

Investigation of the Aggregation of Three Disazo Direct Dyes by UV-Vis Spectroscopy and Mathematical Analysis

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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 for both, thermodynamic and kinetic studies. The nature of aggregation is dependent on the structure of each particular dye. In the present work, the UV-visible absorption spectroscopy was used in order to study the intermolecular interactions of the three disazo direct dyes (IDH, PDP, and RDC). The molecular aggregation of the studied dyes has been studied in aqueous solutions as a function of dye concentration. All studied dyes showed signs of aggregation at lower concentrations. The mathematical obtained data confirms the aggregation of the studied dye.

Keywords: disazo dye, dye aggregation, absorption matrix

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 self associate in solution to form aggregates. The self association of solubilised dyes can lead to formation of *n*-mers through the combined effect of van der Waals and hydrogen bond interactions. The exhaustion kinetics and the equilibrium adsorption of a dye can be affected by the dye aggregation. An important factor in the dyeing process is the fast diffusion of dye molecules into the fibre. It is well known that the accessible area on cellulosic substrate is a function of the dye molecule size. Some parts of the fibre surface become inaccessible for the aggregated dye. Therefore the aggregation of azo dyes in aqueous solution has received significant attention [1, 2]. The self-aggregation of dyes in solution has been investigated by several methods including: conductometry, polarography, measurements of diffusion coefficients, osmometry, as well as by optical techniques, ¹H- and ¹⁹F-NMR, and most frequently by UV/Vis spectroscopy [3-6]. The dye aggregation is a function of temperature, electrolyte concentration, surfactant type, and dye concentration [7]. The increase of the dye concentration, of the electrolyte concentration and the decrease of the temperature enhance the molecular aggregation.

In the present work, spectrophotometric analysis was used to investigate the aggregation of a three disazo direct dyes, as a function of dye concentration.

Experimental part

Material and methods

The synthesis of the studied dyes involves the direct bis-diazotisation of 4,4'-diamino-benzanilide, and two coupling reactions of the resultant bis-diazonium salt with different coupling components: I acid and H acid for IDH dye; pyrazolone in case of PDP dye [8]; salicylic acid and benzoyl I acid for RDC dye [9]. The dyes were purified by several recrystallizations from distilled water and characterized by thin layer chromatography and electronic spectra.

UV-visible absorption spectra of IDH, PDP and RDC dyes in aqueous solution were recorded across a range of different initial concentrations. The samples were placed

in an oven to sit over night. The absorption spectra of the dyes were recorded on a CECIL CE 7200 spectrometer at room temperature. The quartz cuvettes of path lengths ranging from 0.1 to 1 cm were necessary in order to keep the absorption within a useful range.

The data for each dye were stored in spectral files as matrices of size *n* (wavelengths) and *m* (concentrations), and then processed by using MATHCAD 2000 packages.

Results and discussions

The dyes used in this study were disazo direct dyes: I acid ← 4,4'-diamino-benzanilide → H acid (IDH), pyrazolone ← 4,4'-diamino-benzanilide (PDP), salicylic acid ← 4,4'-diamino-benzanilide → benzoyl I acid (RDC), with the chemical structures shown in figure 1.

The absorption spectra of the studied dyes in aqueous solutions, at 10 different concentrations ranging from $8 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M was recorded at room temperature. Absorption spectra of all samples at different concentrations in water solutions are given in figure 2.

The visible absorption spectra of the IDH dye changed with dye concentration showing isosbestic point at 620 nm. This fact indicates that a single equilibrium exists in the concentration range examined [10]. The extinction coefficient decreased with increasing dye concentration.

For the PDP dye the maximum absorption wavelength of the principal peak shifts to lower wavelength as the concentration is increased and the extinction coefficient decreased, signifying that the molecules are beginning to aggregate. An isosbestic point is observed at 500 nm, indicating the existence of equilibrium between two species, monomer and dimer form, of the dye. The spectrum corresponding to $1.42 \cdot 10^{-5}$ M dye concentration does not fit the isosbestic point, indicating the appearance of a new species - probably a trimer.

