

## Short communication

## Determination of the dimerization constant of pinacyanol: Role of the thermochromic effect

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## Abstract

Pinacyanol (PIN), as other cyanine dyes, has demonstrated a unique ability to form associates such as dimers, and H- and J-aggregates. This association is strongly favoured in water, and even at low dye concentrations, dimers and superior order aggregates are present. As a consequence, the determination of the dimerization constant involves sometimes a significant error when these aggregates are neglected. As an increase in temperature shifts the equilibrium among the different species towards the lowest order aggregates, we have obtained the spectra of PIN at several temperatures. By extrapolating some spectral characteristics at high temperatures, a spectrum of the dimer without any contribution of other aggregates was obtained. From this spectrum and that of the monomer, the dimerization constant was calculated, as well as the Gibbs energy change associated to the reaction. The enthalpy and entropy changes of the dimerization were determined from the dependence of the dimerization constants on the temperature. From these results it can be inferred that the driving force of the dimerization is of enthalpic origin.

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## 1. Introduction

Cyanine dyes have been frequently used as optical probes in the study of solvents, surfactants and micellar systems, membranes, proteins and amyloid fibrils [1–13]. The aggregation of cyanine dyes is extremely favoured by strong attractive dispersion forces derived from the high polarizability of the chromophoric chain in aqueous solution. Moreover, the high dielectric constant of water facilitates the aggregation process by reducing the electrostatic repulsion between similarly charged dye molecules [14–17]. Aggregation of cyanines occurs also in mixed solvents [18–21] and in heterogeneous media, e.g. micelles [22,23] or vesicles [24]. Moreover, DNA is able to act as template for the supramolecular assembly of cyanines [25].

Pinacyanol (1,1'-diethyl-2,2'-carbocyanine) chloride (PIN), is a cationic dye that belongs to the class of conjugated cyanine dyes (Fig. 1a). The theoretical PIN monomer geometry determined by minimal energy analysis using the MM2 molec-

ular mechanics and the molecular orbital calculations shows a resulting structure with a dihedral angle  $\psi$  of  $\sim 36^\circ$  between the rings of both sides of the central aliphatic chain (Fig. 1b and c). This torsion confers non-planar properties to PIN monomer that can affect its self-association. Similar dihedral angles have been observed in other planar dyes [26,27]. PIN is soluble over a very wide range of solvents and shows a bathochromic absorbance shift with reducing solvent polarity [4]. PIN aggregates in water taking place an equilibrium between nonaggregated (monomer) and aggregated forms (dimers, trimers, and aggregates of superior order).

In aqueous solution, the visible absorption spectrum of PIN consists of three overlapping spectral bands, with the most intense band red-shifted relative to the others. These bands are centered at 600, 550 and, approximately, at 520 nm. The first of them is usually interpreted as the vibrationless electronic  $S_0 \rightarrow S_1$  transition, and the other two as the same electronic transition under vibration cooperation. With increasing dye concentration, the spectrum undergoes some variations: the peak at 600 nm diminishes, whereas that at 550 nm increases [28,29].

In determined circumstances, such as very high PIN concentration (near to solubility limit), or in low sodium dodecyl sulfate (SDS) submicellar concentration, or when the dye is adsorbed on colloidal surfaces, all these bands decrease with

