

INFLUENCE OF THE AROMATIC SUBSTITUENTE ON THE AGGREGATION PROPERTIES OF DIRECT DYES DERIVED FROM 4,4'-DIAMINOSTILBENE-2,2'-DISULPHONIC

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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 main factors influencing aggregation are dye concentration, electrolyte concentration, and temperature. In the present work, the influence of the coupling component structure on the dye aggregation is presented. 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 coupling component structure was changed in the dye molecule. From the matriceal analysis, the number of chemical species presented in the system (in domain of concentrations studied) was determined. The mathematical calculations confirm the experimental data regarding the aggregation of the investigated dyes.

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 a direct dye, as a function of dye concentration. For the quantitative characterization of the aggregates, the matriceal analysis was used.

RESULTS

The chemical structures of the investigated dyes molecule are presented in Figure 1. These dyes are synthesised and characterized in our laboratory, and are homologues of benzidinic direct dyes.

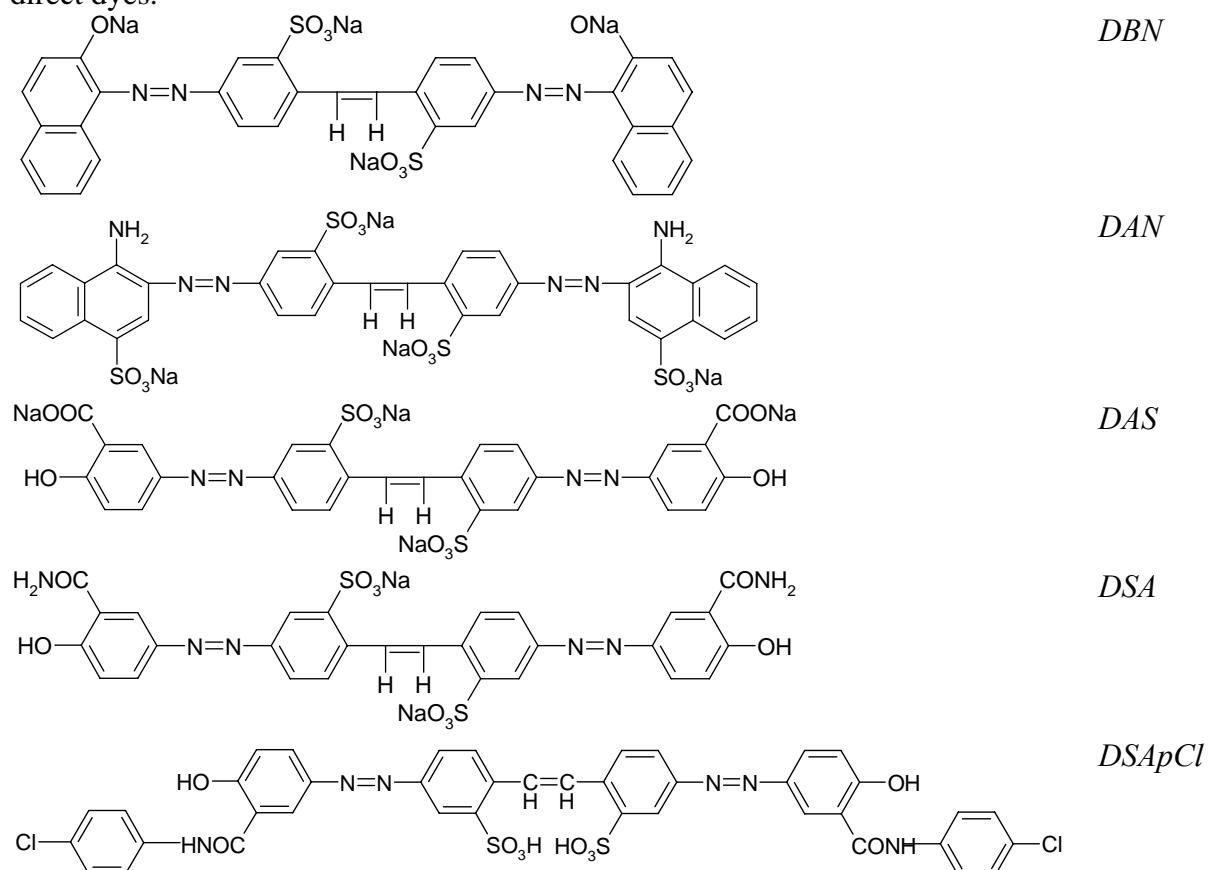
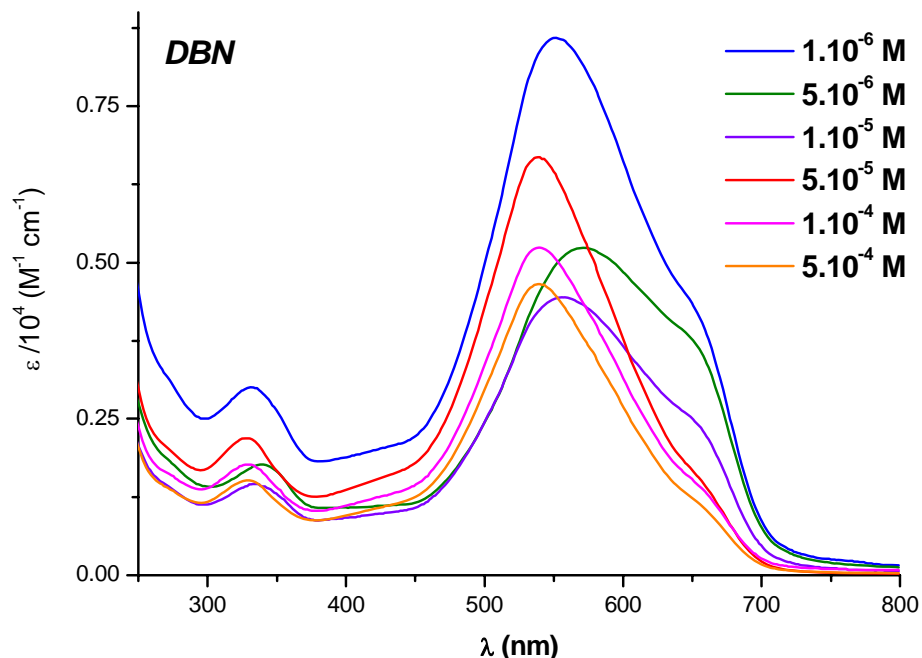


