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Thermodynamics Study Of The Dimerization Equilibria Of Methylene Green In Different Ionic Strengths By Photometric Titration And Chemometric Method



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ABSTRACT

The monomer–dimer equilibrium of an asymmetric cyanine dye has been investigated by means of UV-Vis spectroscopy. The dimerization constants of methylene green have been determined by studying the dependence of their absorption spectra on the temperature in the range 20–90 °C at different total concentrations of methylene green (9.85×10^{-5} to 2.98×10^{-4}) and different concentrations of NaCl as supporting electrolyte. The equilibrium parameters of the dimerization of methylene green have been determined by chemometrics refinement of the absorption spectra obtained from thermometric titrations performed at different ionic strengths. The quantitative analysis of the data of undefined mixtures, was carried out by simultaneous resolution of the overlapping spectral bands in the whole set of absorption spectra. The dimerization constants are varied by changing the ionic strength and the degree of dimerization are increased by increasing of the ionic strengths of the medium. The enthalpy and entropy of the dimerization reactions were determined from the dependence of the equilibrium constants on the temperature (van't Hoff equation).

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INTRODUCTION

Dyes are a kind of organic compounds which can bring bright and firm color to other substances. Synthetic dyes usually have a complex aromatic molecular structure which possibly comes from coal tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. The complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade^[1,2]. Today there are more than 10,000 dyes available commercially^[3]. Synthetic dyes have been increasingly used in the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and food industries.

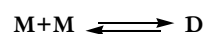
The thiazine dyes are used for dyeing paper and office supplies and also for the preparation of color lakes. In addition, the thiazine dyes have important photochemical applications. They can be used as sensitizers in photopolymerization as a component of a silver free direct-positive color bleaching-out system, because they are reduced by the action of light and thereby bleach-out indigoid dyes also present. If the thiazine dyes is bonded to the polymer chain, photo- or thermochromic polymers are obtained. Methylene green is obtained by the action of nitric acid on methylene blue and derivative of the thiazine dyes class, which are among the oldest and most commonly used of all synthetic dyes that, of their application were using in cloth and food colouring. The special photophysics properties of these types of molecules cause the vast and increasing up applications in chemistry and physics. Methylene green and other phenothiazine dyes are used as photo reducible dyes in galvanic cells. They are also used in the leuco form as oxygen detectors for the detection of the undesired admission of air, for example in vacuum-packed foodstuffs. The methylene green have long been used for staining in medicine, bacteriology, and microscopy^[4,5].

It is well known that solutions of dyes in polar organic solvents at room temperature follow Beer's law over an extended concentration range, but that in water large deviations from the law are observed. For many classes of dye in aqueous solution, the band of highest intensity in dilute solution becomes weaker as the concentration is increased, and new

bands appear at other wavelengths. These spectral changes have long been attributed to aggregation of the dye molecules in water to form dimers and higher polymers under the influence of the strong dispersion forces associated with the high polarizability of the chromophoric chain. The dominant role of water as the solvent most favorable to aggregation at room temperature is no doubt associated with the effect of its high dielectric constant in reducing the repulsive force between the similarly charged dye cations or anions in the aggregate; the absence of aggregation in organic solvents of high dielectric constant at room temperature suggests that solvation interferes with the aggregation, and in such solvents aggregates are stable only at low temperatures under conditions of high viscosity^[6].

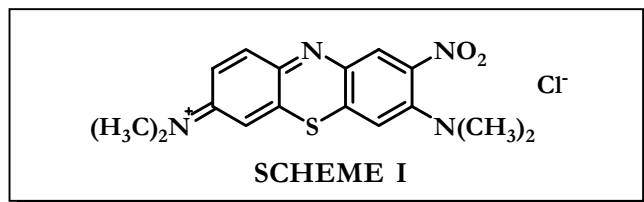
Aggregation is one of the features of dyes in solution^[7-15], affecting their colouristic and photophysical properties and therefore being of special interest. It is well known that the ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates. 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^[15]. 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.

The UV-vis absorption spectroscopy is one of the most suitable methods for quantitative studying the aggregation properties of dyes as function of concentration. In the commonly used concentration range (10^{-3} to 10^{-6} M) the main equilibrium is monomer-dimer reaction.



In this work, we used some physical constraints to determine the dimeric constants of methylene

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green dye (SCHEME I) in pure water and at different ionic strengths. Data analysis was carried out by DATAN package that developed by Kubista group^[16-25].