The UV-Vis absorption spectra of RDC dye shown existence of an isosbestic point at 570 nm, the decrease of the extinction coefficient with increasing dye concentration, although the maximum absorption wavelengths of the principal peak wavelength remain stable, all these signs demonstrating that RDC dye aggregates at low concentrations.

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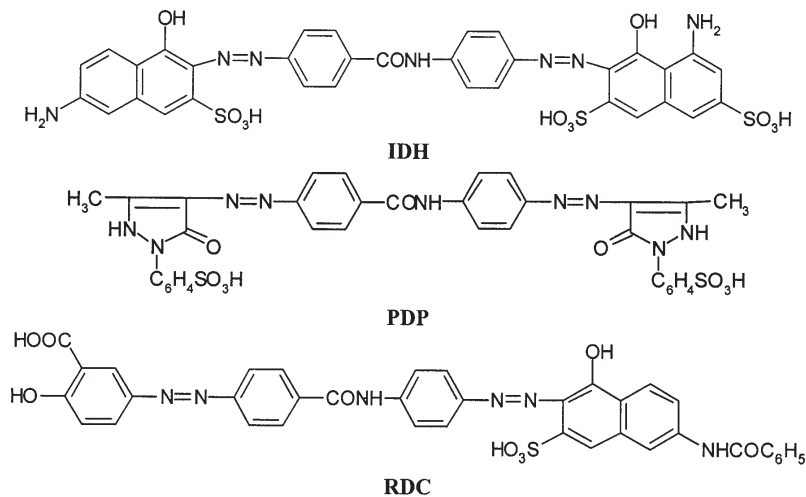