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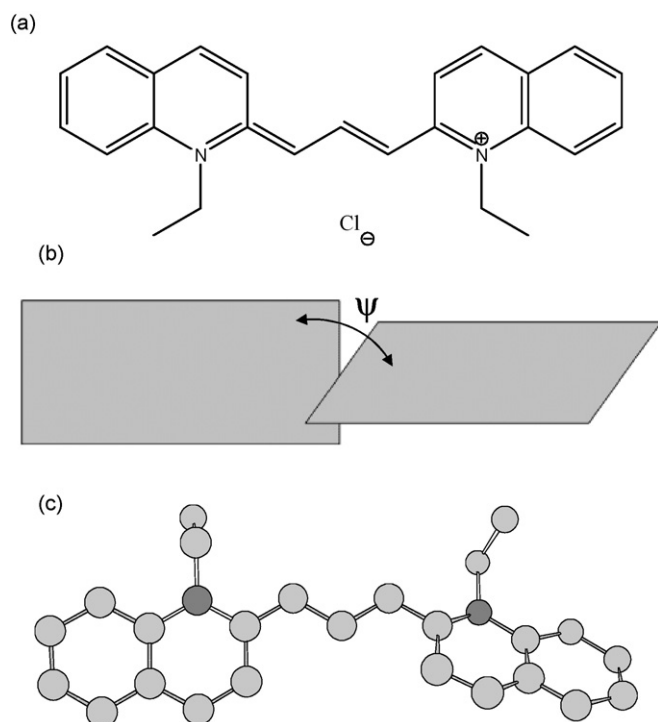


Fig. 1. Structural representations of isolated pinacyanol monomer. (a) Structure of pinacyanol, (b) schematic rotational representation, and (c) geometrical monomer optimization.

simultaneous appearance of a new absorption band centered at 495 nm [15,30]. This behaviour is suggestive of self-aggregation of PIN molecules. Among these aggregates, there are the so-called H-aggregates [31] that are characterized by a one-dimensional array of molecules in which the transition moments of individual monomers are aligned parallel to the line joining their centers (end-to-end arrangement). The association of several monomers entails the formation of different possible dye structures that may be explained by exciton chromophore coupling, based on the coupled oscillator theory (see Supplementary material) [32].

At low dye concentrations, the observed spectrum of an aqueous solution of PIN is mainly a superposition of the spectra of the monomer and the dimer, which concentrations are determined by the dimerization constant. However, other higher order aggregates can be present and contribute to the resulting spectrum. Hence, considering only the presence of dimers and monomers, the calculated dimerization constant bears an undetermined associated error. Moreover, PIN in water presents a thermotropic effect, which results from the equilibrium between the chemical species present. Hence, increasing the temperature entails the increase of monomers in relation to the dimers, and of dimers in relation to aggregates of superior order.

Many photophysical processes and photochemical reactions of organic molecules involve associated molecules. Photoreactions in natural processes, e.g. photosynthesis in green plants and photosynthetic bacteria, as well as in certain technical processes, e.g. spectral sensitization of silver halide emulsions, occur with aggregates of the photosynthetic pigments and cyanine dyes, respectively [33]. Flavins are coenzymes and photoreceptors that

play an important role in numerous basic biological processes. One of the most important flavin coenzymes, flavin mononucleotide, can act as trap for excitation energy when it is in dimer form [34]. Thus, the accurate quantitative estimation of the dimerization constant is of great importance in many process and reactions.

Here, we present a way of circumventing the contribution of aggregates of superior order to the PIN spectrum and, in consequence, of correcting the dimerization constant. This approach is based on the determination of apparent dimerization constants at different temperatures. An increase of temperature shifts the equilibrium to the formation of monomer species, that is, the ratio monomer/dimer increases, but, in turn, the ratio dimer/higher order species also increases. In these circumstances it is possible to consider a zone of the visible spectrum where only the monomer and dimer species have a significant influence, and from these data to obtain a more realistic value of the dimerization constant, as well as the thermodynamic quantities associated to the dimerization process.

## 2. Experimental

### 2.1. Materials

PIN was obtained from Sigma (St. Louis, MO, USA). Solutions were prepared in double-distilled water purified through a Milli-Q system (Millipore, USA).

### 2.2. Solution preparation

Stock solutions of PIN were prepared in chloroform. When necessary, the required amount was placed in round-bottomed flask and evaporated at reduced pressure. To remove chloroform traces, the residue was freeze-dried overnight and then the appropriate aqueous solution was prepared. All PIN preparations were kept in the dark and wrapped in aluminum foil to avoid photodecomposition during storage. To minimize dye adsorption, glassware and cuvettes were silanated with 1% (v:v) dichloromethylsilane:toluene solution and then rinsed with methanol.