2. Theory

The theory and application of physical constraints method was discussed by Kubista et al. in several papers^[16-27]. However, the general principal will be outlined briefly.

Spectra recorded at different temperature are arranged as rows in an $n \times m$ matrix A , where n is the number of temperature intervals and m is the number of data points in each spectrum. A , is decomposed into an orthogonal basis set by NIPALS or any equivalent method^[16,28]:

$$A = TP^T + E \approx TP^T = \sum_{i=1}^r t_i p_i^T \quad (1)$$

Where t_i ($n \times 1$) are orthogonal target vectors and p_i^T ($1 \times m$) are orthogonal projection vectors. These are mathematical constructs and do not correspond to any physical property of the system. r is the number of spectroscopically distinguishable components, and E is the error matrix containing experimental noise, if the right value of r is selected. For a well-designed experiment, E is small compared to TP^T and can be discarded.

Assuming linear response the recorded spectra are also linear combinations of the spectral responses, v_i ($1 \times m$), of the components:

$$A = CV + E \approx CV = \sum_{i=1}^r c_i v_i \quad (2)$$

Where c_i ($n \times 1$) are vectors containing the component concentrations at the different temperatures. The two equations are related by a rotation:

$$C = TR^{-1} \quad (3)$$

$$V = RP^T \quad (4)$$

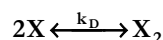
Where R is an $r \times r$ rotation matrix. For a two-

component system:

$$R = \begin{bmatrix} r_{11} & r_{12} \\ r_{21} & r_{22} \end{bmatrix} \text{ and } R^{-1} = \frac{1}{r_{11}r_{22} - r_{12}r_{21}} \begin{bmatrix} r_{22} & -r_{12} \\ -r_{21} & r_{11} \end{bmatrix} \quad (5)$$

Since a single sample is studied, the total concentration must be constant, constraining matrix R ^[29]. For a monomer–dimer equilibrium, the total concentration of monomers is constant:

$$c_x(T) + 2c_x(T) = c_{\text{tot}} \text{ or } c_x + 2c_{x2} = c_{\text{tot}} \quad (6)$$



Combining Eq. (6) with Eq. (3), we obtain:

$$\frac{1}{r_{11}r_{22} - r_{12}r_{21}} (t_1 r_{22} - t_2 r_{21} - 2t_1 r_{12} + 2t_2 r_{11}) = c_{\text{tot}} \quad (7)$$

which can be written as:

$$f_{11}t_1 + f_{12}t_2 = c_{\text{tot}} \quad (8)$$

Where

$$f_{11} = (r_{22} - 2r_{12})(r_{11}r_{22} - r_{12}r_{21})^{-1} \quad (8a)$$

And

$$f_{12} = (2r_{11} - r_{21})(r_{11}r_{22} - r_{12}r_{21})^{-1} \quad (9)$$

These can be determined, for example, by fitting the target vectors to a vector with all elements equal to c_{tot} . Eqs. (8) and (9) provide two relations between the elements of matrix R , hence making two of them redundant. In most cases, the spectra of some of the components can be determined in separate measurements. For example, monomer–dimer equilibrium can, in general, be diluted sufficiently to make the dimer concentration negligible. This makes it possible to record the monomer spectrum, which, of course, should be used as a constraint in the analysis. Normalizing the monomer spectrum to the same total concentration as the analyzed sample. We obtain from Eq. (4):

$$v_{\text{monomer}} = r_{11}p_1^T + r_{12}p_2^T = f_{21}p_1^T + f_{22}p_2^T \quad (10)$$

Where $f_{21} = r_{11}$ and $f_{22} = r_{12}$ are determined by fitting the two projection vectors to the monomer spectrum. Eq.(9) also provides two relations between the elements of matrix R .

These are not independent of Eq. (7), and the two equations cannot be combined to solve for all the elements of matrix R , but they can be used to express R in a single element, below arbitrarily cho-

sen to be r_{21} .

