Experimental and Mathematical Study of the Aggregation of a Green Trisazo Direct Dye

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*Dye ions have a tendency to self-associate in aqueous solutions. The main macroscopic factors influencing the aggregation are: dye concentration, electrolyte concentration, and temperature. In the present work, the aggregation characteristics of a trisazo direct dye (**VD**) have been investigated by spectrophotometric and mathematical analysis. The molecular aggregation of **VD** dye has been studied in aqueous solutions as a function of dye concentration ($1.077 \cdot 10^{-3} \div 8.975 \cdot 10^{-6}$ M) and solution pH (4 ÷ 10). As the concentration increases, the spectra flattening out as well as a second peak begins to form off the main one signifying that the molecules are beginning to aggregate. The variation of the solution pH, determines a change of the spectral maximum, which confirms the aggregation of the studied dye. The mathematical processing of the data confirms the presence of three species in the studied range of concentration.*

Keywords: trisazo dye; dye aggregation; absorption matrix

Adsorption of dyes on solid adsorbents is influenced by the physicochemical properties of the dyes solutions. The ionic dyes have a tendency to aggregate in diluted solutions leading to dimer or higher order aggregates [1]. The possible causes for this tendency are the different types of interactions, such as van der Waals forces, $\pi-\pi$ interactions, hydrogen bonding, and hydrophobic effects [2]. Since almost all textile dyes are applied from aqueous systems it is important to understand the association of dyes in water for both thermodynamic and kinetic studies [3]. At the molecular level the aggregation tendency increases as the molecular weight and the length of the aromatic structure of the dye increases. At the macroscopic level aggregation is promoted by rise in dye concentration and the presence of added electrolytes, e.g. sodium chloride, sodium sulfate. It is reduced by the presence of organic solvents, e.g. ethanol, and by the increasing in temperature [4]. Several techniques have been developed to measure the degree of aggregation of water soluble dyes in aqueous solution: polarography, osmometry, ^{19}F-NMR, spectroscopy, optical techniques and other [5-9].

Direct dyes are generally large molecules, containing two or more azo groups, and several sulfonic groups which provide solubility in water. In the present work, the aggregation characteristics of a trisazo direct dye (**VD**) - a homologue of the benzidinic C. I. Direct Green 8, have been investigated by spectrophotometric analysis and mathematical analysis.

Materials and methods

The synthesis of the **VD** dye involves three steps: the direct bis-diazotisation of 4,4'-diamino-benzanilide; and two subsequent coupling reactions of the resultant bis-diazonium salt - the first with salicylic acid and, the second with a monoazo compound prepared by the coupling reaction of the diazonium salt of *p*-nitroaniline with 1-amino-8-hydroxy-3,6-naphtalin-disulfonic acid (H acid). Direct Green (**VD**) dye was purified by repeated recrystallization from distilled water and characterized by thin layer chromatography, electronic spectra and mass spectroscopy [10].

Aqueous **VD** dye solutions were prepared by dissolving the studied dye in distilled water, using a magnetic stirrer. The visible spectra of **VD** in water, in the concentration range $1.077 \cdot 10^{-3}$ to $8.975 \cdot 10^{-6}$ M (11 concentrations) were recorded. In order to obtain the desired pH value (3.89 ÷ 9.45) the dye solutions ($3.787 \cdot 10^{-5}$ M) were prepared by adding either sodium hydroxide or acetic acid (0.02 M), using a magnetic stirrer. 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 300 to 800 nm. Quartz cuvette of pathlengths 1, 0.5 cm, and 0.1 cm were used in order to obtain absorbance values not exceeding 2. All measurements were carried out at 27 ± 2°C.

Results and discussions

The chemical structure of the dye molecule used in this study, salicylic acid ←4,4'-diaminobenzanilide→1-amino-8-hydroxy-3,6-naphtalindisulfonic acid ←*p*-nitroaniline (**VD**) a trisazo direct dye is presented in figure 1.

The molecular aggregation of **VD** dye has been studied in aqueous solutions as a function of dye concentration and solution *p*H.

Using the 9 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. Dramatic changes take place in the absorption spectra beginning with the dye concentration

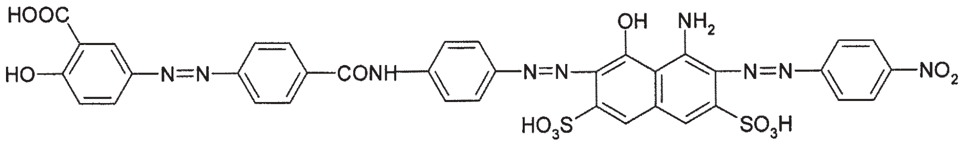

Fig. 1. Molecular structure of the direct green dye VD

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$7.5 \cdot 10^{-4}$ M. These are obvious signs of the aggregation suffered by the **VD** dye (fig. 2).

