

DOES AN AROMATIC CHLORIDE SUBSTITUTE POSITION INFLUENCE THE AGGREGATION PROPERTIES OF DIRECT DYES?

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ABSTRACT

Dyes ions have a tendency to self-associate in aqueous solutions. The main factors influencing aggregation are dye concentration, electrolyte concentration, and temperature. In the present work, the influence of the chloride position in the dye structure on the dye aggregation was investigated. The molecular aggregation has been studied spectrophotometrically in aqueous solutions as a function of dye concentration ($10^{-6} \div 10^{-3}$ mol/L). As the concentration increases, different changes were observed in the dyes UV-vis spectra indicating that the molecules are beginning to aggregate. The shapes of the obtained spectra were totally different as the position of the chloride was changed in the dye molecule.

INTRODUCTION

Direct dyes are generally large molecules, containing two or more azo groups, and sulfonic groups which provide solubility in water. They can adopt a planar structure, and tend to form dye-substrate intermolecular interactions that can facilitate aggregation under some experimental conditions [1]. It is important to understand dye aggregation in aqueous solution in order that the dyeing process will be successful. An important factor in the dyeing process is the fast diffusion of dye molecules into the fiber, a process which requires the disaggregation of the dye molecules. The aggregation of dyes presents a considerable interest and has been investigated by many researchers [2, 3]. The UV-Vis spectroscopy is the usually used method for investigation of the dye aggregation [4]. The dye aggregation is a function of temperature, electrolyte concentration, surfactant type, and dye concentration [5, 6]. In the present work, spectrophotometric analysis was used for the qualitative investigation of the aggregation of three direct dyes, as a function of chloride position in the dyes structure.

MATERIALS and METHODS

Three disazo direct dyes derived from 4,4'-diaminostilbene-2,2'-disulphonic acid were investigated. The dye was purified by several recrystallizations from distilled water and characterized by thin layer chromatography, electronic spectra and mass spectroscopy.

The visible spectra of the investigated dyes, in the concentration range between 5×10^{-6} to 3×10^{-3} mol/L were recorded in water. The samples were placed in an oven to sit over night.

UV-visible absorption spectra were obtained using a CECIL CE 7200 spectrometer in the wavelength range 200 to 800 nm. The quartz cuvette of pathlengths 1, 0.5 cm, and 0.1 cm were used in such a manner that the absorbance values did not exceed 2. All measurements were carried out at 27 ± 2 °C.

RESULTS

The chemical structures of the investigated dye molecules are presented in Figure 1.

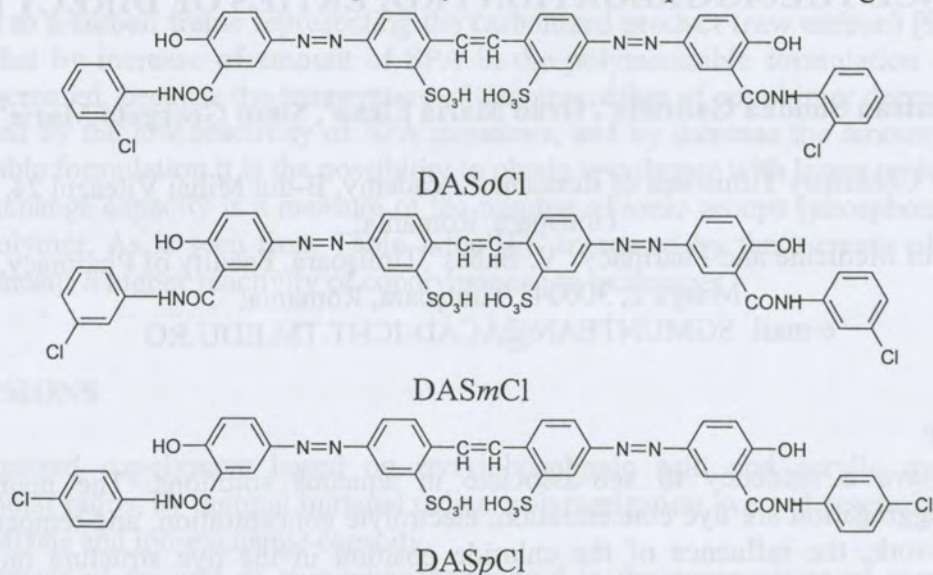


Figure 1. Molecular structure of the investigated dyes

The obtained UV-visible absorption spectra's in aqueous solution are graphed together in Figure 2, plotted as $\epsilon = A/C \cdot l$.