Fig. 1. Molecular structure of the studied dyes

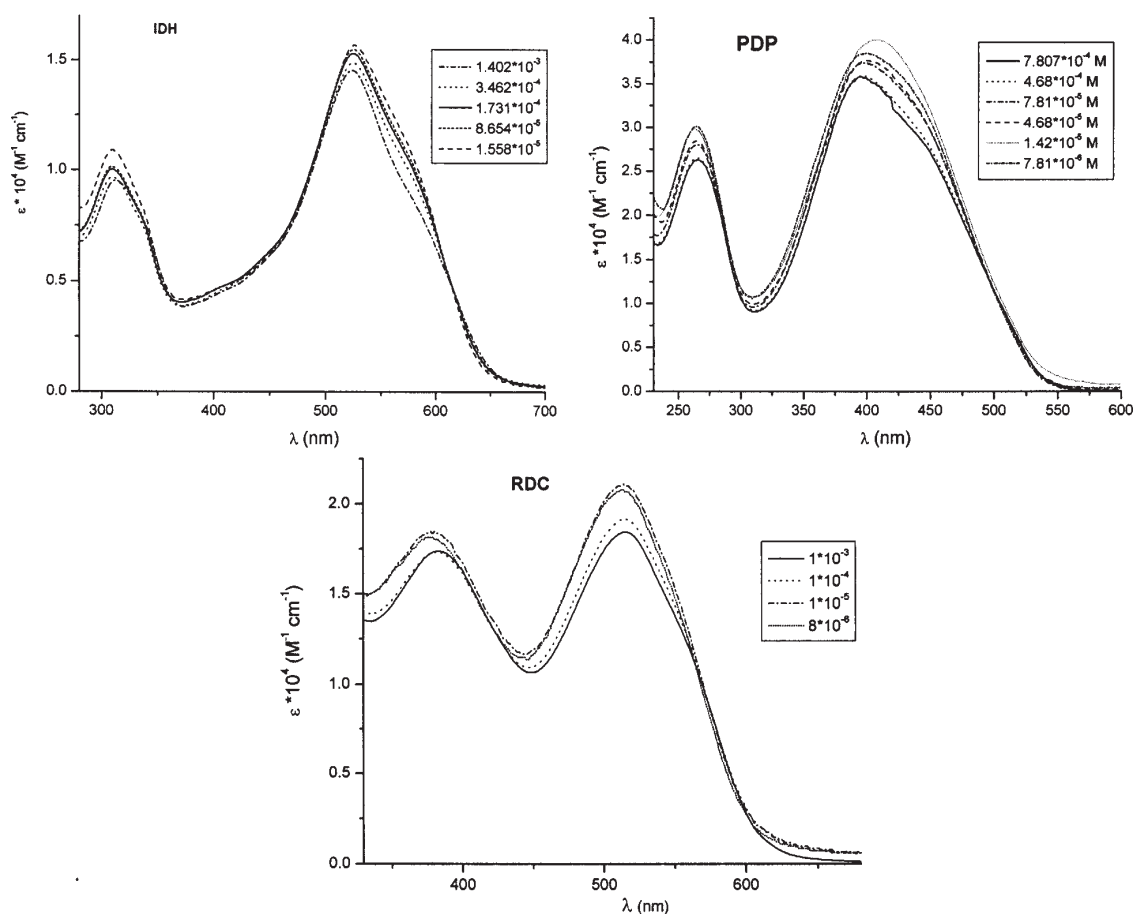


Fig. 2. Absorption coefficients in the UV-visible range for different concentrations of studied dyes

Figure 3 shows the dependence of ϵ at the maximum absorption wavelength of the dilute solution on the dye concentration, C_0 .

For all three dyes, ϵ decreased with increasing dye concentration, but the manner of the change varied from dye to dye, probably due to the interaction between the aromatic rings of the adjacent dye molecules.

For accuracy, the absorption coefficient was plotted as a function of peak wavelength (fig. 4).

For **PDP** dye the graphs shows a clear trend in the changes of the maximum absorption wavelength peak with concentration, but for the **IDH** and **RDC** dyes the principal peak wavelength of absorption remains constant.

Using the experimental absorbance values, an $n \times m$ (n : wavelength, m : concentrations) dimension matrix was build. The rank of this matrix is equal to the chemical

species existing in the system, in the considered concentration domain. In order to determine the rank of this matrix [11], it was multiplied 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 matrix different from zero (within accepted experimental errors) is equal to the chemical species (monomer, dimer, etc.) present in the system (table 1.).

Taking into account that the absorbance values are significant at most to the second decimal, the eigenvalues less than 0.01 may be considered zero. From the obtained data it can be estimated, in case of **IDH** and **RDC** dyes the presence of two species - monomer and dimer, and for **PDP** dye the presence of three species, probably monomer, dimer and trimer.

