An EIS and UV-Vis Spectroscopy Assay for Aggregation of Monoazo Acid Dye

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The qualitative and quantitative analysis of the aggregation of monoazo acid dye (I) (sulfanilic acid → phenol) has been studied by UV-Vis spectroscopy and electrochemical impedance spectroscopy (EIS) in aqueous solutions as a function of dye concentration (1 × 10-6 - 1 × 10-3 M). From the spectroscopic analysis, qualitative information about the monoazo dye I aggregation were obtained. As the concentration increases, the maximum extinction coefficient increased until dye concentration reached at 3 × 10-4 M; after this concentration, the extinction coefficient decreased with increasing dye concentration. The shape of the absorption spectra starts to change at dye concentration 6.25 × 10-4 M. All these shifts indicate that the molecules are beginning to aggregate in the range of concentration investigated. Also, the changes in the dielectric properties of the monoazo acid dye (I) in aqueous solutions as a result of molecular rearrangements caused by the aggregation process that alter the current circulation pathways and the electric dipole distribution were analyzed.

Keywords: EIS, UV-Vis, aggregation, azo dye

The aggregation of dyes presents a considerable interest and has been investigated by many researchers [1-4]. Direct dyes are generally large molecules, containing two or more azo groups, and sulfonic groups which provide solubility in water.

The azo compound class accounts for over 60% of all dyes. They all contain an azo group, -N=N-, which links two sp2 hybridized carbon atoms. Often, these carbons are part of aromatic systems and most azo dyes contain only one azo group, but some contain two (disazo), three (trisazo) or more [5]. In theory, azo dyes can supply a complete rainbow of colours. Azo compounds are usually of yellow or orange color, since their main absorption band in the visible spectrum is typically in the blue region. They can adopt a planar structure, and tend to form dye-substrate intermolecular interactions that can facilitate aggregation under some experimental conditions. It is important to understand dye aggregation in aqueous solution so that the application process will be successful (for the paint, textile, and photographic industries) [6,7].

For example, in the dyeing process an important factor is the fast diffusion of dye molecules into the fiber, a process which requires the disaggregation of the dye molecules. The dye aggregation depends on chemical dye structure and is a function of temperature, electrolyte concentration, surfactant type, and dye concentration [8]. The self-aggregation of dyes in solution has been investigated by a whole bunch of methods, including: conductometry, polarography, measurements of diffusion coefficients, osmometry, as well as by optical techniques, 1H- and 13C-NMR, and most frequently by UV-Vis spectroscopy [9-12].

Grafting ionic groups on the skeleton of the dye dissolved, especially sulfonic group decrease aggregation, while introducing alkyl groups increases the hydrophobic interactions due to increased aggregation [13]. The aggregation occurs through maximum overlapping aromatic systems by a planar arrangement of two molecules with sulfonic groups at the opposite ends of the dimer. The degree of aggregation will increase due to the group -OH, group which increases the interaction between molecules, polarization and electron delocalization [14-17].

Electrochemical impedance spectroscopy (EIS) is a technique, used for characterizing the electrical properties (electron-transfer resistance and capacitance) of electrode-electrolyte interfaces. In the case of dye solution as the dye aggregate on the electrode surface, the impedance is altered and the change can be used to analyze the aggregation behaviour. Two distinct polarization responses can be induced in an insulating material when a time-dependent external field \( \mathbf{E} \) is switched on. One is electronic in origin, with a typical time constant \( \sim 10^{-6} \) s, and a slower one associated with the reorientation of the electrical dipoles [12,16,17]. Energy is adsorbed at a range of different frequencies: for the electronic component of the response - in the ultraviolet domain and for the molecular rearrangement terms - in the radio and microwave. The structural response usually studied by electrical impedance spectroscopy (EIS) techniques, which can be conveniently described in terms of dissipative and polarization components, respectively related to the imaginary \( \varepsilon' \) and real parts of the frequency-dependent dielectric constant \( \varepsilon \). H.P. de Oliveira and co-workers investigated the aggregation process of methyl orange by EIS [16], and presented the results of an electrical impedance spectroscopy investigation of the evolution of the aggregation process of methyl orange dye in aqueous solutions, as dimers and then oligomers formed when the concentration of the dye, is progressively increased. They have adopted the constant phase element (CPE) approximation to model the electrical response of the dye solutions as an equivalent RC electrical circuit and show how the corresponding resistive and capacitive terms

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reveal the existence of specific signatures associated with the successive steps of aggregate formation.