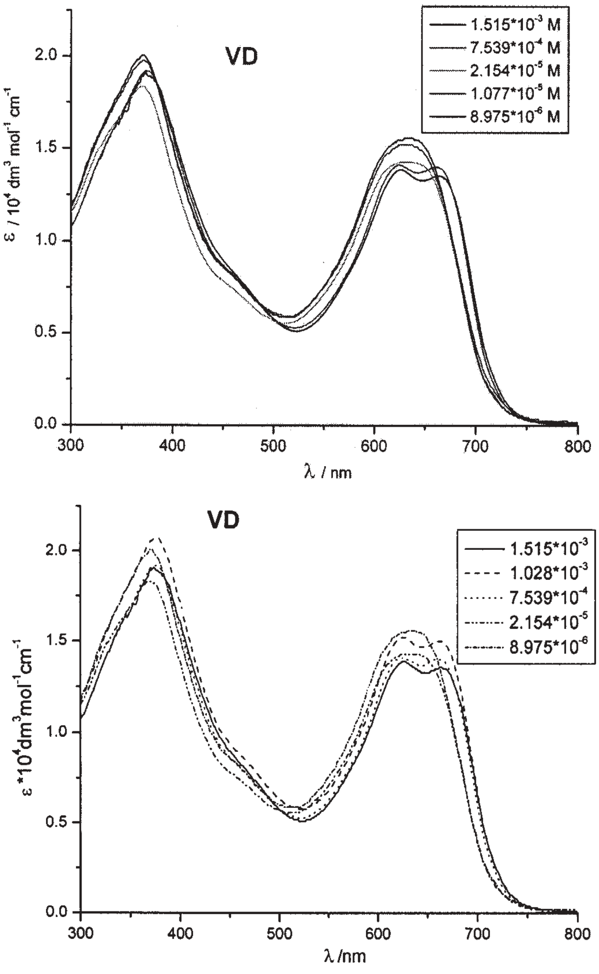

Fig. 2. Direct VD dye absorption spectra at different concentrations

As the concentration increases, the maximum absorption wavelength at 633.8 nm is shifted to lower wavelength 625.4 nm, the extinction coefficient at this wavelength decreased, as well as a second peak begins to form off the main one. All these phenomena indicate that the molecules are beginning to aggregate. The isobestic point at 490 nm indicates the existence of an equilibrium between the two species, monomer and dimer form, of the dye. The spectrum corresponding to $2.154 \cdot 10^{-5}$ M dye concentration doesn't fit the isosbestic point, indicating the appearance of a new species - probably a trimer.

For accuracy, the absorption coefficient at 625 nm was plotted as a function of concentration (fig. 3).

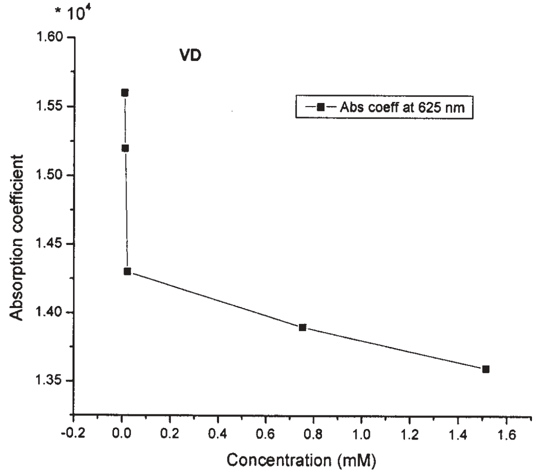

Fig. 3. The trend in VD's absorption coefficient at different concentrations

Initially the graph possesses a very steep slope which shows the major change in the absorption coefficient. From this graph it is obvious that the absorption coefficient changes even at low concentration, signifying that molecules are beginning to aggregate.

By graphing the maximum absorption wavelength vs. the concentration, a clear trend in the changes is also noticed (fig. 4).

