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Spectroscopic studies on aggregation phenomena of dyes

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ABSTRACT

In this article, aggregation (self association) phenomena of some dyes that have been investigated by spectroscopic studies were surveyed. Equilibrium constants and thermodynamic parameters of self association phenomena of the dyes are obtained by classic (like Benesi-Hildebrand) and chemometrics (like Kubista method) methods with the spectroscopic investigations. In general, the self association phenomena are classified into two types, H- and J-aggregates. The aggregation phenomena of dyes: rhodamine B, rhodamine 6G, Neutral Red, Nile Blue A, Safranine T, Thionine, Methylene blue, methylene green, thiazole orange and TO-3 which have been studied by spectroscopic investigations were surveyed in this paper.

Keywords: Aggregation phenomena, Self association, Kubista method, Benesi-Hildebrand method, Spectroscopic study, Chemometrics, Equilibrium constant

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INTRODUCTION

Many dyes demonstrate ability for self-association which is one of the features of dyes in solution [1-10]. This phenomenon that is called aggregation, affect on colouristic and photophysical properties of dyes and therefore being of special characteristics [11]. The aggregation phenomenon in solution or at the solid-liquid interface is a frequently encountered phenomenon in dye chemistry owing to strong intermolecular van der Waals-like attractive forces between the molecules. It is well known that the ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates. In such a case the molecular nature of dye is strongly affected by, and therefore related to such parameters as dye concentration, structure, ionic strengths, temperature and presence of organic solvents [10]. Although dyes are very individualistic as structure and, of course behavior, certain broad rules are well established regarding the aggregation in general. It may increase with an increase of dye concentration or ionic strengths; it will decrease with temperature rising or organic solvents adding; addition to the dye structure of ionic solubilizing groups will decrease aggregation, whereas the inclusion of long alkyl chains increase aggregation because of higher hydrophobic interaction in solution. Dye aggregates have played important roles in both fundamental science and technological applications such as optical memory, organic solar cells and organic light emitting diodes [12-14]. The xanthene dyes class, which are among the oldest and most commonly used of all synthetic dyes that, of their applications were using in cloth and food colouring [15]. The special photophysics properties of these types of molecules cause the vast and increasing up applications in chemistry and physics. They are applied as probes in biochemistry, monitoring of membrane fusion, for determination of the

aggregations distance in biology, as fluorescent probes of protein in detecting protein orientation because of their high time-zero anisotropy, photostability and also red emission making them ideal for use in microscope [16, 17]. A class of dyes which are called cyanine have great aptitude to form aggregates in polar solvents was discovered in the thirties [14, 18] and has afterwards been the subject of many studies [19-27] based mostly on the analysis of the effects of concentration on absorption and emission spectra. The majority of the authors paid maximum attention to the dimerization process occurring in a certain concentration range which precedes the formation of more complex aggregates. Organized assemblies of cyanine dyes act as molecular functional units in many processes of technological interest like spectral sensitization in photography [28], size-enhancement of nonlinear optical polarizabilities [29,30], sensitization of semi-conductor materials [31], etc. In these cases aggregates are formed on solid surfaces or in monomolecular layers at the air–water interface [32, 33], where the chromophore packing is assisted by specific dye–substrate interactions.

In general, they are classified into two types, H- and J-aggregates [19, 34, 35]. Extensive studies on J- and H-aggregates have resulted in the proposal that these aggregates exist as a one-dimensional assembly in solution that could be in (a) brickwork, (b) ladder, or (c) staircase type of arrangement. The pattern of the assembly is shown in the fig 1.

Fig1. Schematic representation of the different arrangement of cyanine dyes in the solid surface and in solution

Maskasky based on the study of J-aggregates proposed the brickwork model of polymethine dyes on silver halide grains by polarized fluorescence microscopy. The aggregation behavior of cyanine dyes has been studied extensively since these are the best-known self-aggregating dyes. It is generally agreed that both H- and J-aggregates are composed of parallel dye molecules stacked plane-to-plane and end-to-end and form two-dimensional dye crystals. The dye molecules may aggregate in a parallel way (plane-to-plane stacking) to form a sandwich-type arrangement (H-dimer) or in a head-to-tail arrangement (end-to-end stacking) to form a J-dimer. Dimers as the simplest aggregates are the subject of many studies concerned with the thermodynamics of monomer–dimer equilibrium and photo-physical properties [2-8, 10, 36]. The aggregates in solution exhibit distinct changes in the absorption band from those of the monomeric molecules. From the spectral shifts, various aggregation patterns of the dyes in different media have been proposed.