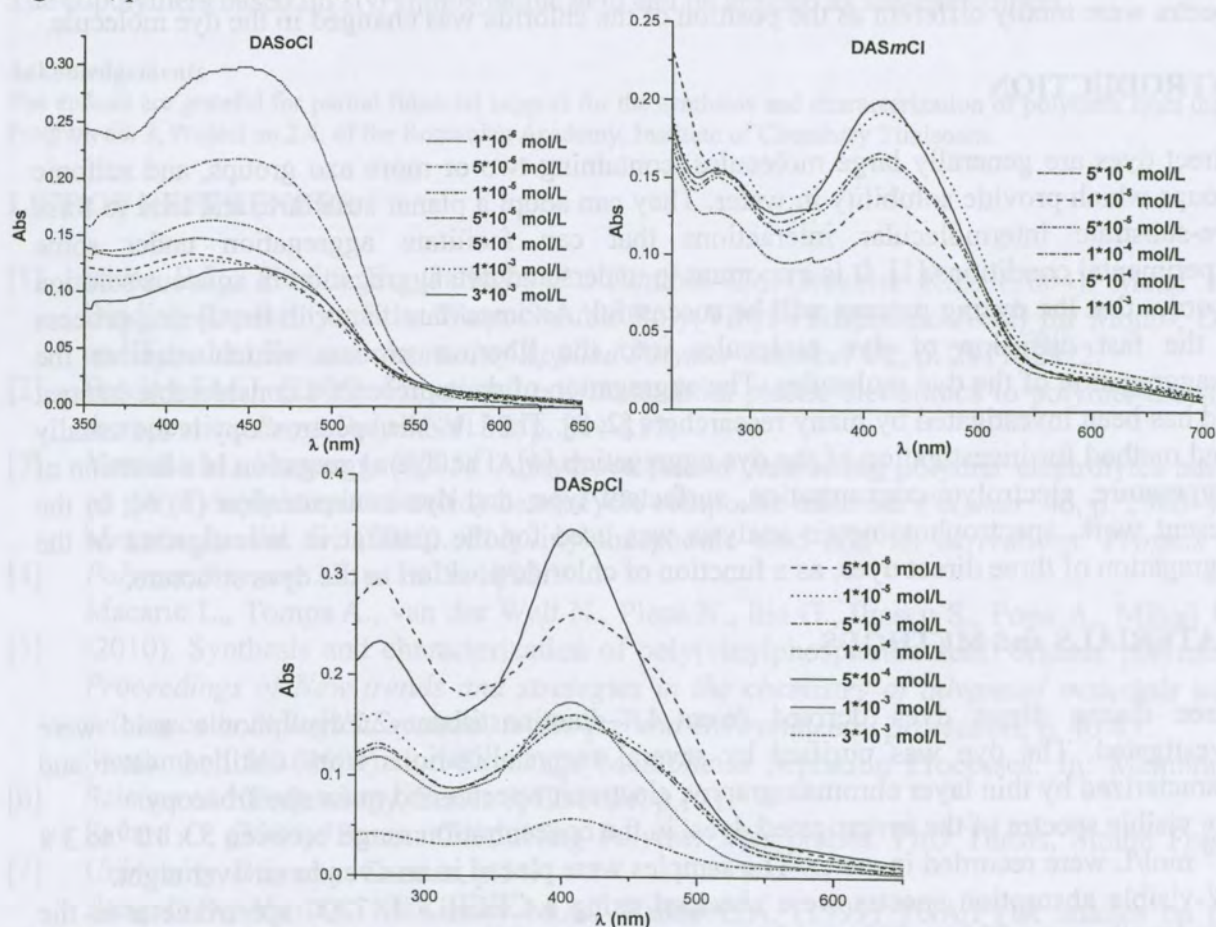


Figure 2. The absorption spectra of DASoCl, DASmCl, and DASpCl dye, at different concentrations

As can be seen in Figure 2, as the dye concentration increases, the maximum absorption wavelength shifted but the shape and the manners are very different. In case of DASoCl the maximum extinction coefficient decrease as the concentration increased.

For the DASoCl dye the extinction coefficient decreased, and the maximum absorption wavelength of the principal peak shifts to lower wavelength till the concentration 5×10^{-4} mol/L and, at higher concentrations shifts to higher wavelength signifying that the molecules are beginning to aggregate.

In case of DASmCl dye the extinction coefficient increase with increasing the dye concentration, although the maximum absorption wavelengths of the principal peak wavelength remain stable.

As can be seen in Figure 2, for DASpCl dye, in concentration range $5 \times 10^{-6} \div 1 \times 10^{-4}$ mol/L and $5 \times 10^{-4} \div 3 \times 10^{-3}$ mol/L, as the concentration increases, the extinction coefficient at 409.6 nm decreased. Between concentrations $1 \times 10^{-4} \div 5 \times 10^{-4}$ mol/L a major change was observed, when the shape of the spectra was changed, and an increase of the molar absorption coefficient was observed.

For accuracy, the absorption coefficient at 416.8 nm was plotted as a function of concentration (Figure 3).

