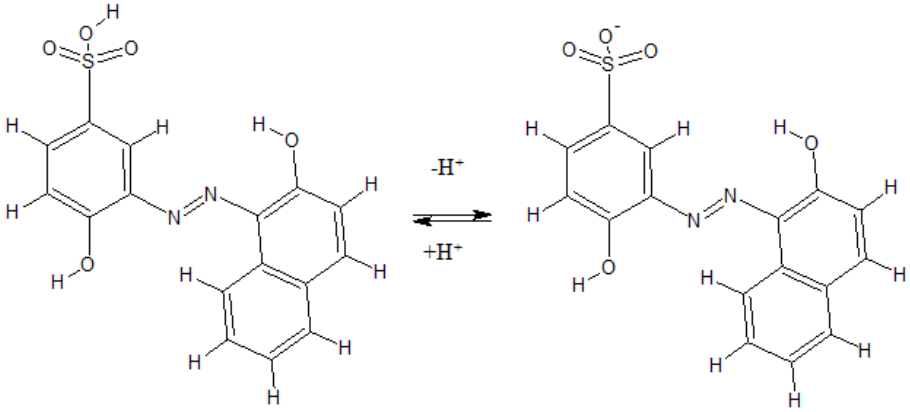
Data analysis was carried out by DATAN package that developed by Kubista group [11-13], called the physical constraints approach, which provides a unique solution by needing that the calculated concentrations obey an assumed equilibrium expression and shows it's applicability by determining the acidity constants of two and four protolytic forms of fluorescein. A possible advantage of the Kubista et al. method is that it mixes a soft-modeling

approach with a hard-modeling approach. This might be better and more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constraints method calculates spectral profiles, concentrations and equilibrium constants by utilizing equilibrium expressions that related the components.

The theory and application of the physical constraints method were discussed by Kubista et al., in several papers. In previous papers, algorithms and theory of DATAN is presented [14-24].

Azo dyes comprise the largest group of organic reagents used in spectrophotometric analysis. They also are found in a variety of industrial applications, mainly because of their color fastness and low price. These dyes are characterized by chromophoric azo groups (-N=N-) offering a wide spectrum of colors. Azo dyes are also used for coloring numerous consumer goods, such as leather, clothes, food, toys, plastics and cosmetics [25].

In this work, the physical constraints approach has been used for spectrophotometric determination of the acidity constant of 4-hydroxy-3-(2-hydroxy-1-naphthylazo) benzene sulphonic acid (acid alizarin violet n) in pure water (see **Scheme1**). The acid alizarin violet N (AVN) is belonging to dye class azo. The color change of this dye occurs at pH 6.5 (orange-red) to 9.0 (violet). The physical form has reddish-violet crystals and soluble in water and ethanol. This dye has a maximum wavelength at 545nm.



Scheme1. Chemical structure representation of the equilibrium between the forms of AVN

MATERIALS AND METHODS

Instruments and reagents

A Hewlett–Packard 8453 diode array spectrophotometer controlled by a Hewlett–Packard computer and equipped with a 1-cm path length quartz cell was used for UV–Visible spectra acquisition. Data acquisition between 190 and 700 nm were performed with UV–Visible ChemStation program, running under Windows 7. A Metrohm 692 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 4.00 and 10.00. The acid alizarin violet n ($C_{16}H_{11}N_2O_5SNa$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and potassium nitrate (KNO_3) were purchased from Merck. All the reagents used were of analytical reagent grade. The stock solutions of 10^{-4} mol L^{-1} of AVN were prepared by dissolving appropriate amounts of AVN in double-distilled de-ionized water.

Spectrophotometric measurements

For the solution of AVN (4.0×10^{-5} Mol L^{-1}) in pure water, absorption spectra were measured with a titration setup consisting of a computer interfaced to a spectrophotometer. The pH values were varied from 1.50 to 10.00 by step of 0.20 using convenient universal buffer. The absorption spectra at 44 pH values were related to each sample. All measurements were carried out at 25 ± 0.5ºC. Ionic strength was maintained at 0.1molL^{-1} by adding appropriate amounts of KNO3.