1. UV-Vis spectroscopy and dyes

The absorption UV-Vis spectroscopy is one of the most suitable methods for quantitative studying the aggregation properties of dyes as function of concentration, since in the concentration range used (10^{-3}– 10^{-6}M) mainly monomer-dimer equilibrium exists. Spectroscopic methods are in general highly sensitive and are as such suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of the equilibrium constant is trivial. However, in many cases, the spectral responses of two and sometimes even more components overlap considerably and the analysis is no longer straightforward [37-41].

2. Benesi-Hildebrand method

The determination of association constants using spectroscopic measurements is commonly accomplished by the method of Benesi–Hildebrand that was first developed by Benesi and Hildebrand in 1949 [42-45]. This analysis requires that the concentration of one of the associating species be kept very much lower than the other, and it assumes that the dissociated species do not contribute significantly to the measured analytical signal (i.e. <5%). This method has been typically applied to reaction equilibria that form one-to-one complexes. The theoretical foundation of this method is the assumption that when either one of the reactants is present in excess amounts over the other reactant:

$$H + G \rightleftharpoons HG \tag{1}$$

$$A = A^{HG} + A^{G} + A^{H} \tag{2}$$

With the assumption that the initial concentration of the guest (G_0) is much larger than the initial concentration of the host (H_0), then the absorbance from H_0 should be negligible:

$$A = A^{HG} + A^{G} \tag{3}$$

The absorbance can be collected before and following the formation of the HG complex. This change in absorbance (ΔA) is what is experimentally acquired, with A_0 being the initial absorbance before the interaction of HG and A being the absorbance taken at any point of the reaction:

$$\Delta A = A - A_0 \tag{4}$$

$$\Delta A = \epsilon^{HG}[HG]b + \epsilon^{G}[G]b - \epsilon^{G}[G]_0 b \tag{5}$$

Due to the previous assumption that $[G]_0 >> [H]_0$, one can expect that $[G] = [G]_0$. Δε represents the change in value between ε^{HG} and ε^{G}:

$$\Delta A - \Delta\epsilon[HG]b \tag{6}$$

However, in many cases, the spectral responses of two and sometimes even more components overlap considerably and analysis is no longer straightforward. The single-point measurements are usually made at the edge of an absorption band, where the spectral overlap is least. However, in many cases, the spectral responses is much lower than at the absorption maximum, the noise level may be considerable and association constants determined by Benesi–Hildebrand method are accompanied with more systematic errors [46].

3. Chemometrics method

Using chemometric methods one can analyze whole spectra, thereby utilizing all spectral information. The approach is superior to any single-point measurement since several hundreds of data points per spectrum can be treated simultaneously [47]. More accurate and precise association constants, thermodynamic parameters and spectral information are determined by characterizing a single sample containing components in chemical equilibrium. In this method by utilizing the Vant-Hoff relation [48], which describes the dependence of equilibrium constant on temperature, the spectra recorded at different temperatures are deconvoluted into contributions from the individual components [49] as well as thermodynamic parameters are determined.