Defined this way, matrix R produces C and V matrices that are consistent with the total sample concentration and the spectral response of the monomer. The value of r_{21}

$$\mathbf{R} = \begin{bmatrix} f_{21} & f_{22} \\ r_{21} & 2f_{22} + (2f_{21} - r_{21}) \frac{f_{11}}{f_{12}} \end{bmatrix} \quad (11)$$

determines the dimer spectrum and the monomer concentration profiles. Although all values of r_{21} produce mathematically acceptable solutions, 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^[30]:

$$K_D(T) = \frac{c_{x2}(T)/c^\circ}{(c_x(T)/c^\circ)^2} \quad (12)$$

Where $c^\circ = 1 \text{ mol dm}^{-3}$. Assuming that the dimerization constant $K_D(T)$ depends on temperature according to the van't Hoff equation^[30],

$$\frac{d \ln K_D(T)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \quad (13)$$

Where ΔH is the molar enthalpy change, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ the universal gas constant, and T the Kelvin temperature. r_{21} can now be determined by requiring that matrix R should rotate the target vectors to give concentration vectors (Eq. (3)) that produce an equilibrium constant whose logarithm is a linear function of $1/T$. In practice, the solution is found by a simple search procedure. r_{21} is given an arbitrary value, for which a trial rotation matrix is calculated (Eq. (11)). This is used to calculate trial concentration profiles (Eq. (3)), which are combined to a trial equilibrium constant (Eq. (12)). A linear regression of equilibrium constants with respect to $1/T$ is then performed (Eq. (13)), which determines a trial enthalpy change of the reaction. Each trial

rotation matrix also determines trial spectral responses (Eq. (4)). The procedure is repeated for various values of r_{21} to find a range that produces reasonable concentration profiles and spectral responses. This is done rather arbitrarily since there is no simple way to estimate r_{21} . Once a range has been found, r_{21} is varied gradually in this range, and a χ^2 (a regression coefficient) is calculated for each regression of $\ln K_D(T)$ with respect to $1/T$. The r_{21} that produces the best fit determines matrix R . The analysis is readily performed with the DATAN program^[31]. Several studies based on the application of this algorithm and program using spectrophotometric data have been reported^[10, 11, 16-27].

EXPERIMENTAL

Material

All the chemicals used were of analytical reagent grade. Subboiling, distilled water was used throughout. Methylene green (for microscopy grade) were purchased from Fluka and were used without any additional purification. A stock solution ($5 \times 10^{-2} \text{ M}$) was prepared by dissolving solid methylene green in water. In all experiments the ionic strengths were maintained constant by NaCl (Fluka) at 0.3 to 4.5 mol l⁻¹.

Apparatus

Absorption spectra were measured on UV S-2100 (Scinco) Spectrophotometer using 0.1 nm bandwidth and along with a temperature controller and were digitized with five data points per nanometer. Conventional quartz cells (10 and 2 mm) were used throughout. The cuvettes were treated with repel saline prior to measurements to avoid dye adsorption.

Computer hardware and software

All absorbance spectra were digitized at ten data points per nanometer in the wavelength range 500-750 nm and transferred (in ASCII format) to an Athlon 2000 computer for analysis by MATLAB (Mathworks, Version 6.1) or for processing by using DATAN package^[31].