RESULTS AND DISCUSSION

The outputs of DATAN (**Version 5.0, 2013**) program are pKa values, the number of principal components, concentration distribution diagrams and pure spectrum of each assumed species. By inspection of the experimental spectra, it is hard to guess the number of species participating in the equilibrium. The principal component analysis of all absorption data matrices obtained at various pH shows at least two significant species (HL and L^-). These species could be attributed to dissociation equilibrium of the mono-protic acid of AVN. The two calculated

significant projection vectors with clear spectral features (as compared to the noise) are also an evidence of the presence of two spectroscopically distinguishable components in the equilibrium. Typical absorption spectra of AVN at different pH values (from pH = 1.50 to pH = 10.00) in pure water is shown in **Fig.1**. AVN is a well-known chelating reagent which is used as an indicator in acid–base titrations. The AVN has one acidity constant. This is due to the ionizable $–SO_3$-H group (**Scheme 1**). The pure spectra and distribution diagram of AVN solution with different pH ranging from1.50–10.00 are shown in **Figs. 2** and **3**. According to **Fig.3,** the pKa value of AVN is 6.25.

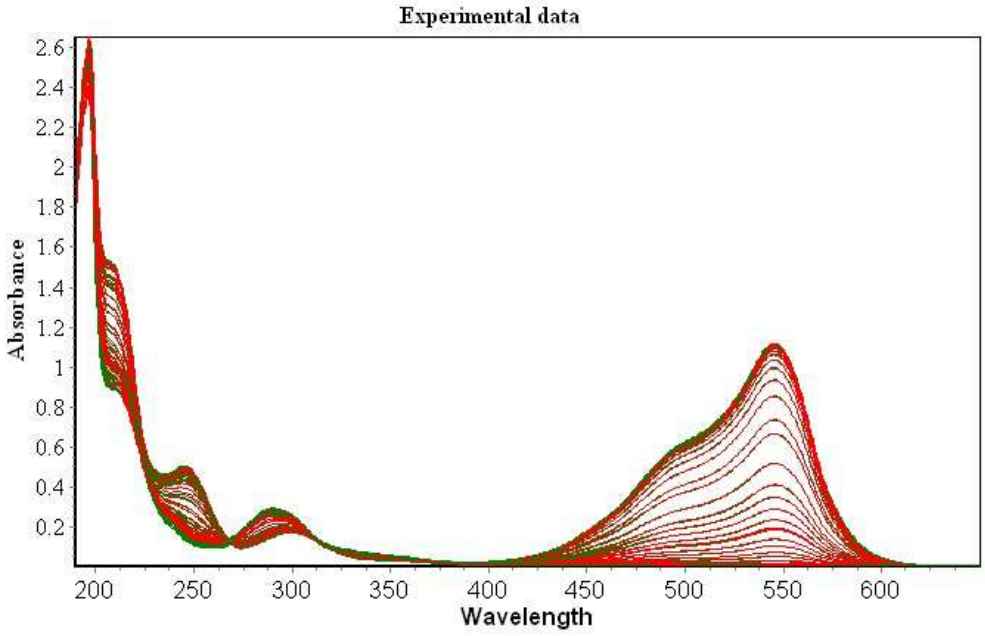


Figure 1. 2D-plot of acid alizarin violet spectra at pH range 1.5-10

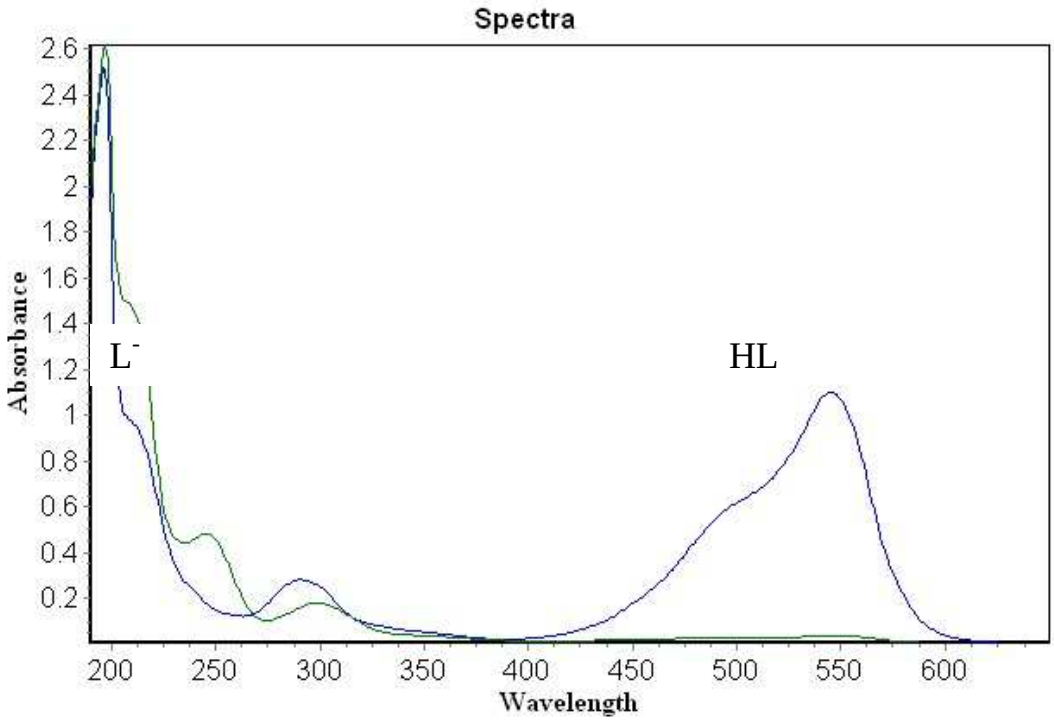


Figure 2. Pure spectra of acidic and basic forms of AVN

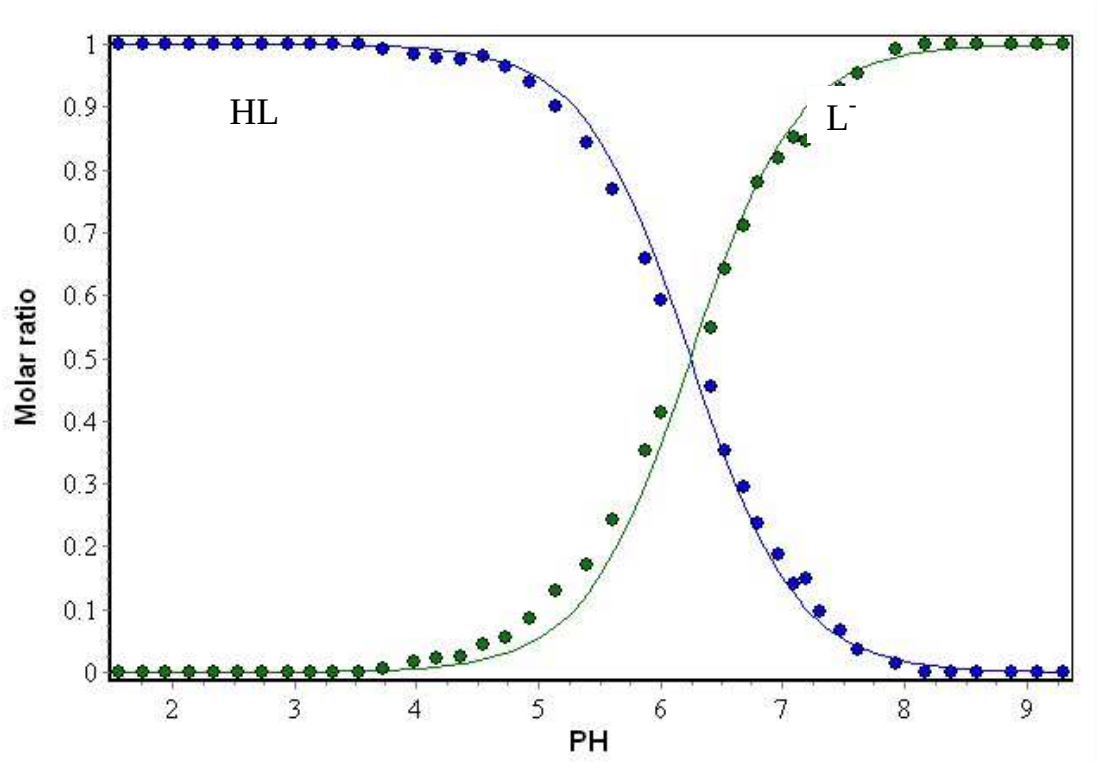


Figure 3. Plot of distribution of major species of AVN, as a function of pH for the spectral data in pure water

CONCLUSION

In this study, we distinguish the behavior of acidity constant of acid Alizarin Violet N in pure water, at 25ºC and ionic strength of 0.1 $molL^{-1}$ that are studied by the multiwavelength spectrophotometric method. It was also demonstrated that DATAN is a useful tool for resolution of different species present in equilibrium systems. By using this method and without any prior knowledge about the system, concentration profiles and pure spectra can be obtained from the experimental data.

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