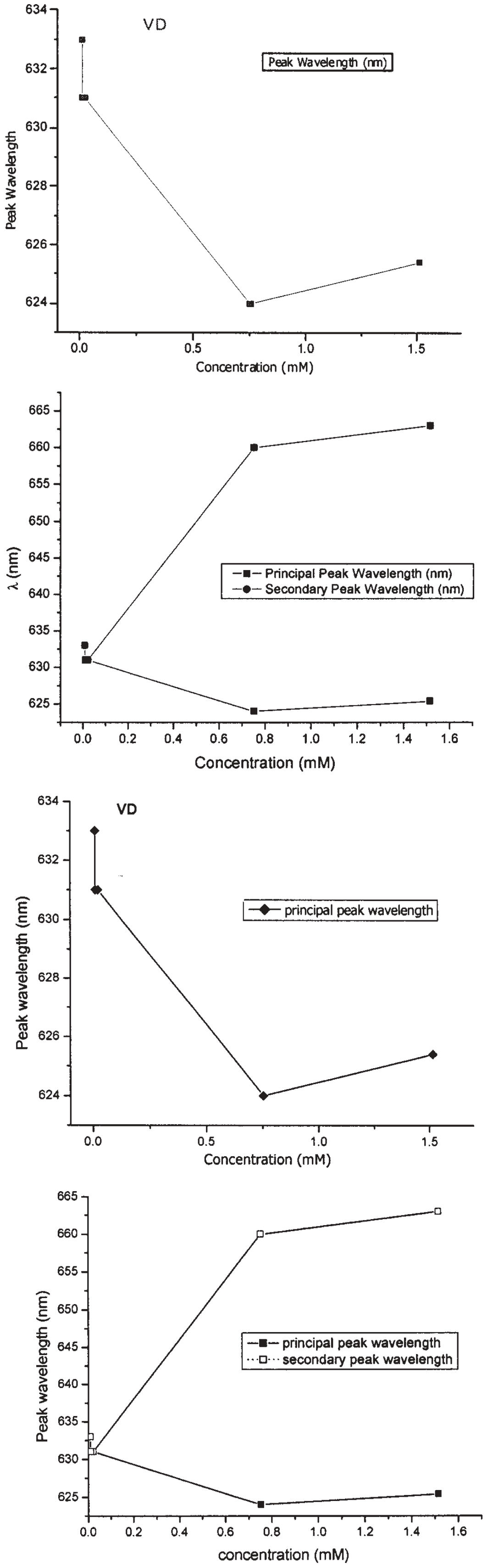

Fig. 4. Change in peak wavelength at different concentrations

The analysis was extended to solutions with various pH values. Adding to solutions of 3.787 · 10^{-5} M, either NaOH or acetic acid (0.02M) in proper amounts, we obtained the desired *p*H value, between 10 and 4. As the pH increases, in acid medium (*p*H 3 ÷ 7) (fig. 5) the maximum from 366 nm undergoes a hyperchromic and bathocromic shift. The maximum at 627 nm undergoes a hyperchromic shift while the secondary peak from 673 nm dissapears. These are also signs of the dye aggregation.

In the basic medium (*p*H 7÷10) there are no major changes of the spectral maximum (fig. 6).