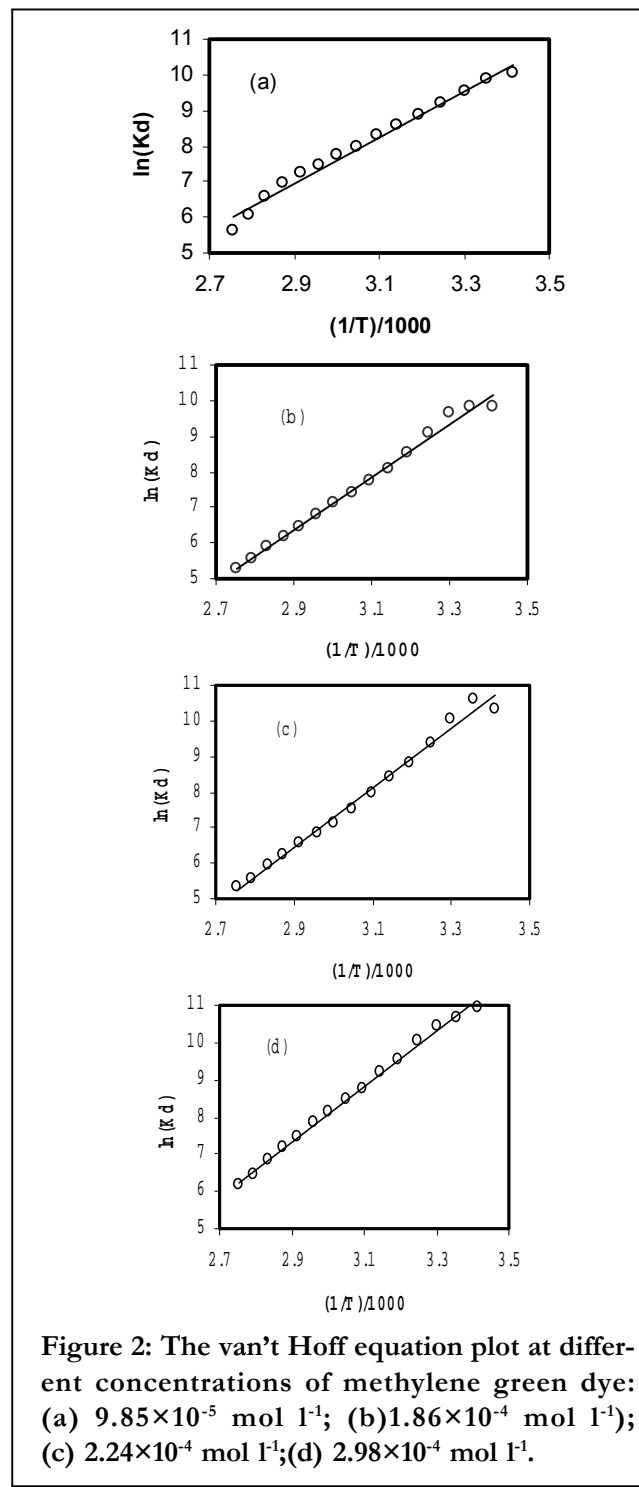
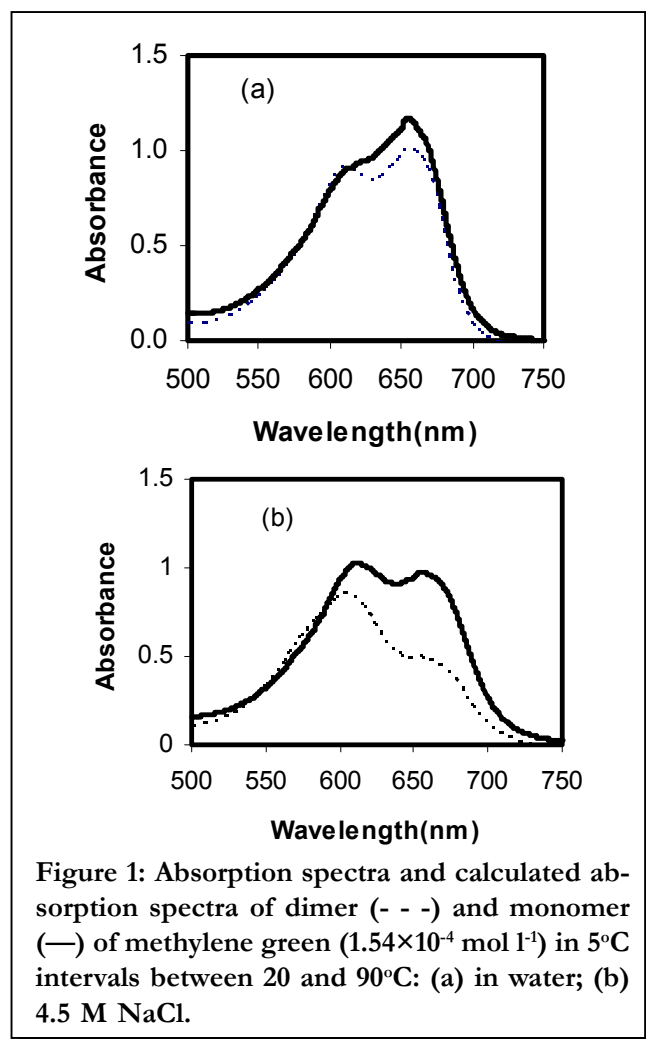
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RESULTS AND DISCUSSION

The absorption spectra of methylene green, at different total dye concentrations and ionic strengths, were recorded in the wavelength 500–750 nm and temperature 20–90 °C at 5 °C intervals. The sample absorption spectra are shown in figure 1. As it is expected, by increasing the temperature and decreasing the concentration, the monomer form would be predominant over the dimer form. So it is wise to choose the spectrum of the dye at the highest temperature and at lowest concentration as an initial estimate for the monomer in the subsequent calculations. Then according to Esq. (1) – (13), the DATAN program starts with a trial value of r_{21} , at predefined interval, and iterates all the calculation steps. The iteration stops when all r_{21} values in the preset interval are tested. The K_p , dimer spectrum, ΔS and ΔH ,

correspond to minimum value of the χ^2 statistics, are selected as the final results. The χ^2 is the sum of squared residuals^[17] and generally used as a goodness of fit criterion and its value indicate the predictability of the model, i.e. how well the monomer spectrum and r_{21} are determined.