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{7}$$

where H◦ is the molar enthalpy change, S is the molar entropy change , R = 8.31 $Jmol^{-1}$ K^{-1} the universal gas constant, and T the Kelvin temperature. A linear regression of equilibrium constants with respect to 1/T is then performed, which determines a trial enthalpy change of the reaction. One of the methods in chemometrics which is used to calculate equilibrium constant and thermodynamic parameters is Kubista method [49-58]. The absorption spectra are digitized and arranged as rows in a matrix A. Matrix A is then decomposed into an orthogonal basis set using, for example, the NIPALS routine [51]:

$$\boldsymbol{A} = \boldsymbol{TP} + \boldsymbol{E} \approx \boldsymbol{TP} = \sum_{i=1}^{r} \boldsymbol{t}_i \boldsymbol{p}_i' \tag{8}$$

where ti are orthogonal target vectors and pi are orthogonal projection vectors, E is the error matrix, and r the number of spectroscopically distinguishable components, which is two in this case. Assuming linear response the recorded spectra are also linear combinations of the spectral responses, vi, of the components:

$$\boldsymbol{A} = CV + \boldsymbol{E} \approx CV = \sum_{i=1}^{r} \boldsymbol{c}_i \boldsymbol{v}_i \tag{9}$$

where ci are vectors containing the component concentrations at the different temperatures. Eqs. (10) and (11) are related by a rotation:

$$C = T\boldsymbol{R}^{-1} \tag{10}$$

$$V = \boldsymbol{R}P \tag{11}$$

where R is an r×r rotation matrix, for which a two-component system has the element:

$$\boldsymbol{R} = \begin{bmatrix} r_{11} & r_{12} \\ r_{21} & r_{22} \end{bmatrix} \tag{12}$$

Two constraints are used to determine three of the element in R. The first is the spectrum of monomer, which is measured separately, and the second is the constant total concentration of the dye:

$$c_x(T) + 2c_{x_2}(T) = c_{\text{tot}} \tag{13}$$

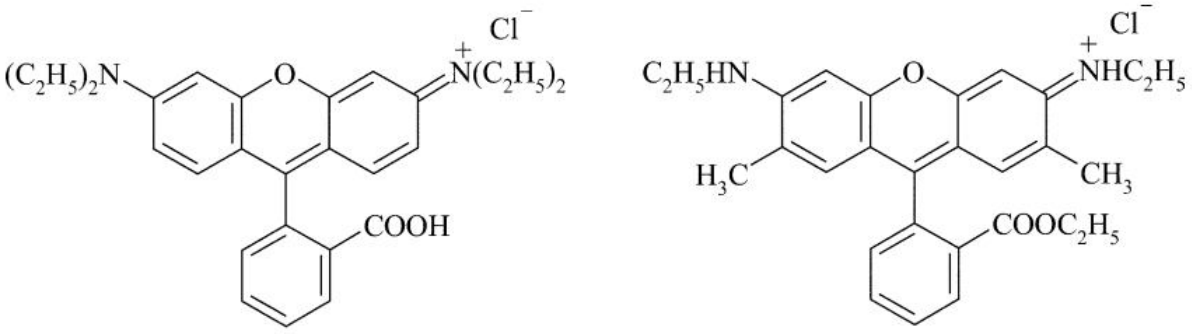
Matrix R can now be described by a single scalar r_{21}, and other factors that are determined by the constraints. The value of r_{21} determines the dimer spectrum and the monomer concentration profiles. Although many values of r_{21} produces a mathematically acceptable solution, reasonable results in terms of spectral intensities and non-negative concentrations, and spectral responses are obtained in a relatively narrow range of r_{21} values. Still, the range is, in general, too large for a quantitative analysis. The final constraint, which produces a unique solution, is the thermodynamic relation between temperature and the equilibrium constant. The components' concentrations are related by the law of mass action [48]:

$$K_{\text{D}}(T) = \frac{c_{x_2}(T)/c^{\circ}}{(c_x(T)/c^{\circ})^2} \tag{14}$$

where $c^{\circ} = 1\text{mol/dm}^3$. The thermodynamic parameters are calculated by application of vant Hoff equation similar above said procedure. Several studies based on the application of this method to spectrophotometric data have been reported [59-61].

