

# Spectrophotometric determination of acidity constants of Alizarine Red S in water, water-Brij-35 and water-SDS micellar media solutions

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## Abstract

The acidity constants of Alizarine Red S in water, water-Brij-35 and water-SDS micellar media solutions at 25 °C and an ionic strength of 0.1 M 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. DATAN program applied for determination of acidity constants. Results show that the  $pK_a$  values of Alizarine Red S are influenced as the percentages of a neutral and an anionic surfactant such as Brij-35 and SDS, respectively, added to the solution of this reagent. Effect of surfactant on acidity constants and pure spectrum of each component are also discussed.

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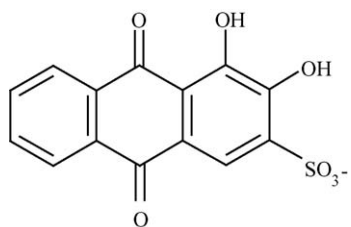
## 1. Introduction

Aqueous micellar media are widely used in different areas of analytical chemistry and several reviews concerning their analytical applications have been published [1–4]. One important property of micelles is their ability to solubilize a wide variety of compounds which are insoluble or slightly soluble in water. The incorporation of a solute into micellar systems can lead to important changes in its molecular properties. Another important effect of micellar systems is that they can modify reaction rates and, to some extent, the nature of the products. Micelles can inhibit or accelerate reaction rates (by up to several orders of magnitude) and also shift equilibria (acid–base). Surfactants usually affect spectral parameters: the intensity and shifts in the absorption bands can be increased and shifts in the absorption maxima of reagents are observed [5,6]. Micelles can affect the apparent  $pK_a$  values of the reagents due to a combination of electrostatic and microenvironmental effects of the micelle [7–9]. Moreover, the acid–base equilibria involved in these systems are also influenced by surfactants [10–12].

Acid dissociation constants (i.e.  $pK_a$  values) can be a key parameter for understanding and quantifying chemical phenomena such as reaction rates, biological activity, biological uptake, biological transport and environmental fate [13]. There have been several methods of the determination of acidity constants, including the use of potentiometric titration, spectrophotometry, capillary electrophoresis, and so on. Spectroscopic methods are in general highly sensitive and as such are suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of the equilibrium constant is trivial [14].

For many systems, particularly those with similar components, this is not the case, and these have been difficult to analyze. Therefore, to overcome this problem we have to employ the graphical and computational methods. Up to the middle of the 1960s, the evaluation of equilibrium measurements was based on the different graphical methods. These methods were reviewed in considerable details by Rossotti and Rossotti [15]. Starting from middle of the 1960s, computers acquired ever-greater importance in the evaluation of equilibrium measurement data using multiple wavelengths or full spectrum to determining the stability and acidity constants. The most relevant reports are on SPECFIT [16], SQUAD [17] and HYPERQUAD [18]. All these computational approaches are based on an initial proposal of

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Scheme 1. Chemical structure of Alizarine Red S.

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 [19] introduced chemometrics based method for spectral analysis. These approaches are free from the restriction of the mass-action law and do not require an initial model of species to be set up.

Data analysis was carried out by DATAN package that developed by Kubista group [20–22], called the physical constraints approach, which provides a unique solution by requiring that the calculated concentrations obey an assumed equilibrium expression and demonstrates its 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 best 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 physical constraints method was discussed by Kubista et al. in several papers [23–34].

In this work, we applied the physical constraints approach to determine the acidity constants of Alizarine Red S (Scheme 1) in pure water, water-Brij-35 and water-SDS micellar media solutions at 25 °C and an ionic strength of 0.1 M spectrophotometrically. The effects of polyoxyethylenaurylether (Brij-35) as nonionic surfactant and sodium *n*-dodecyl sulfate (SDS) as anionic surfactant were studied on the dissociation constants and pure spectrum of Alizarine Red S. The analysis is readily performed with the computer program DATAN [20].

## 2. Experimental

### 2.1. Materials

Alizarine Red S, Brij-35, SDS, hydrochloric acid, sodium hydroxide and potassium nitrate were analytical grade commercial products from Merck. These reagents were used without further purification. Standard stock solution of  $8.0 \times 10^{-4}$  M of Alizarine Red S was prepared by dissolving appropriate amounts of Alizarine Red S in water. The stock solutions of surfactants prepared by dissolving weighted amounts of substances in appropriate amounts of water. All the solutions were prepared in deionized water.

### 2.2. Instrumentation

A Perkin-Elmer (Lambda 25) spectrophotometer controlled by a computer and equipped with a 1 cm path length quartz cell was used for UV–vis spectra acquisition. Spectra were acquired between 370 and 700 nm. A HORIBA M-12 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 3.00 and 9.00 (which pH adjustment contains error with respect to the direct use of the buffer solutions).

### 2.3. Computer hardware and software

All absorption spectra were digitized at five data points per nanometer in the wavelength 370–700 nm and transferred (in ASCII format) to an AMD 2000 XP (256 Mb RAM) computer for subsequent analysis by MATLAB software, version 6.5 (The MathWorks) or for processing by using DATAN package.

### 2.4. Spectrophotometric titrations

For the Alizarine Red S ( $2 \times 10^{-4}$  M) in pure water, water-Brij-35 and water-SDS mixtures titrations, absorption spectra were measured with a titration set-up consisting of a computer interfaced to a spectrophotometer. After each pH adjustment, solution is transferred into the cuvette and the absorption spectra are recorded. Ionic strength was maintained at 0.1 M by adding appropriate amounts of KNO<sub>3</sub>. All measurements were carried out at the temperature ( $25 \pm 0.5$  °C).

## 3. Results and discussion

The absorption spectra of Alizarine Red S in pure water at various pH values at 370–700 nm intervals were recorded. In order to determine the influence of the nonionic surfactant (Brij-35) and the anionic surfactant (SDS) in acidity constants, a series of experiments were run at different Brij-35 and SDS concentrations, above the cmc. Sample spectrum of Alizarine Red S at different pH values in pure water, water-Brij-35 and water-SDS are shown in Figs. 1–3. The principal component analysis of all absorption data matrices obtained at various pH values

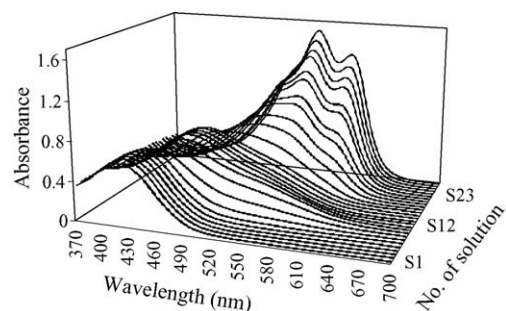


Fig. 1. Absorption spectra of Alizarine Red S in pure water at different pH values: (1) 0.85, (2) 1.49, (3) 1.91, (4) 2.42, (5) 2.90, (6) 3.40, (7) 3.90, (8) 4.40, (9) 4.95, (10) 5.42, (11) 5.92, (12) 6.46, (13) 6.94, (14) 7.30, (15) 7.85, (16) 8.36, (17) 8.94, (18) 9.41, (19) 9.70, (20) 10.06, (21) 10.32, (22) 10.49, (23) 10.79, (24) 11.00, (25) 11.31, (26) 11.55, (27) 12.02.

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