With increasing temperature the absorption peak



655 nm grows and the absorption shoulder around 600nm decreased (Figure 1). We analyzed the temperature titrations assuming monomer–dimer, monomer–dimer–trimer and even some models including higher order aggregates, and it was found that a monomer–dimer model most adequately describes the data in these ranges of dyes concentrations. The presence of exactly two species is also evidenced by appearing of the isosbestic points at 615 nm.

The dimerization constants (K_D) were calculated at different temperatures and dye concentration in pure water. As expected K_D decreased with increasing temperature, while it is virtually independent of total dye concentration. From the dependence of $\log K_D$ on $1/T$ (Figure 2), ΔH° and ΔS° values were determined.

TABLE 1: Dimeric constant (K_D) and thermodynamic parameters values of methylene green dye at different concentrations in water.

Methylene Green (mol l ⁻¹)	Ave. Log K_D (25°C)	Ave. $-\Delta H^\circ$ (kJmol ⁻¹)	Ave. $-\Delta S^\circ$ (jmol ⁻¹ k ⁻¹)
9.85×10 ⁻⁵	4.35	53.72	98.13
1.54×10 ⁻⁴	4.39	74.89	140.99
1.86×10 ⁻⁴	4.46	60.21	126.10
2.24×10 ⁻⁴	4.61	71.19	151.9
2.98×10 ⁻⁴	4.50	61.62	122.24

TABLE 2: Dimeric constant (K_D) and thermodynamic values of methylene green (1.54×10⁻⁴ mol l⁻¹) dye at different concentrations of salt.

NaCl mol l ⁻¹	Log K_D (25°C)	$-\Delta H^\circ$ (kJmol ⁻¹)	$-\Delta S^\circ$ (jmol ⁻¹ k ⁻¹)
0.3	4.19	49.13	86.66
0.6	4.23	52.56	96.27
0.9	3.92	41.27	63.46
1.2	4.31	52.14	93.12
1.5	4.25	35.15	93.19
1.8	4.64	61.8	118.2
2.1	4.24	47.52	78.32
2.4	4.30	42.68	60.59
2.7	4.38	48.68	79.22
3	4.81	55.75	95.9
3.3	4.65	50.69	81.62
3.6	4.74	53.68	89.76
3.9	4.56	45.75	64.88
4.2	4.95	58.04	100.9
4.5	4.97	41.87	45.4

terminated. The dimerization constants at 25°C and at different concentrations and thermodynamic parameters of the dimerization reactions of the methylene green dye are listed in TABLE 1. The ΔH° values ranges from -53.72 to -74.89 kJ mol⁻¹ with mean -64.33 kJ mol⁻¹, while ΔS° ranges from -98.13 to -151.9 J mol⁻¹ K⁻¹ with mean -127.87 J mol⁻¹ K⁻¹ for methylene green. As described above dimerization is presumed to be the dominant form of aggregation in applied concentration ranges in aqueous methylene green solutions. This is corroborated by the constancy of the apparent enthalpy of association. In general, the extent of aggregation depends reciprocally on the temperature of the solution and is fully reversible. The observed relationship between entropy and enthalpy reflects an electrostatic nature of the dimerization phenomenon of methylene green dye. The relative dependence of the concentrations of the monomer and dimer of methylene green on the temperature in different concentrations are shown diagrammatically in figure 3. The sample calculated absorption spectra of methylene green in monomer and dimer forms are shown in figure 1. For studying the effect of ionic strengths on the dimerization of methylene green, the different concentrations of sodium chloride was selected and dimerization was investigated. Also, according to findings of Mchedlov-Petrosyan et al.^[32] the dominant species around this pH (7.50) is zwitterion, which bears positive and negative charge simultaneously and has a tautomeric isomer with zero charge especially in some nonaqueous solutions. Hydrogen bonding, hydrophobic forces, and electrostatic interactions are all may consider important for the dimerization. What effect we expected from the increasing of the ionic strength on the dimerization constants according to extended Debye–Huckel equation^[33,34], is totally depend on the relative changing in the total charge of the dimer species with respect to the two monomer moieties. As it can be seen from the data obtained at different ionic strength (TABLE 2), the increasing of the ionic strength results in increasing of the dimerization constants. The dimeric constants at 25°C and thermodynamic parameters values of methylene green dye at different ionic strengths of sodium chloride medium are listed in TABLE 2.