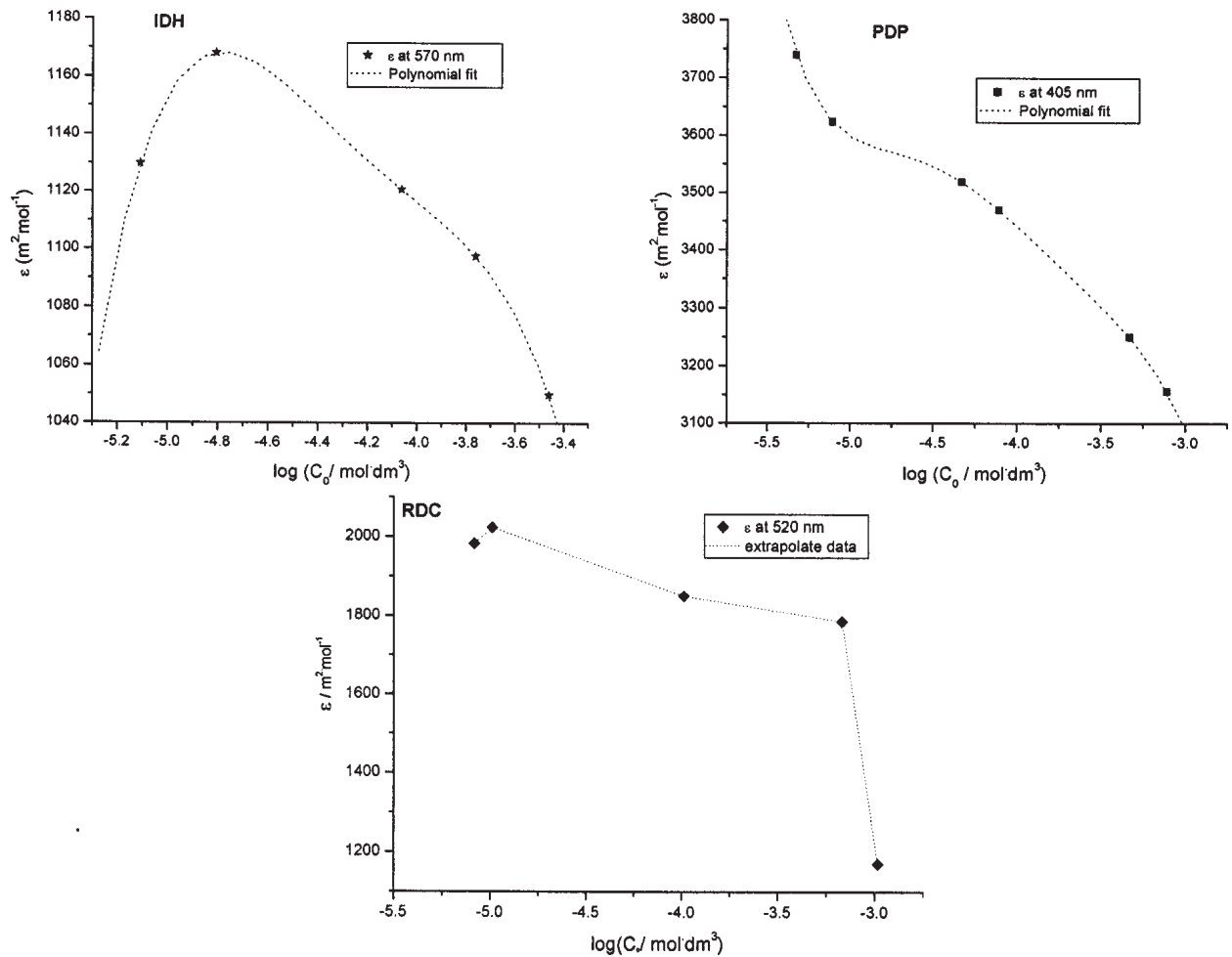


Fig. 3. Dependence of ϵ at fixed nm on the dye concentration

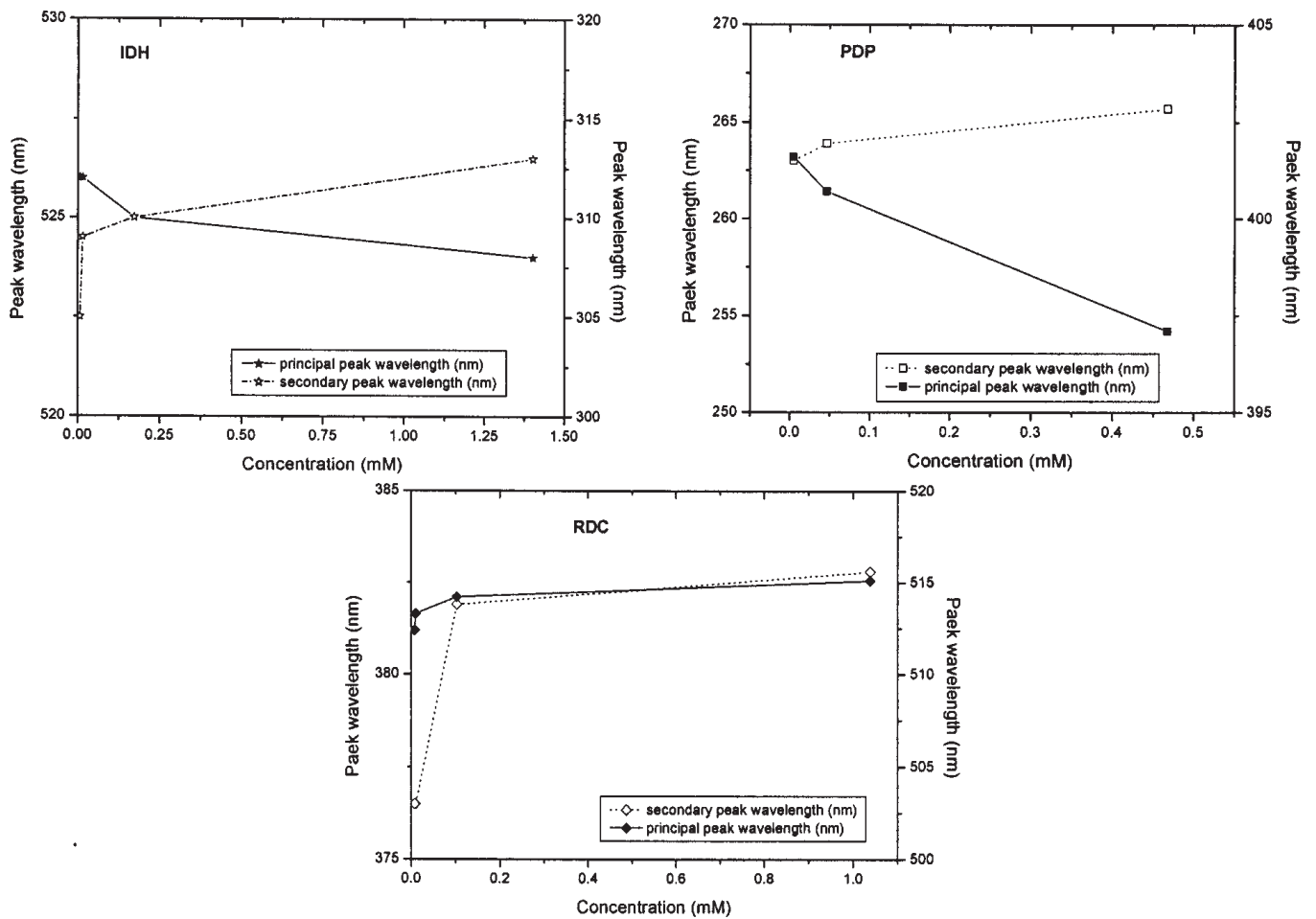


Fig. 4. Change in peak wavelength at different concentrations

Table 1
THE EIGENVALUES VALUE OF THE ABSORPTION MATRIX

The eigenvalues value function of Absorption		
IDH	PDP	RDC
7.354e-15	-1.422e-14	6.447e-15
-7.768e-15	2.854e-13	-6.511e-15
-2.975e-13	-2.429e-12	1.426e-13
6.147e-13	2.435e-3	-3.219e-13
3.038e-3	4.570e-3	1.805e-12
5.604e-3	0.038	2.096e-4
0.041	0.196	0.011
0.533	0.492	0.152
1.165e3	2.409e3	1.077e3

Conclusions

UV-Vis spectroscopy has been used to study the structure and bonding of three bis-azo direct dyes, **IDH**, **PDP** and **RDC**, in solution. The experimental results indicate that all three studied dyes showed signs of aggregation at lower concentrations. From the absorption spectra graphs, it is easy to see that spectra of each dye shifted as the concentration changed, which is to be expected from aggregating dyes.

The mathematical analysis has provided information about the formation of the dimers and trimers for the

studied dyes. The results indicate that, in the concentration domain considered, **IDH** and **RDC** dyes exist as monomer and dimer, and in case of **PDP** dye exist also trimer species.

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