AGGREGATION OF TWO DIRECT DYE DERIVED FROM 4,4'-DIAMINOSTILBENE-2,2'-DISULPHONIC ACID. SPECTROSCOPIC AND MATHEMATICAL STUDIES

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ABSTRACT
Dyes ions have a tendency to self-associate in aqueous solutions. Since almost all textile dyes are applied from aqueous systems, it is important to understand the association of dyes in water, and to determine the number of chemical species presented in the system. The aggregation of the dyes in aqueous solution is influenced by: the dye concentration, electrolyte concentration, and temperature. In the present work, the qualitative and quantitative analysis of the aggregation of two disazo direct dyes (*DSA*, and *DAS*) is presented. The molecular aggregation of studied dye has been studied spectrophotometrically in aqueous solutions as a function of dye concentration ($10^{-6} \div 10^{-3}$ M). In case of *DSA* dye, in concentration range $1 \cdot 10^{-6} \div 1 \cdot 10^{-5}$ M and $5 \cdot 10^{-5} \div 1 \cdot 10^{-3}$ M, as the concentration increases, the extinction coefficient at 416.5 nm decreased. Between concentrations $1 \cdot 10^{-5} \div 5 \cdot 10^{-5}$ M an increase of extinction coefficient was observed, and the shape of the spectra changed; all this shifts indicate that the molecules are beginning to aggregate. In case of *DAS* dye, a change in the absorption spectra shape was observed at concentrations bigger than $5 \cdot 10^{-5}$ M. From the mathematical obtained data the number of species presented in the system, in domain of concentrations investigated, was determined. The mathematical calculations confirm the experimental data regarding the aggregation of the *DSA*, and *DAN* dyes. From the matriceal analysis, the number of chemical species presented in the system (in domain of concentrations studied) was determined to be three in case of *DSA* dye, respectively four in case of *DAN* dye.

Keywords: direct dye, aggregation, matriceal analysis

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. According to literature data, the 4,4'-diaminostilbene 2,2'-disulphonic acid is considered to be a suitable middle component in the synthesis of direct dyes [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]. In the present work, spectrophotometric analysis was used for the qualitative investigation of the aggregation of two direct dye, as a function of dye concentration. For the quantitative characterization of the aggregates, the matriceal analysis was used.

RESULTS

The chemical structure of the dye molecule used in this study 4,4'-diaminostilbene-2,2'-disulphonic acid $\rightleftharpoons$ salicilamide (*DSA*), and 4,4'-diaminostilbene-2,2'-disulphonic acid $\rightleftharpoons$ naphthionic acid (*DAN*) are presented in Figure 1. The synthesis and characterization of the dyes were presented in a previously paper [6].
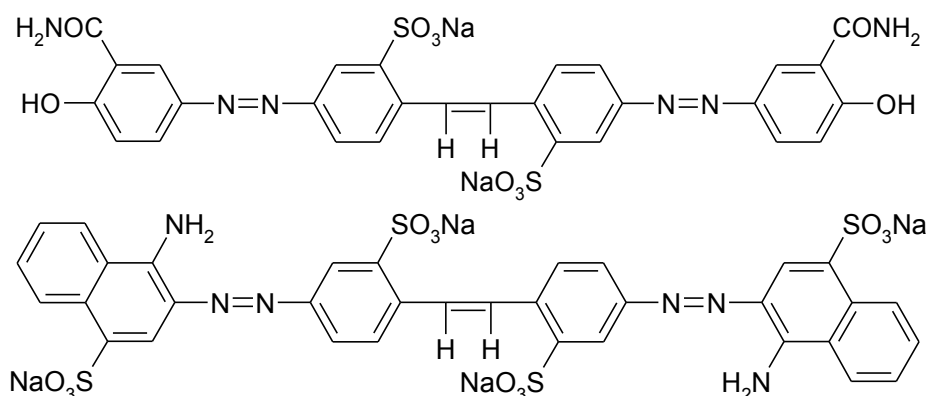