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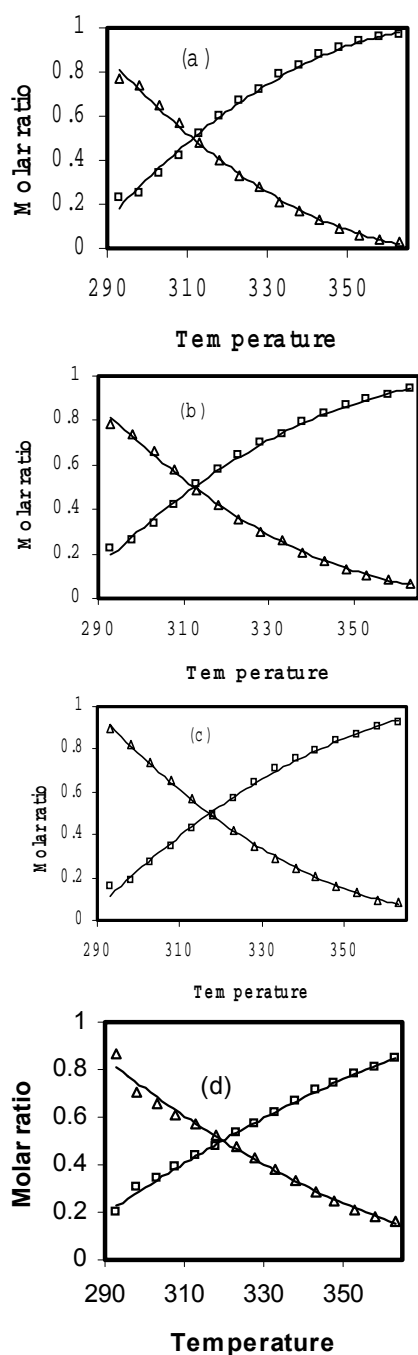


Figure 3: Molar ratio of methylene green dye monomer (\square) and dimer (Δ), compared to molar ratios predicted by the temperature dependence of the equilibrium constant (shown as line) at different concentrations of methylene green dye: (a) $9.85 \times 10^{-5} \text{ mol l}^{-1}$; (b) $1.85 \times 10^{-4} \text{ mol l}^{-1}$; (c) $2.24 \times 10^{-4} \text{ mol l}^{-1}$; (d) $2.98 \times 10^{-4} \text{ mol l}^{-1}$.

One of the most interesting points of the changing of the ionic strength on the dimerization reactions of the methylene green dye is the spectral changing of the dimer form. The dimer spectra of the methylene green show enhancement of the intensity of the spectral band with λ_{max} around 655 nm as compared with those in water. Patil et al.^[35] reported a similar spectral changing from the effect of the addition of some solutes to the aqueous solution of methylene blue. They showed that these spectral variations are depending on the angle between the two dye molecules planes which in turn is depend on the concentration of the inert solutes. The decrease in dimer formation constant values with increasing in the concentration of sodium chloride also indicates the increased tendency of the methylene green molecules to undergo aggregation. The random variations in the formation constants by changing ionic strengths (TABLE 2) may be return to the presence of the some un-accounted interactions such as anion-cation (methylene green – Cl^-) attractive type interactions, etc. in addition to monomer-dimer equilibrium.

CONCLUSIONS

In this paper we report, for the first time, to our knowledge, a thermodynamics study of the dimerization equilibrium of the methylene green dye in different ionic strengths. Dimerization constants, concentration and spectral responses profiles for the monomer and dimer forms obtained by computer refinement of temperature photometric titrations data matrix. The thermodynamic parameters, enthalpy and entropy of dimerization reaction were calculated from the dependence of dimeric constant on the temperature (van't Hoff equation). To obtain more reliable estimates of the thermodynamics parameters we performed all experiments at four different total concentrations and different ionic strengths of the dye.

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