### 2.3. UV/vis spectroscopic measurements

Visible absorption spectra were recorded with a Shimadzu UV-2401 PC UV–vis spectrophotometer (Shimadzu, Japan) using a matched pair of glass cuvettes of 1 cm optical length placed in a thermostated cell holder kept at different temperatures.

### 2.4. Spectral overlapping peaks determination

From the fourth derivative spectrum of PIN we obtained previously that any PIN spectrum was formed by three bands (actually, the number of bands was five, but two of them were so little that it is acceptable to neglect them). Hence, PIN spectra (from dimer or from monomer) were fitted to three overlapping Gaussian curves and the amplitude, center and bandwidth at half

of the maximum amplitude and area of each Gaussian function were been calculated using a non-linear peak fitting program (PeakFit package, Systat Software, San Jose, CA, USA).

### 2.5. Determination of the dimerization constant

Assuming the only existence of dimers and monomers of PIN in an aqueous solution, the equilibrium between monomer and dimer ( $2M \leftrightarrow D$ ) at a temperature  $T$  is described by the dimerization constant  $K_D$ , which is given by the ratio between the molar concentrations of dimers,  $C_D$ , and monomers,  $C_M$ , at equilibrium:

$$K_D = \frac{C_D}{C_M^2} \quad (1)$$

On the other hand, the total absorbance of a PIN solution per unity of optical length at a given wavelength ( $A(\lambda)$ ) is:

$$A(\lambda) = \varepsilon_M(\lambda)C_M + \varepsilon_D(\lambda)C_D \quad (2)$$

where  $\varepsilon_M$  and  $\varepsilon_D$  represent the molar absorption coefficients of monomeric and dimeric species, respectively, at a wavelength  $\lambda$ .

From Eqs. (1) and (2) and considering the mass balance of PIN in the volume dispersion, the following equation is obtained:

$$A(\lambda) = \varepsilon_D(\lambda) \left( \frac{C}{2} - \frac{-1 \pm \sqrt{1 + 8K_D C}}{8K_D} \right) + \varepsilon_M(\lambda) \left( \frac{C}{2} - \frac{-1 \pm \sqrt{1 + 8K_D C}}{4K_D} \right) \quad (3)$$

where  $C$  is the total analytical concentration of PIN.

By plotting the measured absorbances as a function of dye concentration at any wavelength, the molar absorptivity of monomer,  $\varepsilon_M(\lambda)$ , and dimer,  $\varepsilon_D(\lambda)$ , as well as the dimerization constant,  $K_D$ , were calculated using a non-linear least-squares fitting routine program.

## 3. Results and discussion

### 3.1. Dimerization constant determination

From spectral data of PIN at different concentrations, we have obtained the values of dimerization constant (Table 1) and the molar absorptivities of monomer and dimer. However, it is

Table 1

Real ( $K_D$ ), apparent ( $K_D^{app}$ ) dimerization constants, dimerization constant variations ( $\Delta K_D$ ) and standard Gibbs energy change of dimerization ( $\Delta_r G^\circ$ ) at different temperatures

| $T$ (K) | $K_D$ (L mol <sup>-1</sup> ) | $K_D^{app}$ (L mol <sup>-1</sup> ) | $\Delta K_D$ (%) | $\Delta_r G^\circ$ (kJ mol <sup>-1</sup> ) |
|---------|------------------------------|------------------------------------|------------------|--|
| 294.16  | 35,002                       | 31,307                             | 10.56            | -25.59                                     |
| 297.16  | 28,745                       | 27,266                             | 5.15             | -25.36                                     |
| 303.16  | 20,820                       | 19,304                             | 7.28             | -25.06                                     |
| 310.16  | 14,037                       | 13,368                             | 4.77             | -24.63                                     |
| 318.16  | 10,024                       | 8,255                              | 17.65            | -24.37                                     |
| 325.16  | 6,744                        | 6,466                              | 4.12             | -23.84                                     |