4. Rhodamine B and rhodamine 6G

In 2005thermodinamic characteristics and dimerization equilibria of rhodamine B and 6G (Scheme 1) in different ionic strengths by photometric titration and chemometrics method were studied. Rhodamine B and rhodamine 6G are derivatives of the xanthene dyes class, which are among the oldest and most commonly used of all synthetic dyes that, of their applications were using in cloth and food colouring [15]. The special photophysics properties of these types of molecules cause the vast and increasing up applications in chemistry and physics. They are applied as probes in biochemistry, monitoring of membrane fusion, for determination of the aggregations distance in biology, as fluorescent probes of protein in detecting protein orientation because of their high time-zero anisotropy, photostability and also red emission making them ideal for use in microscope [16,17].



Scheme 1.

Solutions of rhodamines are the most popular gain media in organic dye lasers. Rhodamine 6G was employed in the first flashlamp-pump dye laser, and in the first continuous wave dye laser [62,63]. The dimerization and/or the aggregation as whole of the rhodamines in the solutions have serious disadvantages in their application in lasing media. Generally too prevent of formation of aggregation a detergent such as Triton X-100 is added [63]. Against to the laser application the monomer–dimer equilibrium of the rhodamines plays a fundamental role in biochemical research. The advantage is the drastically change in fluorescence intensity accompanying the monomer–dimer transition [64]. In addition to the above-mentioned unique optical properties rhodamines have very important role in several fields of scientific researches. Nowadays, they serve as water tracing agents [65], fluorescent markers formicroscopic studies of complex cellular processes and structure [66], as photosensitizers [15], laser dyes, and since recently, as chromoionophores in optical chemical sensors [2]. The absorption spectra of rhodamine B and 6G, were recorded in the wavelength 450–620 $_{nm}$ (for rhodamine B) and 440–580 $_{nm}$ (for rhodamine 6G) and temperature 20–80 $^{\circ C}$ at 5 $^{\circ C}$ intervals and pH 7.50. The sample absorption spectra are shown in figs.2 and 3.

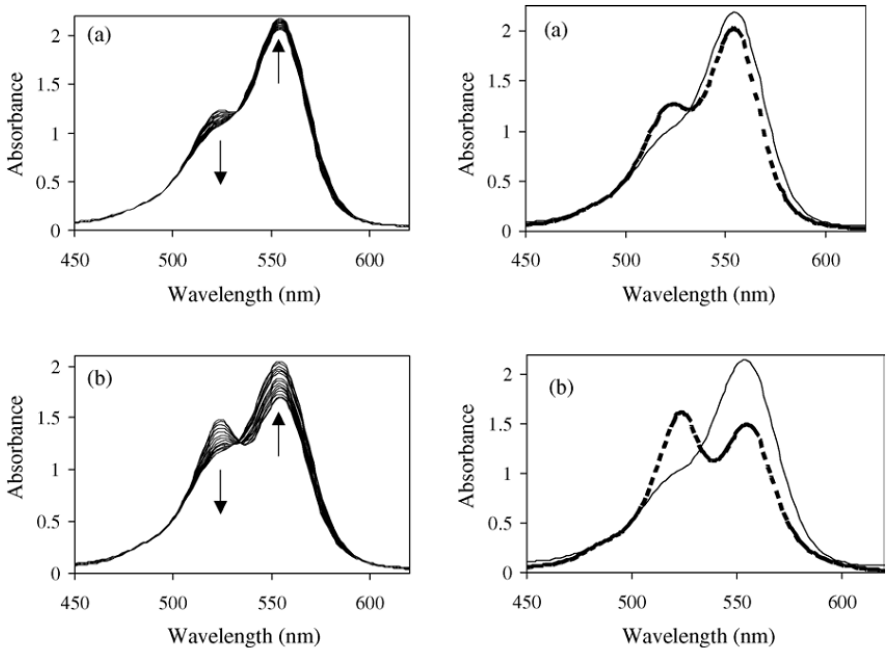


Fig. 2. Absorption spectra and calculated absorption spectra of monomer (- - -) and dimer (—) of rhodamine B (2.4×10^{-4} mol l^{-1}) in 5 $^{\circ C}$ intervals between 20 and 80 $^{\circ C}$ at pH 7.50: (a) in water; (b) 3M NaCl