Fig. 1. Molecular structures of the investigated direct dyes

Using different initial concentrations, varying between $1 \cdot 10^{-6}$ and $3 \cdot 10^{-3}$ M, the samples were analyzed using a CECIL CE UV-Vis spectrometer, in order to obtain the absorption spectra

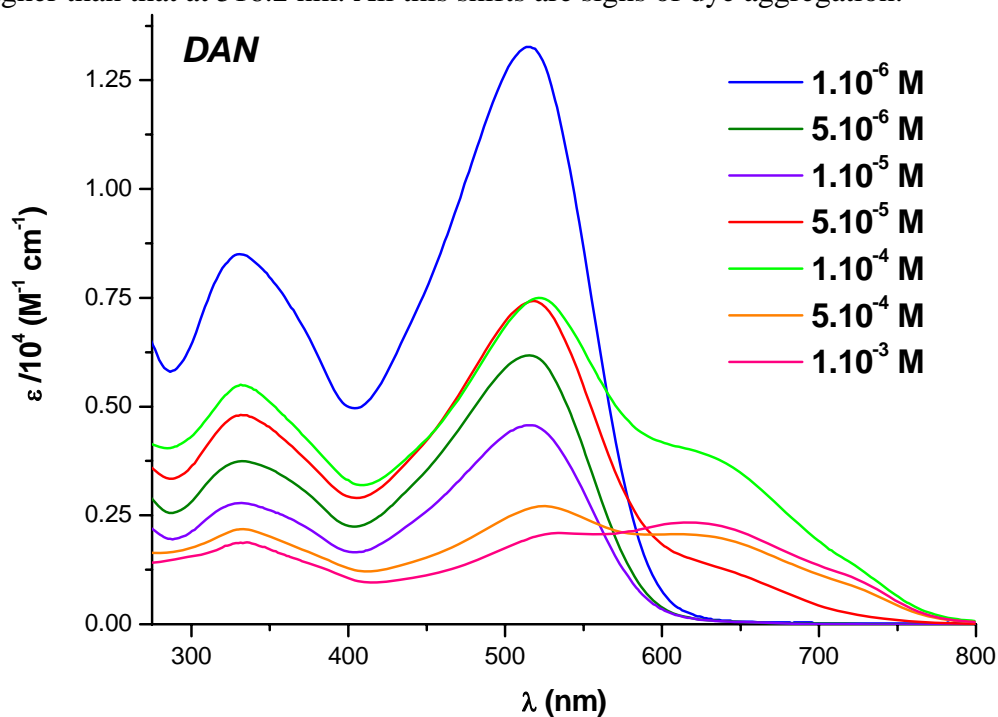
and to study the trends in these spectra. The obtained results are graphed together plotted as $\epsilon = A/C \cdot l$.