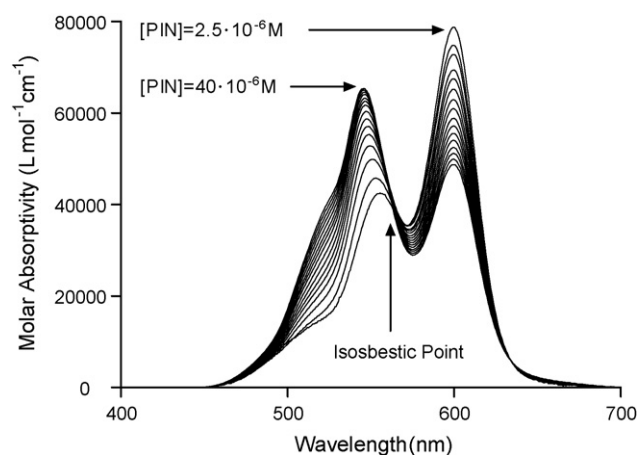


Fig. 2. Apparent variation of the molar absorptivity of PIN as a function of dye concentration at 310.16 K.

known that PIN has a natural tendency to aggregate spontaneously in solution when its concentration is increased or the temperature is lowered. In this way, when dye molecules aggregate, the absorption spectrum undergo a change in comparison with the one obtained with the monomer, and, apparently, the Lambert–Beer law is not obeyed (Fig. 2). As the aggregation process starts at relative low concentrations, at the first stages it is possible to study the equilibrium between monomer and dimer, since they represent the main species present in solution. However, considering that the equilibrium monomer–dimer is the unique equilibrium existing at low concentration is only a simplification. Thus, the dimerization constants obtained directly from Eq. (3), are, actually, apparent dimerization constants, and if one wants to achieve a more precise characterization of the monomer–dimer equilibrium and a more exact value of the dimerization constant, it is essential to consider the presence of aggregate species of superior order.

We have employed a simple method to obtain more realistic values of the dimerization constant. The method consisted in determining the apparent dimerization constant and molar absorptivities at several temperatures. Once the molar absorptivities were obtained, the theoretical spectrum of monomer (Fig. 3a) and dimer (Fig. 3b), were generated. It is important to remark that while the monomer spectrum remains without changes in the temperature range used, that of the dimer changed as a function of temperature, and an isosbestic point appeared, which indicates the existence of a thermotropic effect which results from the equilibrium between two chemical species. Such thermotropic effect is different of a thermotropic shift, which is the gradual displacement of the absorption or emission spectrum of molecules according to the temperature of the solvent. In a thermotropic shift there is no isosbestic point; the maximum of the spectrum moves continuously with the temperature.

The dimer spectrum presents a strong band at 550 nm and a weak band at 625 nm. The first is blue-shifted with respect to the monomer transition and it can be considered an H-band, whereas the additional red-shifted band is a J-band. A two-band absorption spectrum is explained by the Davidov splitting [35] and it is observed when two chromophore molecules are arranged in a