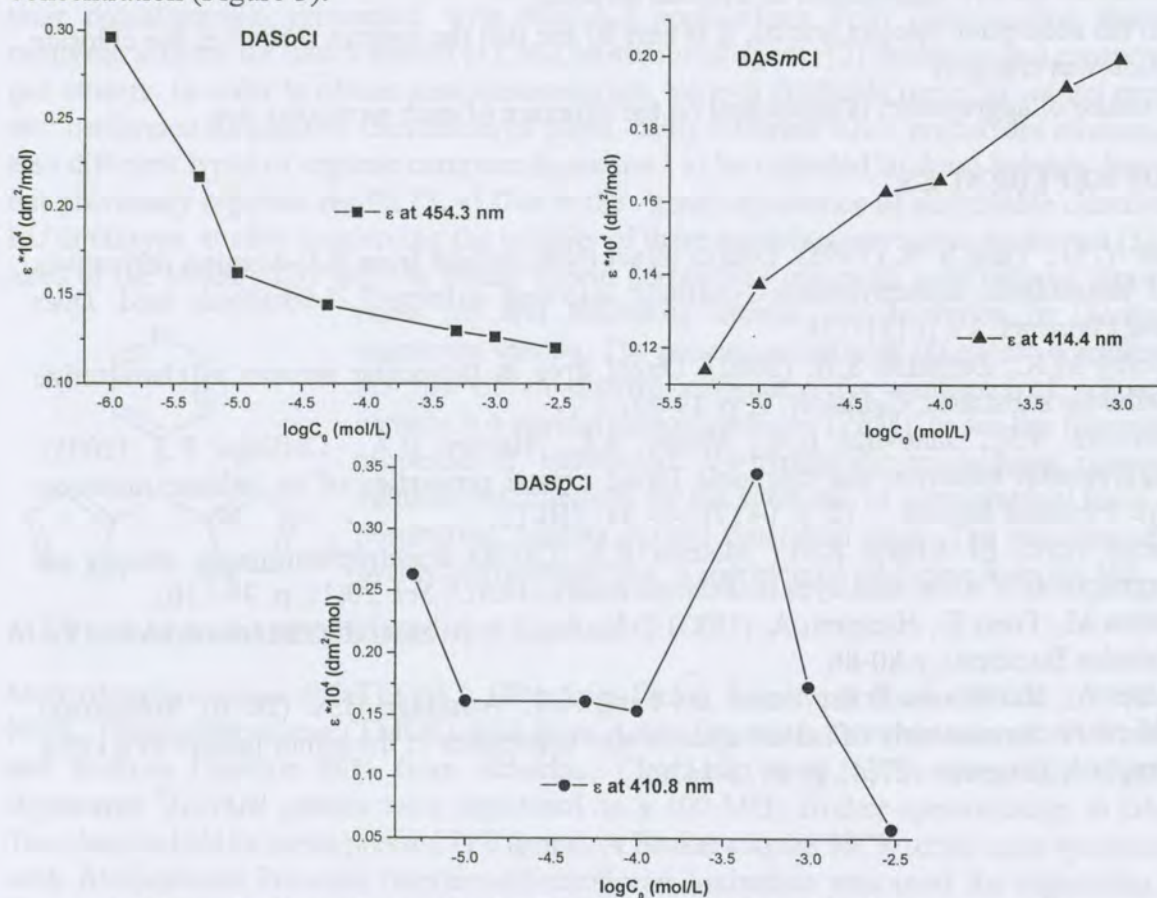


Figure 3. Dependence of ϵ (at fixed wavelength) on the dye concentration

From these graphs it is obvious that the absorption coefficient changes even at low concentration, signifying that molecules are beginning to aggregate, but the manner of changes is very different from dye to dye.

By graphing the wavelength vs. concentration, for DASoCl dye a clear trend in the changes is noticed (Figure 4).

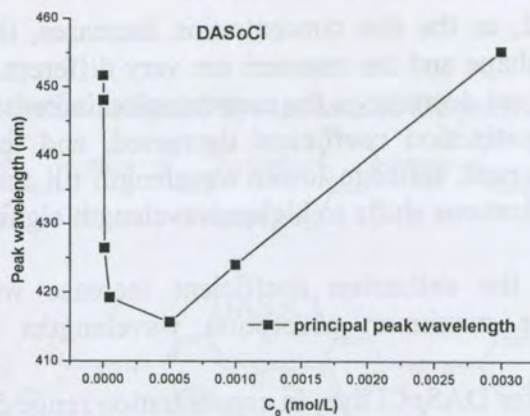


Figure 4. Change in peak wavelength at different concentrations

CONCLUSIONS

- UV-Vis spectroscopy was used to study the effect of chloride position from the dye structure on the dye aggregation in aqueous solution.
- From the absorption spectra graphs, it is easy to see that the spectra shifted as the chloride position was changed.
- The nature of aggregation is dependent on the structure of each particular dye.

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