In case of *DBN* dye as the dye concentration increases, the maximum absorption wavelength at 570.8 nm shifted to lower wavelength 538.6 nm. Between concentrations $1 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ M, and also in the range of concentrations $5 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$ M with increasing the concentration a decrease of the extinction coefficient was observed.

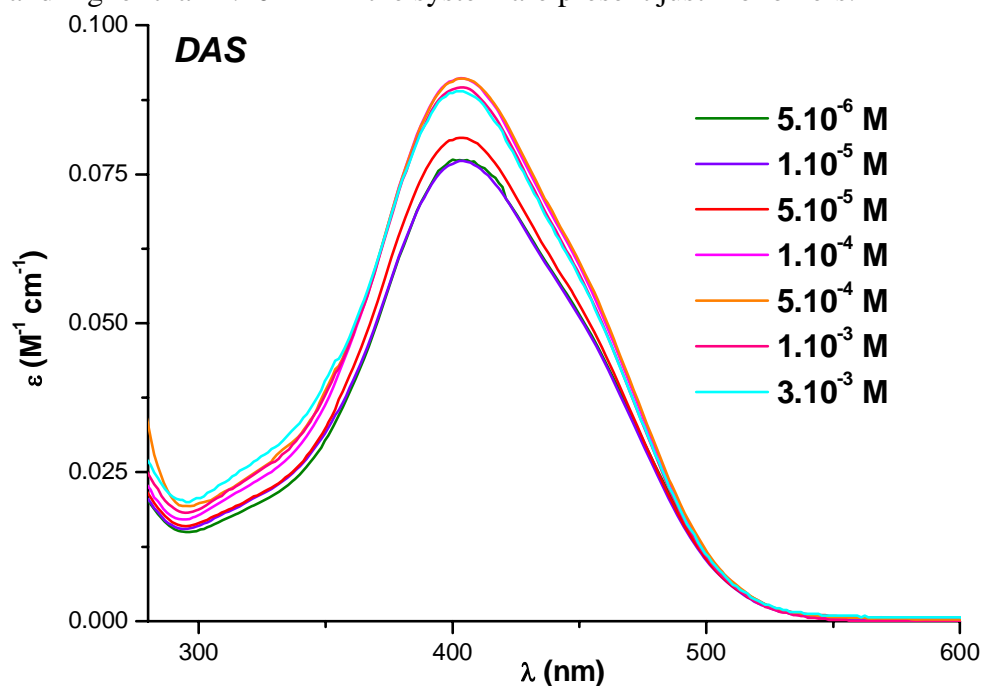


Between concentrations $1 \cdot 10^{-5} \div 5 \cdot 10^{-5}$ M the extinction coefficient increased with increasing the concentration and also the shape of the spectra is changed. All this shifts indicate that the molecules are beginning to aggregate.