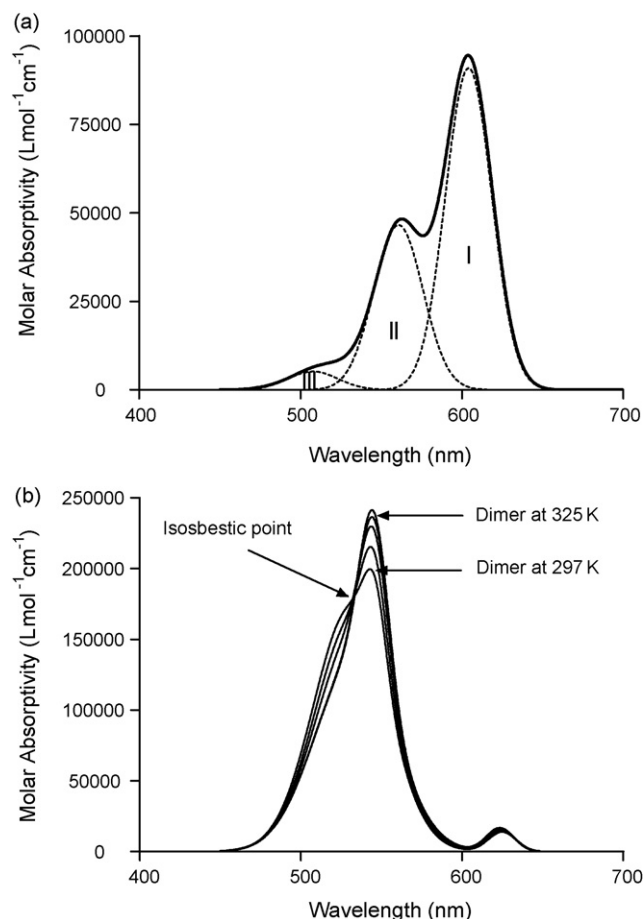


Fig. 3. Absorption spectrum of (a) monomer, and (b) dimer at different temperatures.

nonzero angle between their transition dipole moments. The two absorption bands correspond to the sum (H-band) and difference (J-band) of the transition dipole, and the tilt angle between the molecules determines the intensity of both bands [36–39].

The dimer spectrum showed two important features: first, the peak at 550 nm increased with the temperature. This increase is however lower temperature. Upon temperature increase, the band at 550 nm exhibited a little hypsochromic shift. This behaviour has been also observed in a well-related dye, merocyanine, and it is suggested that it arises because, at high temperatures, the electronic structure of the ground state of cyanines approaches that of neutral polyenes, whereas at low temperatures, this structure is similar to the structure of ideal polymethine [40]. Second, spectra from 550 to 650 nm were almost identical, independently of the temperature.

There are two main reasons to explain the existence of a changing dimer spectrum as a function of temperature: the formation of dimer species with an oblique association, or the contribution of order superior aggregates in the dimer spectrum. If the arrangement of the two chromophores in a dimer is neither in-line (J-aggregates) nor parallel (H-aggregates), it results in either a broadened band spectrum or a two-band spectrum. The broad band is obtained when the chromophores are chi-

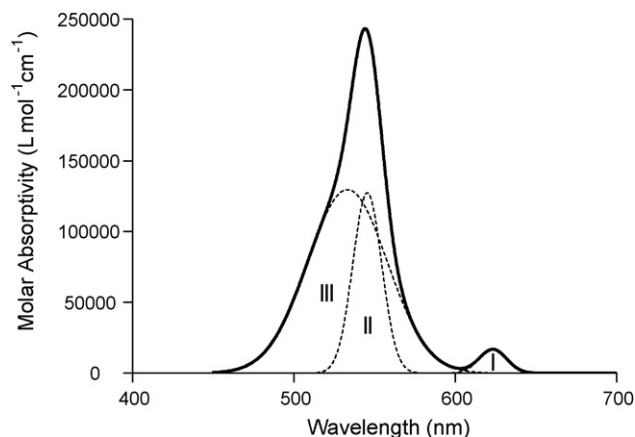


Fig. 4. Absorption spectrum of the pure dimer of PIN in aqueous solution. This spectrum was generated after obtaining the dimerization constant in absence of any species of superior order ( $K_D$ ).

rally disposed (see Supplementary) [16,17,41,42]. In this case, the splitting is easily determined by circular dichroism [43,44]. We have not observed this effect when the circular dichroism spectrum was obtained. However, the absence of a CD-signal does not contradict the existence of H-aggregates with oblique orientations of the respective monomers.