The process of aggregate formation in colloidal systems can be investigated by techniques as different as nuclear magnetic resonance, absorption spectroscopy, and measurements of surface tension and electrical conductance of the solutions [13,15], and it has been determined that dimers are formed when dye concentration reaches 0.0158 mM, causing a slight, but noticeable blue shift in the maximum of the UV–visible absorption spectrum.

In the present work, the qualitative and quantitative analysis of the aggregation of a monoazo acid dye (I) is presented. Spectroscopic analysis was used for the qualitative investigation of the aggregation of an azo dye, as a function of dye concentration. For the quantitative characterization of the aggregation process of monoazo acid dye (I), the EIS analysis was performed based on the changes in the dielectric properties of the dye in aqueous solutions as a result of molecular rearrangements caused by the aggregation process that alter the current circulation pathways and the electric dipole distribution.

Experimental part

Materials and methods

The monoazo acid dye (I) (sulfanilic acid → phenol) was obtained in our laboratory. The synthesis and the characterization of it was presented in a previous paper [18]. The structure of monoazo acid dye (I) (sulfanilic acid → phenol) (NaC₆H₄N₂O₄S; sodium hydroxyazobenzensulfonate) is presented in figure 1.

![Chemical structure of the investigated acid dye (I)](image)

The aqueous solutions of dye were prepared by dissolving the dye (I) in distilled water, using a magnetic stirrer.

The UV-visible spectra of monoazo acid dye (I) in water, in the concentration range 9 × 10⁻⁶ to 5 × 10⁻³ M were recorded. UV-visible absorption spectra were obtained using a CECIL CE 7200 spectrometer in the wavelength range 200 to 800 nm. The quartz cuvette of path lengths 5, 2, 1, 0.5, 0.1, and 0.09 cm were used in such a manner that the absorbance values did not exceed 2. All measurements were carried out at 27 ± 2°C. The dielectric response of monoazo acid dye (I) solutions of variable concentration was measured as a function of frequency. Electrochemical impedance experiments were performed with an Autolab 302N potentiostat/galvanostat equipped with the FRA2 impedance module. All measurements were carried out in a conventional one-compartment three-electrode cell, equipped with two inox counter electrode and an SCE reference electrode. The exposed surface area of the working electrode (inox) used in electrochemical experiments, was 0.567 cm². Electrochemical impedance spectra were recorded at open circuit potentials in progressively diluted aqueous dye (I) solutions starting from a highly concentrated (10 mM) solution of (I) dye. All spectra reported here were measured at the open circuit potential. The tested frequency range was from 0.1 Hz to 100 kHz. The sinusoidal potential amplitude was 10 mV. All electrochemical measurements were performed at room temperature.

Results and discussions

The molecular aggregation of acid dye (I) has been studied in aqueous solutions as a function of dye concentration. The UV-visible absorption spectra of monoazo dye (I) in aqueous solution were recorded across a range of different initial concentrations varying between 9 × 10⁻⁶ and 5 × 10⁻³ M. Using nine initial concentrations, the samples were analyzed using the CECIL UV-Vis spectrometer, in order to obtain their absorption spectra and to study the trends in these spectra. The obtained results are graphed together in figure 2, plotted as ε = A/C.l.

![Absorption spectra of monoazo dye (I) at different concentrations](image)

As can be seen in figure 2, in concentration range 9 × 10⁻⁶ ÷ 3 × 10⁻⁴ M, as the concentration increases, the extinction coefficient at 355 nm increased. Dramatic changes take place in the absorption spectra beginning with the dye concentration 6.25 × 10⁻⁴ M.

As the concentration increases, the extinction coefficient decreased, the maximum absorption wavelength at 355 nm shifted to higher wavelength (390.2 nm), as well as a second peak begins to form off the main one and shifts to lower wavelength (311.2 nm). All these shifts indicate that the molecules are beginning to aggregate. For accuracy, the absorption coefficient was plotted as a function of peak wavelength (fig. 3).