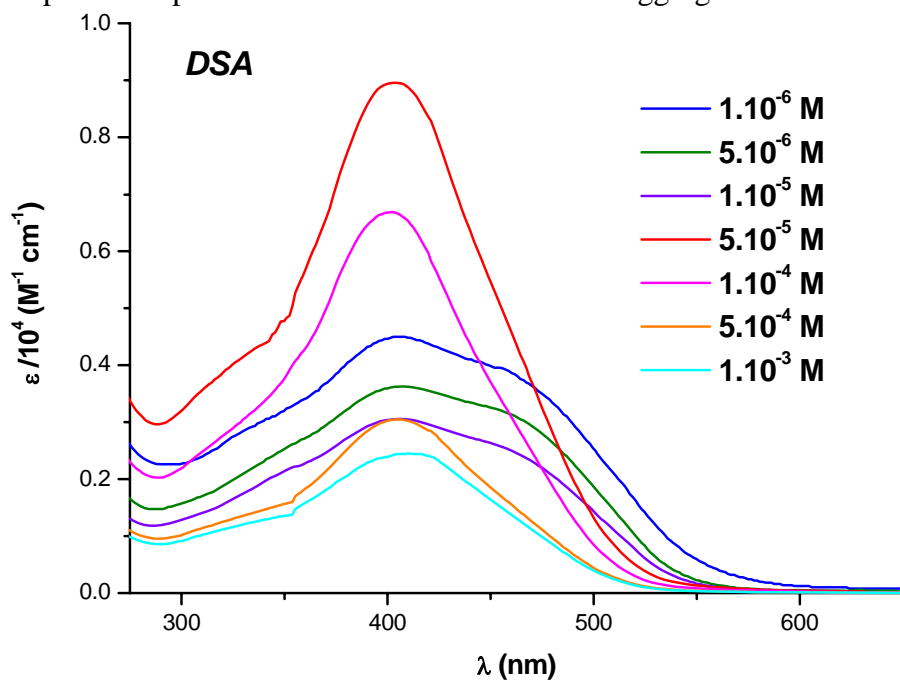
As the concentration increases, in case of *DAN* dye, the extinction coefficient at 516.2 nm decreases. Started from concentration $5 \cdot 10^{-5}$ M a second peak begins to form off the main one at wavelength 619.8 nm. At higher concentration ($1 \cdot 10^{-3}$ M) the extinction coefficient at 619.8 nm is higher than that at 516.2 nm. All this shifts are signs of dye aggregation.



An increase of DAN dye concentration, determined a just a very small change (an increase of extinction coefficient) in the spectra, and only between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ M, indicating that only in this range coexist different of species in the system. At concentrations smaller than $1 \cdot 10^{-5}$ M and higher than $1 \cdot 10^{-4}$ M in the system are present just monomers.

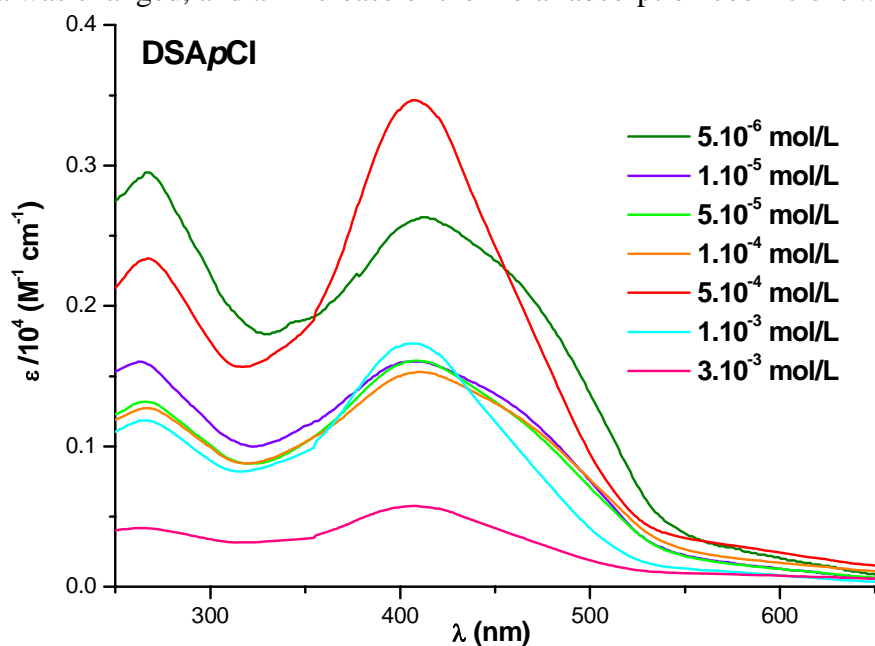


As can be seen in the next figure, for *DSA* dye in concentration range $1 \cdot 10^{-6} \div 1 \cdot 10^{-5}$ mol/L as the concentration increases, the extinction coefficient at 416.5 nm decreased. The same changes are observed in the concentration range $5 \cdot 10^{-5} \div 1 \cdot 10^{-3}$ mol/L, but the spectra's shape is different. Between concentrations $1 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ mol/L an increase of extinction coefficient was observed with increasing the concentration, and in this range started the change in the spectra shape indicated that the molecules are aggregated.