According to Eqs. (7)–(14), the DATAN program start with a trial value of r_{21}, at predefined interval, and iterate all the calculation steps. The iteration stops when all r_{21} values in the preset interval are tested. The K_D, dimer spectrum, S and H, correspond to minimum value of the χ^2 statistics, are selected as the final results. The χ^2 is the sum of squared residuals [52] and generally used as a goodness of fit criterion and its value indicate the predictability of the model, i.e. how well themonomer spectrum and r_{21} are determined. The general formula of the χ^2 is [67]:

$$\chi^2 = \sum_{i=1}^{n} (A_{exp} - A_{calc})^2 / A_{exp} \quad (15)$$

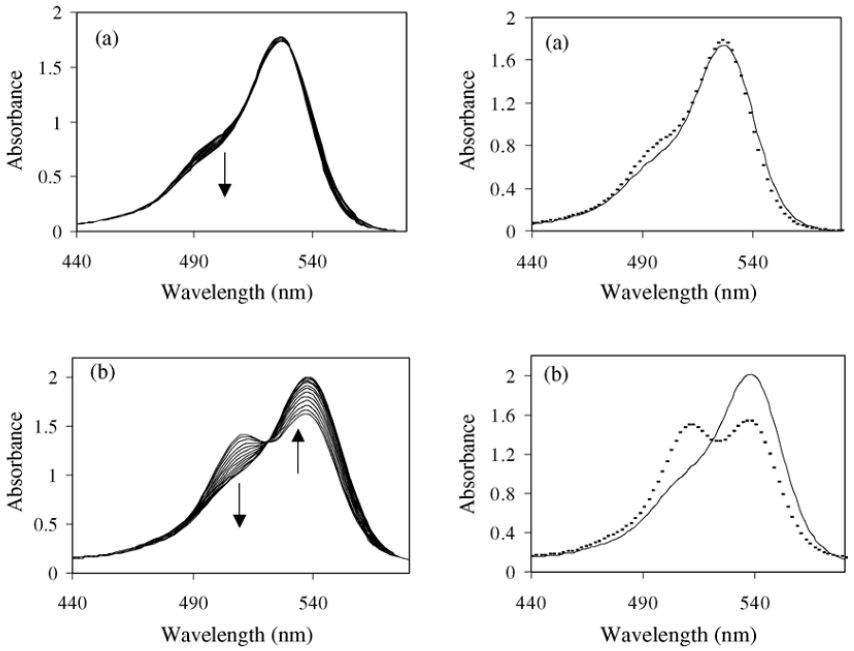
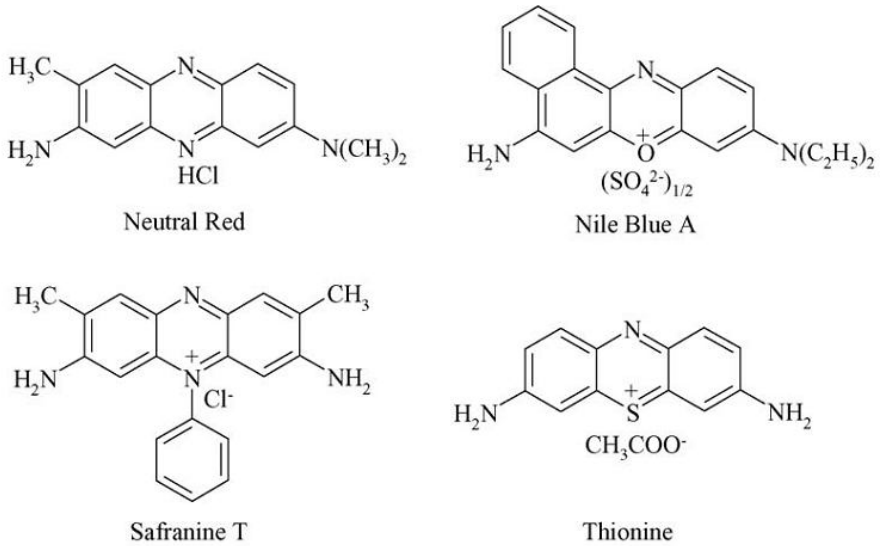