Fig. 1. Molecular structure of the studied direct dye *DSA*, and *DAN*

UV-visible absorption spectra of direct dyes (*DSA, DAN*) in aqueous solution were recorded across a range of different initial concentrations varying between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-3}$ M. Using seven 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 results are graphed together in Figure 2, plotted as $\varepsilon = A/C \cdot l$.
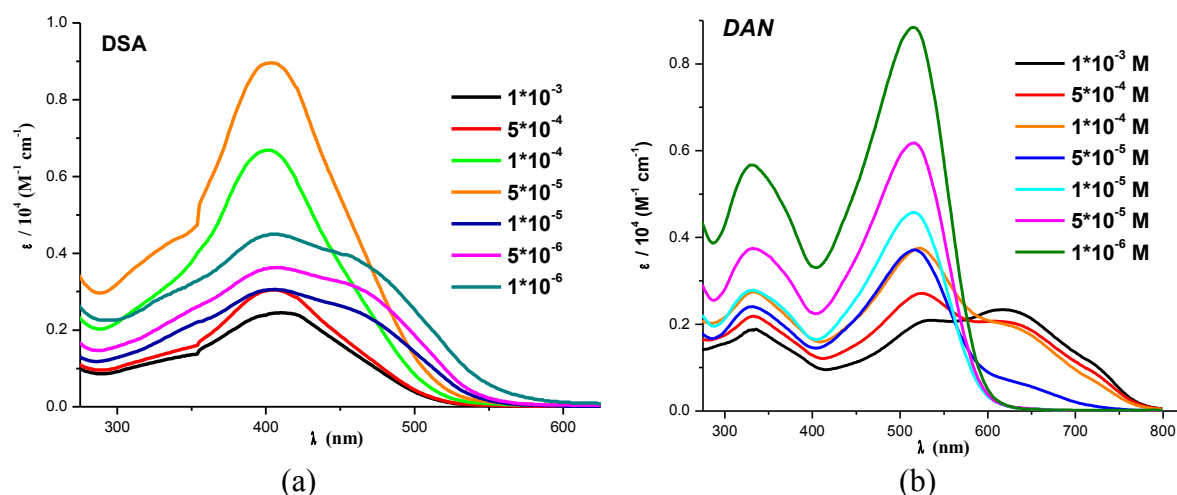
Figure 2. Direct dyes (a) *DSA* and (b) *DAN* absorption spectra at different concentrations

As can be seen in Figure 2a, in concentration range $1 \cdot 10^{-6} \div 1 \cdot 10^{-5}$ M and $5 \cdot 10^{-5} \div 1 \cdot 10^{-3}$ M, as the concentration increases, the extinction coefficient at 416.5 nm decreased. Between concentrations $1 \cdot 10^{-5} \div 5 \cdot 10^{-5}$ M an increase of extinction coefficient was observed, and the shape of the spectra was changed; all this shifts indicate that the molecules are beginning to aggregate. In case of direct dye *DAN* by increasing the concentration from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M the maximum extinction coefficient at 520 nm decreased (Figure 2b). A drastic change in the absorption spectra shape was observed at concentrations bigger than $5 \cdot 10^{-5}$, the maximum absorption wavelength at 520 nm shifted to higher wavelength 619.8 nm. All this shifts indicate that the molecules are beginning to aggregate. For accuracy, the absorption coefficients were plotted as a function of concentration (Figure 3).
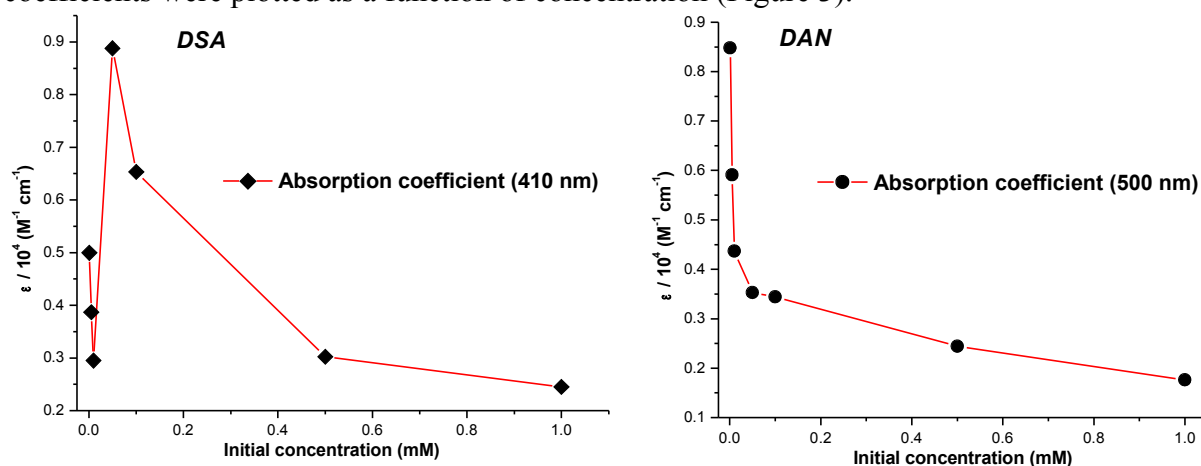