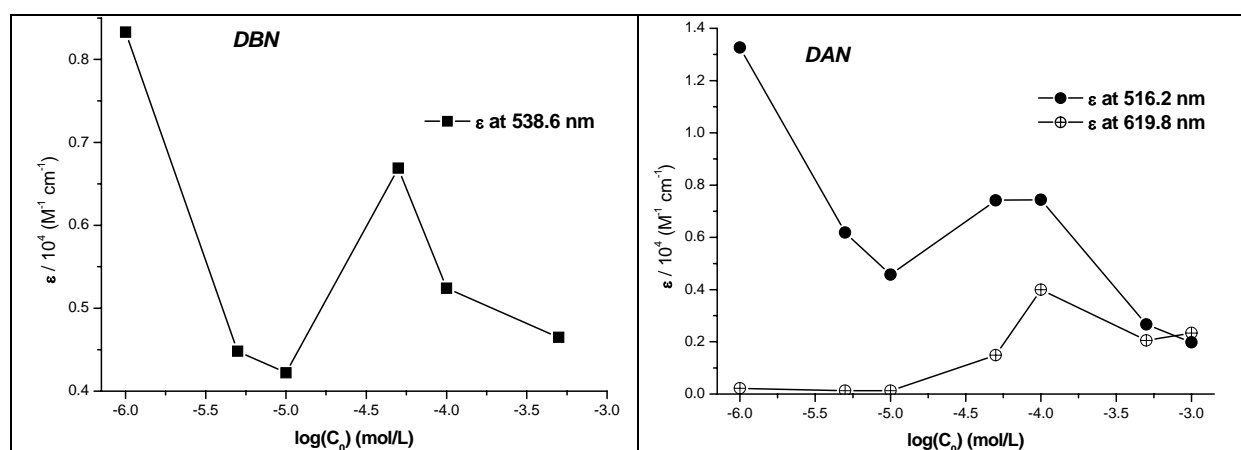
For *DASpCl* dye, between concentration $5 \cdot 10^{-6}$ and $1 \cdot 10^{-4}$ mol/L and also between $5 \cdot 10^{-4}$ and $3 \cdot 10^{-3}$ mol/L, as concentration increases the extinction coefficient at 409.6 nm decreased.

Between concentrations 1.10^{-4} and 5.10^{-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.



From the obtained graphs, it is easy to see that the shapes of the obtained spectra were totally different as the coupling component structure was changed in the dye molecule. Just a little change in the coupling component structure, salicylamide for DSA dye instead of salicylic acid, for DAS dye, determine a major change in the absorption spectra. Comparing the obtained data for DSA dye and DSApCl dye it is obvious that even the shape change tendency is similar, the absorption values are different.

For accuracy, the absorption coefficient at maximum wavelengths was plotted as a function of dye concentration (Figure 2).