Fig. 3. Absorption spectra and calculated absorption spectra ofmonomer (- - -) and dimer (—) of rhodamine 6G (5.89×10^{-5} mol l^{-1}) in 5 °C intervals between 20 and 80 °C at pH 7.50: (a) in water; (b) 2M NaCl



Scheme 2

5. Neutral Red, Nile Blue A, Safranine T and Thionine

The monomer–dimer equilibrium and thermodynamic of several ionic dyes (Neutral Red, Nile Blue A, Safranine T and Thionine (Sheme 2.)) were investigated by means of spectrophotometric and chemometrics methods in 2006. It is well known that the ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates [3-8].

The absorption spectra of Neutral Red, Nile Blue A, Safranine T and Thionine, were recorded between 400 and 650 $_{nm}$, 500 and 720 $_{nm}$, 400 and 650 $_{nm}$, and 450 and 650 $_{nm}$, respectively, in the temperature range 20–75 $^{\circ C}$ at 5 $^{\circ C}$ intervals and pH 7.00; absorption spectra are shown in Fig. 4.

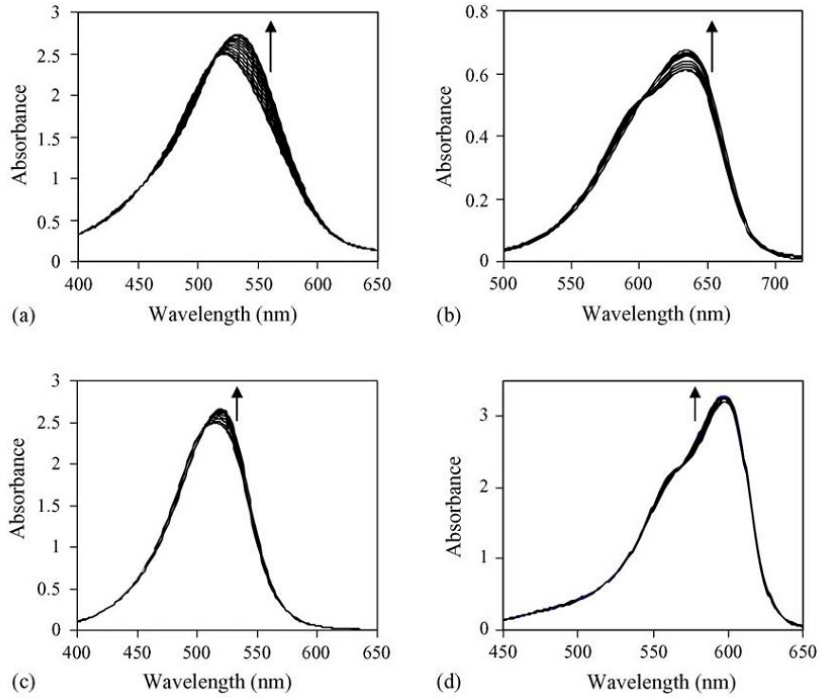
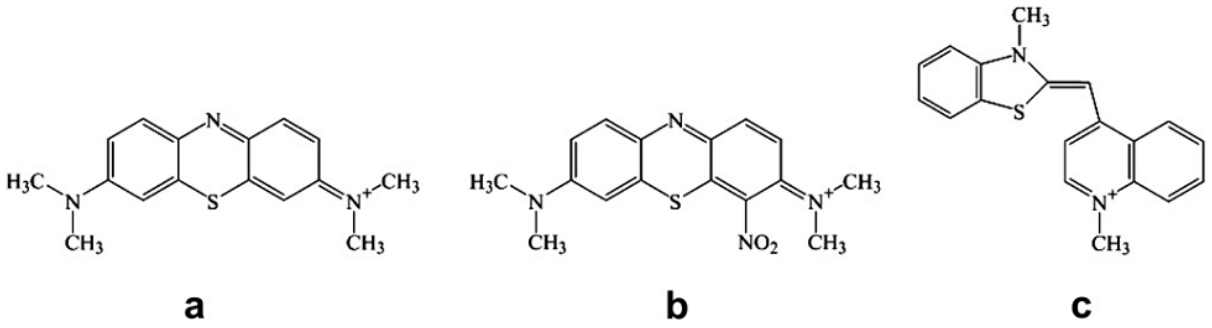