Figure 3. The trend in *DSA*'s, and *DAS*'s absorption coefficient at different concentrations

The graphs confirms the results presented in Figure 2.
The qualitative analysis implies the determination of the number of chemical species (aggregation number) presented in the system. For this reason we applied a mathematical method described by Brigleb [8] and used in the field of charge transfer intermolecular complex compounds. Mathematical analysis was done with the MATHCAD 2000 program and implied determination of the eigenvalues of the absorbance matrix. Using the experimental absorbance values, an n x m (n: values of absorption at different wavelengths, m: concentrations) dimension matrix was build. In order to determine the rank of this matrix [9], it was multiplied to left with its transpose matrix, resulting a symmetric square matrix of dimension n x n. According to theoretical considerations, of linear algebra, the number of

eigenvalues, of this obtained matrix (Table 1), different from zero (within accepted experimental errors) is equal to the chemical species (monomer, dimer, etc.) present in the system.

Table 1. The eigenvalues value of theabsorption matrix for *DSA*, and *DAN* dyes

Eigenvalues value	
DSA	*DAN*
163.642	**116.417**
3.289	**8.339**
0.087	**0.025**
1.00e-3	**2.584e-3**
1.566e-4	3.783e-4
1.399e-13	1.938e-4
3.985e-14	2.371e-5
-3.084e-15	-3.983e-15

Taken into account that the absorbance values are significant at most of the third decimal, the eigenvalues less than 0.002 may be considered zero. The obtained data considering also the experimental errors, strongly suggest the presence of at least three − monomer, dimmer, and trimmer respectively in case of *DSA* dye, and four in case of *DAN* dye (monomer, dimmer, trimmer, and tetramer).

MATERIALS and METHODS

Two symmetric disazo stilbene dyes derived from 4,4'-diaminostilbene-2.2'disulphonic acid were investigated. The dyes were purified by several recrystallizations from distilled water and characterized by thin layer chromatography, electronic spectra and mass spectroscopy.
The visible spectra of dyes in water, in the concentration range $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M (7 concentrations) were recorded. 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 ºC.
The spectroscopic dates for investigated dyes were stored in spectral files as matrices of size *n* (values of molar absorption coefficient at different wavelength) and *m* (concentrations), and then processed by using MATHCAD 2000 packages.

CONCLUSIONS

- UV-Vis spectroscopy has been used to study the aggregation of direct dyes DSA and DAN in aqueous solution.
- From the absorption spectra graphs, it is easy to see that spectra for studied direct dye shifted as the concentration changed, which is to be expected from aggregating dyes.
- The mathematical calculation confirms the experimental data regarding the aggregation of the DSA and DAN dyes.
- Using the matriceal analysis the number of chemical species presented in the system, in the range of concentration studied, was determined.

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