For studied dye (I) the graph shows a clear trend in the changes of the maximum absorption wavelength peak with concentration, and the split of the principal peak. Figure 4 shows the dependence of absorption coefficient (ε) at the maximum absorption wavelength (355 nm) of the dilute solution, on initial dye concentration (C₀).

![Variation of the maximum peak wavelength with dye concentrations](image)
By increasing the initial dye concentration, the extinction coefficient increased till dye concentration reached at $3 \times 10^{-4}$ M; after this concentration, the extinction coefficient decreased with increasing dye concentration. The experimental results indicate that the studied dye showed signs of aggregation at lower concentrations, and the presence of n-mers in the system in the range of concentrations investigated.

From the spectroscopic analysis, we obtained only qualitative information about the monoazo dye aggregation. We extended our research with electrical impedance spectroscopy investigation and compared the aggregation by measured impedance changes.

Starting with a highly concentrated mother solution, we were able to determine the dielectric response of this azobenzene in a wide domain of concentrations at which dimer and oligomer formation are expected to occur. During the dilution process from the motherhood dye solution, the pH of the sample solution remains in the range 6.3 ÷ 5.5.

Consistent trends in impedance changes were observed across all samples, characterized as a general increase in the measured impedance magnitude at 3 kHz. Impedance changes reach a peak approximately at $10^{-4}$ M. These results suggest that changes in impedance spectra are directly influenced by dye aggregation phenomena and that the impedance measurements may provide an online assessment of these.

Impedance spectra were represented in Bode plots. The Bode representation shows the logarithm of the real and imaginary part of impedance as a function of the logarithm of frequency (log f) are displayed in figures 5 a and c. At low frequencies the impedance presents almost the same high value and starts to decrease at a critical frequency (an intermediate frequency domain) and after this value decreased strongly in high frequency domain (fig. 5a). The real part of the impedance of the analyzed solution varies by several orders of magnitude, with the dye concentration; lower value at high concentration values (fig. 5a.). The module of impedance at this critical frequency provides an indication of some modification of the electrodes surface as a result of aggregation of dye molecules and how close and extensively the dye molecules spread on the surface (fig. 5b).

The imaginary part of the impedance shows a shift of the relaxation peak (fig.5c) to lower frequencies as the dye concentration in solution is progressively reduced. The peak shifts slightly to lower frequency, which suggests that dye molecules contacts with electrode surface decrease monotonically with decrease of concentration. The decrease of dye contacts is a result of aggregation process (increase conformational inertia and a longer time of response, is favored when dye concentration increases). At a critical frequency the electrode impedance changes dramatically.

In figure 6 is presented the magnitude of impedance change plotted as a function of dye concentration in solution at the critical frequency ($\sim 3 \times 10^{3}$ Hz). The existence of an evident change in slope is observed when the dye concentration reaches the value of $3.75 \times 10^{-4}$ M where dimers are formed.

The obtained concentration value at which this monoazo acid dye start to aggregate is lower comparatively with other azo dye. In the case of methyl orange the concentration at which this monoazo acid dye start to
The presence of the hydroxyl group instead the dimethyl amino group increases the tendency of aggregation, due to the possibility of hydrogen bonding formation. The aggregation occurs through maximum overlapping aromatic systems by a planar arrangement of two molecules with sulphonic groups at the opposite ends of the dimer.

The degree of aggregation will grow due to this hydroxyl group, which increases the interaction between molecules, polarization and electron delocalization [19].

Conclusions
A qualitative and quantitative analysis on the aggregation of a monoazo dye was performed. From the spectroscopic analysis, was easy to see that spectra of studied dye shifted as the concentration changed, which is to be expected from aggregating dye. All the obtained spectra changes indicate that the dye molecules are aggregated, in the domain of concentration investigated. EIS was a convenient tool for the investigation of aggregation processes of an aqueous solution of dye and indicate the concentration where dimers. The phase angle increases with decrease of concentration and shifts slightly to lower frequency, as a result of dye molecules contacts with electrode surface. The decrease of dye contacts is a result of aggregation process (increase conformational inertia and a longer time of response, is favored when dye concentration increases. The results obtained from UV-Vis spectroscopy are in agreement with those obtained from electrical impedance spectroscopy. Azo red dye has a tendency to aggregate at lower concentration (3.75 × 10^{-4}M) comparatively with other dyes for example methyl orange.

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