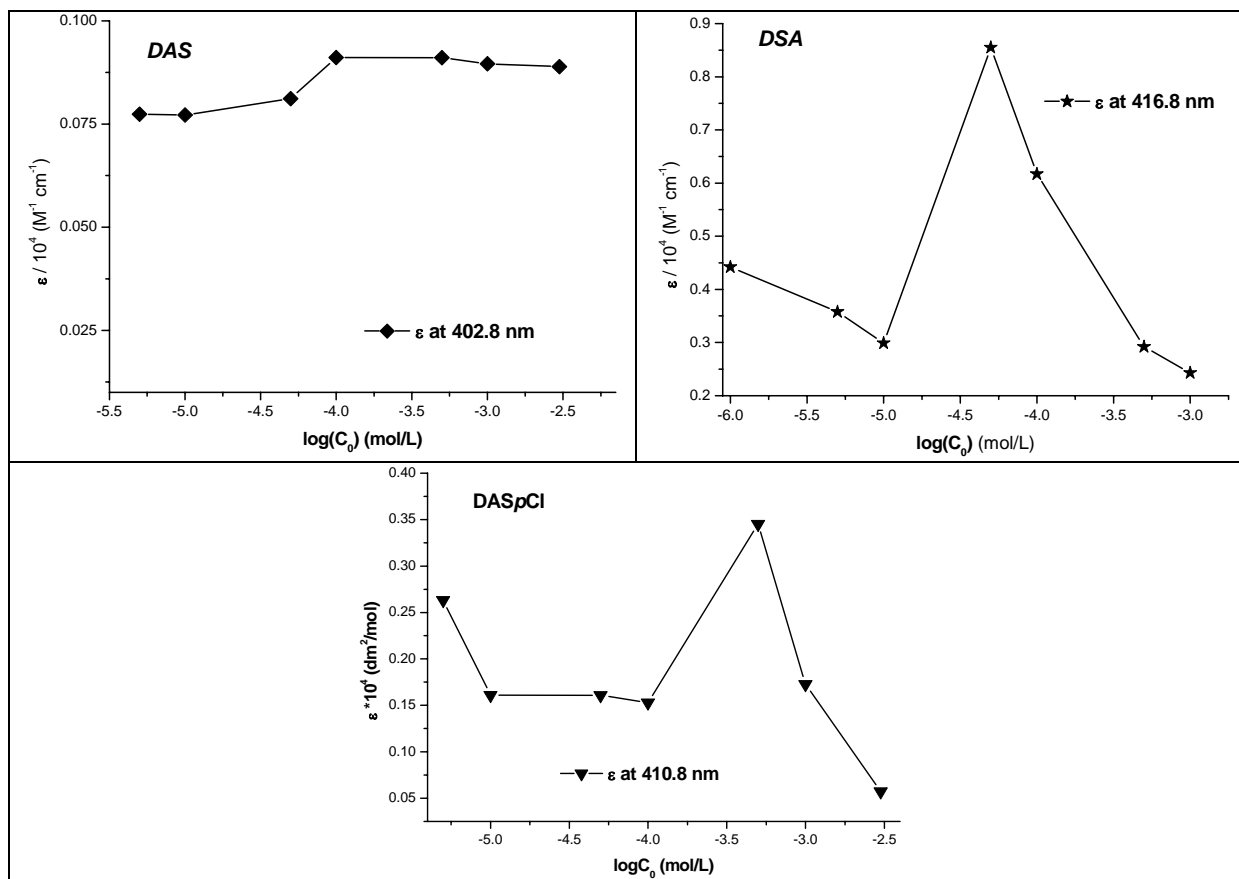


Figure 2. The trend in investigated dye's absorption coefficient at different concentrations

From these graphs it is obvious that the absorption coefficient changes (exception in case of DAS dye) even at low concentration, signifying that molecules are beginning to aggregate.

The spectroscopic analysis gave us just qualitative information about the dye aggregation. The quantitative 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 [6] 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 $n \times m$ (n : values of absorption at different wavelengths, m : concentrations) dimension matrix was build. In order to determine the rank of this matrix [7], it was multiplied to left with its transpose matrix, resulting a symmetric square matrix of dimension $n \times n$. 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 the absorption matrix for investigated dye

Eigenvalues value				
DBN	DAN	DAS	DSA	DSApCl
2.054.10-15	4.752.10-14	1.549.10-15	5.076.10-13	1.529.10-15
9.625.10-14	6.047.10-5	5.494.10-6	1.083.10-3	4.051.10-14
2.671.10-5	3.317.10-4	2.245.10-5	0.022	3.688.10-4
1.927.10-4	8.991.10-4	4.292.10-5	0.054	5.748.10-3
1.391.10-3	3.801.10-3	2.676.10-4	0.169	0.091
4.639.10-3	0.025	1.173.10-3	0.419	0.175

3.115	7.428	2.852.10⁻³	5.149	1.676
160.801	157.173	3.012	301.304	66.509

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 n-mers in the range of concentration investigated, for DBN (trimmers), DAN (tetramers), DAS (dimers), DSA (sexamers), and DSAPCl (pentamers) dyes.

MATERIALS and METHODS

Five symmetrical 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 samples (aqueous dye solutions with different concentrations, between $1 \cdot 10^{-6}$ and $3 \cdot 10^{-3}$ M) 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 5, 1, 0.5, 0.2, 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.

The spectroscopic dates for all 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 for a quantitative study of the direct dyes aggregation in aqueous solution.
- From the absorption spectra graphs, it is easy to see that spectra 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 investigated 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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