To determine the real dimerization constant, it is necessary to know the spectrum of the dimer without any contribution of superior order aggregates. As the increase of absorbance at the maximal wavelength near 550 nm as a function of temperature follows an asymptotical curve (not shown), it is possible to obtain the limit value of this increase, that is, the value at very high temperature when only the dimer is present. From this value, the spectrum of pure dimer can be obtained (Fig. 4). Now, the real value of the real dimerization constant ( $K_D$ ) is determined using Eq. (3) and spectra of pure dimer and monomer (Table 1). To determine a more accurate value of  $K_D$ , only the wavelengths ranging from 550 to 650 nm were used. As indicated above, the contribution of superior order species to PIN spectra is negligible in this range of wavelength. As can be seen in Table 1, the values of the dimerization constants are in the order of  $10^3$ – $10^4$  L mol<sup>-1</sup>, depending on the temperature, which is consistent with literature results [33,45,46]. Moreover, it can be inferred from the table that  $dK_D/dT < 0$ , that is, the dimerization is an exothermic reaction.

The  $\Delta K_D$  (representing the error between  $K_D$  and  $K_D^{\text{app}}$  expressed as a percentage) at the different temperatures is in a range from 4.12 to 17.65% (see Table 1.). This significant variation between  $K_D$  and  $K_D^{\text{app}}$  fully justifies the utilization of a method that allows correcting for the contribution of superior order aggregates.

### 3.2. Thermodynamic parameters determination

As Le Chatelier principle predicts that a system in equilibrium will be tend to shift under the influence of the temperature, it is interesting to determine the thermodynamic parameters associated to the dimerization reaction.



The standard Gibbs energy change of dimerization ( $\Delta_r G^\circ$ ) can be calculated from the expression

$$\Delta_r G^\circ = -RT \ln K_D \quad (4)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature. Table 1 shows the results obtained.

At constant pressure, the standard enthalpy change ( $\Delta_r H^\circ$ ) and standard entropy change of dimerization ( $\Delta_r S^\circ$ ) can be obtained from the van't Hoff equation [47]:

$$\frac{d \ln K_D}{d(1/T)} = -\frac{\Delta_r H^\circ}{R} \quad (5)$$

Plotting  $\ln K_D$  in front of the reciprocal of the absolute temperature, a linear relationship is obtained ( $r=0.9969$ ). The straight line presents a slope of 5.1146 K. This equals to  $-\Delta_r H^\circ/R$ , and therefore,  $\Delta_r H^\circ$  is  $-42.52 \text{ kJ mol}^{-1}$ . In an exothermic reaction,  $-\Delta_r H^\circ/T$  corresponds to a positive change of entropy of the surroundings and favours the formation of the products. When the temperature is raised,  $-\Delta_r H^\circ/T$  decreases, and the increasing entropy of the surroundings has a less important role. Once the enthalpy change is calculated, the entropy change at any temperature within the studied interval can be determined from the expression

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (6)$$

Entropy values range from  $-57.56 \text{ J mol}^{-1} \text{ K}^{-1}$  at 294.16 K to  $-57.45 \text{ J mol}^{-1} \text{ K}^{-1}$  at 325.16 K.

We can affirm that dimerization is driven by enthalpic factors traceable to strong attractive van der Waals interaction between the two large and highly polarizable dye molecules. Conversely, entropic contributions to Gibbs energy change favour the dimer dissociation, but are smaller than the enthalpic ones.

### 3.3. Conclusions

We have studied the influence of the temperature on the spectral properties of PIN, a dye that exhibits a thermotropic effect. An increase of temperature involves a shift of the equilibrium towards the less aggregated species. This fact has allowed to us to obtain the spectrum of the dimer without any interference from aggregates of superior order, and from it, to determine the dimerization constant with high accuracy. Thermodynamic parameters associated to dimerization are concordant with a spontaneous process driven by enthalpic factors.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2007.09.004.

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