Fig. 4. Absorption spectra of: (a) Neutral Red (1.73×10^{-5} M), (b) Nile Blue A (3.94×10^{-5} M), (c) Safranine (6.59×10^{-5} M) and (d) Thionine (6.60×10^{-5} M) in 5 $^{\circ C}$ intervals between 20 and 75 $^{\circ C}$ at pH 7.00 in water
The acquired data were resolved by the Kubista method [68].

6. Methylene blue, methylene green and thiazole orange

Cationic dyes, such as methylene blue (MB) and methylene green (MG) (Scheme 3.), are thiazine type dyes, which were initially used for dyeing silk, leather, plastics, paper, and cotton mordanted with tannin, as well as for the production of ink and copying paper in the office supplies industry, and also for the preparation of color lakes. These dyes have also long been used for staining in medicine, bacteriology, and microscopy [69, 70]. They can be used as sensitizers in photopolymerization and as a component of a silver free direct-positive color bleaching-out system [71]. Furthermore, the reversible equilibrium between the reduced and oxidized forms of MB and MG, renders these compounds useful as redox indicators [72, 73].MB main uses are related with the determination of glucose, O_2 or ascorbic acid [74, 75]. Also previous studies have found that MB molecules existed as a dimer or as aggregates at the surface, as well as a protonated form depending on the concentration and the surface properties [76]. Cyanine dyes are typically based on indole, benzothiazole, benzoxazole and quinoline heterocycles. A widely used intercalating cyanine dye which has an unsymmetrical structure is thiazole orange (TO). Thiazole orange is the oldest synthetic cyanine dyes, today widely used in reticulocyte analysis. The cationic unsymmetrical cyanines such as TO are best known for their fluorogenic behavior in the presence of DNA and RNA [77]. Thiazole orange serves as an ideal scaffold for these conjugates because it is highly fluorescent when bound to DNA. The fluorescence properties of thiazole orange has led to its incorporation into a number of DNA detection or probing systems. This dye was shown to permeate live cell membranes and efficiently stain residual RNA in reticulocytes [78]. In addition, thiazine and cyanine dyes have important photophysical applications [49, 79]. In 2012 the monomer dimer equilibrium and thermodynamics of ionic dyes were investigated by spectrophotometric and chemometric methods. The electronic absorption spectra of MB, MG and TO, at constant total dye concentrations and different surfactant

concentration were recorded over the wavelength range of 500 to 750 $_{nm}$ (for MB and MG) and 350 to 600 $_{nm}$ (for TO) and a temperature range over 15 to 75 ^{C} at 5 ^{C} intervals and pH 7.0.

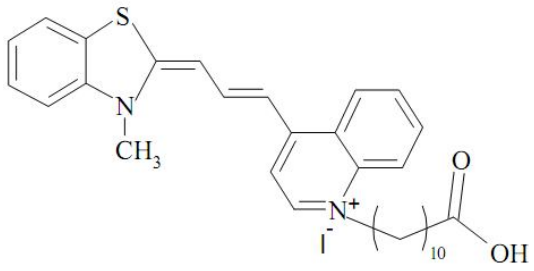


Scheme 3. Dye structures: (a) MB, (b) MG and (c) TO

In this work, it was used the Kubista method [80].

7. TO-3

In 2004 the dimerization constant of 1-carboxydecyl-4-{3-[3-methyl-3H-benzothiazol-2-ylidene]-propenyl}-quinolinium (TO-3) was determined by studying the dependence of absorption spectrum on temperature. A recent analogue of TO is TO-3 iodide salt (Scheme 4.).



Scheme 4. TO-3

Data resolving was done by Kubista method [79].

CONCLUSION

In the present investigation, the aggregation phenomena of some dyes as well as the different methods to obtain equilibrium constants and thermodynamic parameters of equilibrium systems by using the classic methods and chemometrics methods were surveyed.

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