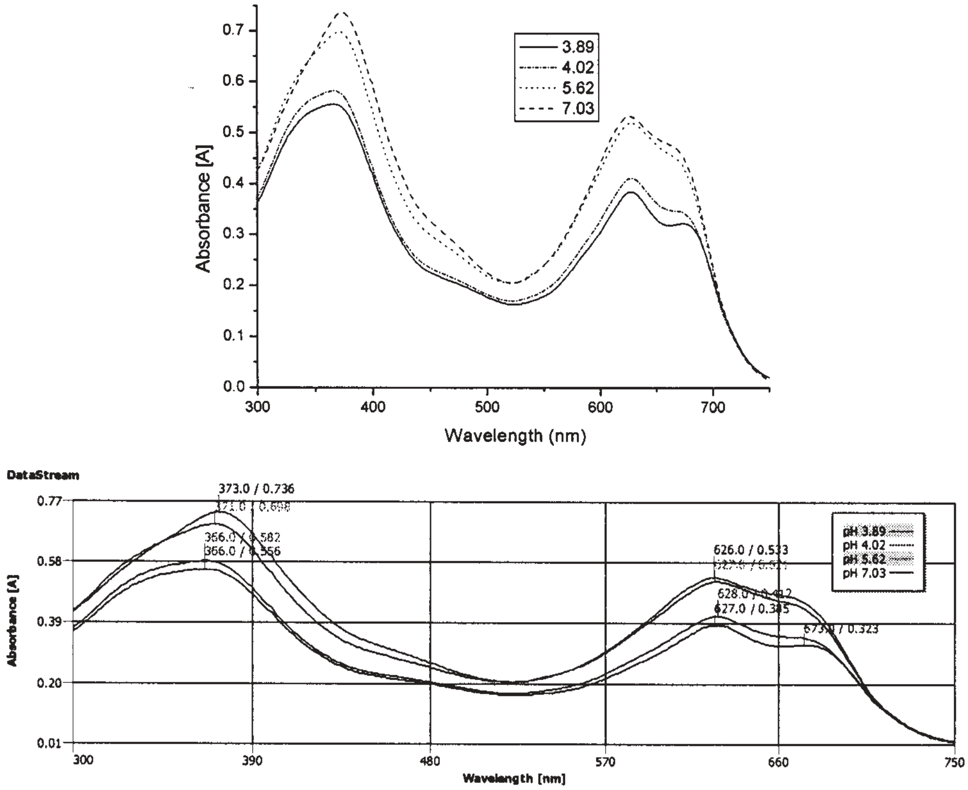

Fig. 5. Absorbance spectra of VD dye in acid medium

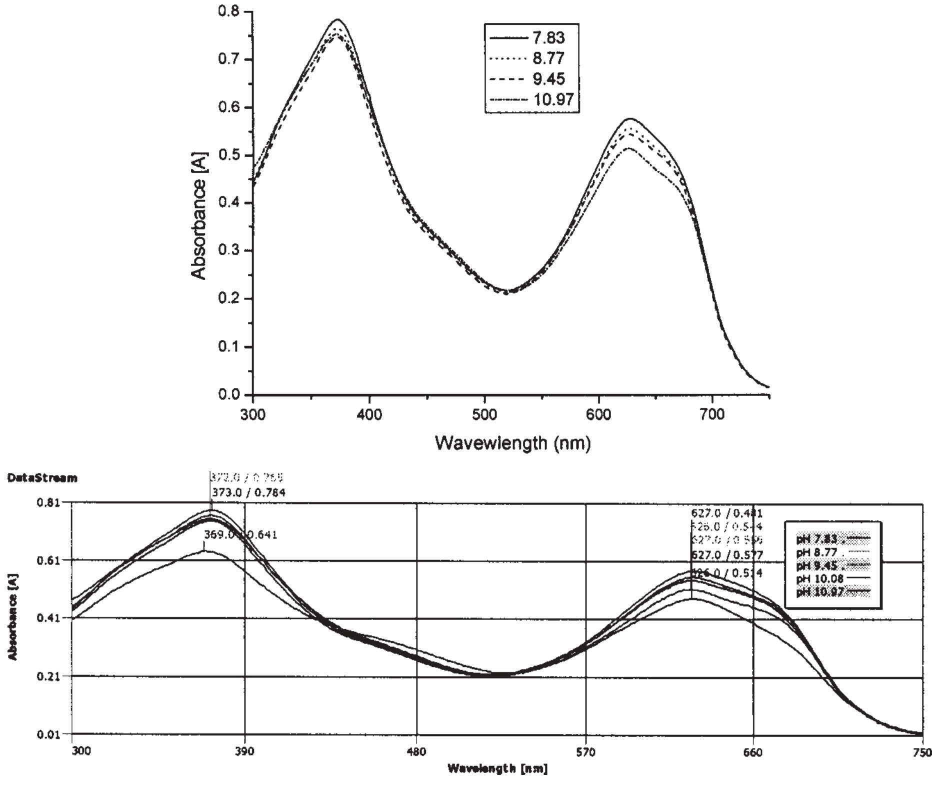

Fig. 6. Absorbance spectra of VD dye in basic medium

Using the experimental absorbance values, an n x m (n: values of absorption at different wavelengths, m: concentrations) dimension matrix was build. The rank of this matrix is equal to the chemical species existing in system, in the concentration domain considered. In order to determine the rank of this matrix [11, 12], it was multiplied to left with its transpose matrix, resulting a symmetric square matrix of dimension n x n (table 1.).

Table 1
THE EIGENVALUES VALUE OF THE ABSORPTION MATRIX

The eigenvalues value function of Absorption
5.429e-15
1.019e-13
-3.518e-13
1.023e-12
9.210e-5
1.950e-3
0.018
0.348
780.913

According to theoretical considerations, of linear algebra, the number of eigenvalues of this matrix different from zero (within accepted experimental errors) is equal to the chemical species (monomer, dimer, etc.) present in the system. Taken into account that the absorbance values are significant at most to 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 species, probably monomer, dimer and trimer. The theoretical modeling of the aggregation (by molecular dynamics) confirms the formation of different species, till to the trimer (to be published).

Conclusions

UV-Vis spectroscopy has been used to study the aggregation of a trisazo dye (**VD**) in aqueous solution.

From the absorption spectra graphs of the trisazo dye (**VD**), it is obvious that the maximums of absorption are shifted as the concentration changed, which is to be expected from aggregating dyes.

Molecular aggregation of the **VD** dye also depends on solution *p*H in the acid medium when a hyperchromic and bathocromic shift is observed.

The mathematical calculation confirms the experimental data regarding the aggregation of the **VD** dye.

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