

## Spectral studies of Pinacyanol Chloride in Sodium Alkyl Sulfate

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### Abstract

Interaction of pinacyanol chloride (PIN) with anionic surfactants at premicellar and postmicellar concentration range was studied by visible spectrophotometry and these interaction produces a blue shift metachromatic band (at  $\sim 490$  nm), which gradually shifted to higher wavelength region as the concentration of sodium alkyl sulfate increased in the premicellar region. PIN-micelle binding constant ( $K_C$  and  $K_C'$ ) was determined from spectral data for post micellar stage and premicellar stage.

**Keywords:** Pinacyanol Chloride; Anionic surfactant; Binding constant.

### 1. Introduction

Pinacyanol chloride (1,1'-diethyl-2,2'-carbocyanine) (PIN) is a cationic dye that belongs to the class of conjugated cyanine dyes. The amphipathic nature of these dyes confers solubility in a wide range of solvents, including water and chloroform. It can form aggregates. A strong dispersion force associated with the high polarizability of the chromophoric chain favors the aggregation of cyanine dyes in aqueous solution. The high dielectric constant of water facilitates the aggregation process by reducing the electrostatic repulsion between similarly charged dye molecules [1]. Cyanine dyes are intensively colored, polymethine dyes and have been frequently used as optical probes in the study of membranes, surfactants, micelles, proteins, amyloid fibrils, and dendrimer-based host systems [2-5]. As a redox indicator, it is used to monitor peroxide activation [6]. In health sciences, it has been observed that PIN causes respiratory immunogenicity [7]. PIN has been used to study bacterial polysaccharides [8].

Aggregation produces new spectral bands, now commonly referred as the J and the H band [9]. H aggregates are spectroscopic entities that are characterized by a blue-shifted absorption band with respect to monomer absorption, whereas J aggregates present a red-shifted band. H aggregates appear at low concentration prior to the formation of the J aggregates. In water, maxima of such spectral components can be located at 600,

550, and  $\approx 520$  nm. The first one 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 enhances.

Surfactants form organized structure both in polar and nonpolar media due to the presence of polar head and nonpolar tail groups [10]. They play key role in synthetic, analytical, pharmaceutical and industrial fields. Surfactants, both in pre- and post- micellar concentration ranges, can affect the electronic absorption spectra of many dyes [11]. Hence, spectroscopic techniques can be used to determine certain physic-chemical properties of surfactant aggregates [12].

A number of research works in the field of the interactions between surfactants and dyes in both aqueous and non-aqueous media have been reported [13-14]. Dye-surfactant interaction has importance in various dyeing processes such as textile dyeing, photography, printing ink and inhibition of dye transfer in detergency as well as in biochemistry, analytical chemistry, and photosensitization. Panda et al [15] have studied the interaction of pinacyanol chloride with binary surfactants in aqueous medium. Sabate *et al.* [16] have located pinacyanol in micellar solutions of N-alkyl trimethylammonium bromide surfactants. The interaction of Coomassie brilliant blue G250 with CTAB was studied by Gao et al. [17].

Although several reports are there on the studies of surfactant and solvent effect on dyes but still such studies are considered to be fragmentary in nature on the basis of spectral behavior of Pinacyanol Chloride with different anionic surfactants and solvents. Despite of numerous applications of Pinacyanol Chloride dye in various areas, information on the spectral properties of the dye in various solvents and different anionic surfactants required for understanding its spectral behavior is incomplete. The aim of this work is to investigate the effect of different anionic surfactants by varying its chain length on the cyanine dye and to evaluate the binding constant between dye and surfactant at pre-micellar and post-micellar stage. The chemical structure of the investigated dye is presented in the inset of Fig. 1.

## 2. Experimental

Pinacyanol Chloride (PIN) was purchased from Sigma-Aldrich (USA) and was used as such. Sodium dodecylsulfate  $C_{12}H_{25}OSO_3^-Na^+$  (SDS), sodium tetradecyl sulfate  $C_{14}H_{29}OSO_3^-Na^+$  (STS) and sodium hexadecyl sulfate  $C_{16}H_{33}OSO_3^-Na^+$  (SHS) were purchased from Sigma-Aldrich (USA). The purity of the sample was > 99%. Absorption spectra of PIN in water, and different solvents were recorded using a Lambda 25

spectrophotometer (Perkin-Elmer, USA). A stock solution of PIN of concentration  $10^{-5}$  mol dm<sup>-3</sup> was prepared using double distilled water and wrapped with black paper kept at 4<sup>0</sup>C. The CMC values are taken from literature [18].

### 3. Results and discussion

#### 3.1. Absorption spectra of PIN in aqueous medium

Visible absorption spectra of PIN in aqueous medium at different concentrations ranging from  $1 \times 10^{-6}$  to  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> showed that the intensity of both monomeric and dimeric bands increased with the increase of dye concentration. The shape of the visible absorption spectrum of PIN in water was dependent on the dye concentration, as we can see in **Fig.1**. At low concentrations, band absorption at 600 nm predominated slightly over that observed at ~558 nm, whereas in more concentrated solutions, this later was clearly higher than the most red-shifted band. This fact provoked a lack of linearity in the plot of absorbance vs dye concentration; that is, the Lambert Beer law did not hold, as a consequence of the presence of monomer molecules of PIN, as well as its dimer form. It was found that there are three overlapping spectral components: the first one at 600 nm (monomer peak), second one at 550 nm (dimer peak) and another at 517 nm (peak for higher aggregates of PIN); which were found to be comparable with the earlier reported results [1].

#### 3.2. Interaction of PIN with anionic surfactants

Effect of anionic surfactants at various concentrations on the absorption spectra of PIN was studied. It was observed that at pre-micellar stage, a new band at ~490 nm (metachromatic band) at the cost of its monomeric and dimeric peaks was observed and on progressive addition of surfactant a red shift in this band along with hyperchromic effect was also observed. After certain concentration of anionic surfactant was reached no further shift in band of PIN was observed; only the intensity of peak increased. **Fig. 2** shows (as representative) the spectra of PIN in the presence of varying concentration of STS in aqueous medium at 298 K. The above result indicates the electrostatic interaction between dye and surfactant. However, in the post-micellar stage, the dye molecules became complexed with anionic surfactants, no further shift of band occurred.

The length of the hydrophobic tail of the sodium alkyl sulfate surfactants affect some properties of the micelles; for example, a decrease in the length increases the cmc, and the degree of micelle dissociation decreases the micellar aggregation number and the thickness of its Stern layer. As a result, the hexadecyl chain

micelles are smaller and less compact and their Stern layers are more ionic than their dodecyl (SDS) chain counterpart.

### 3.3. Determination of binding constant between dye-surfactant systems

The binding constant ( $K_C$ ) was calculated by using the Benesi-Hildebrand equation [19] valid at higher concentration, was used in the following modified form [20-21]:

$$\frac{D_T}{\Delta A} = \frac{1}{\epsilon_m - \epsilon_o} + \frac{1}{K_C(\epsilon_m - \epsilon_o)C_m} \quad (1)$$

where  $D_T$  is the total concentration of PIN,  $\Delta A = A - A_0$ ,  $A$  and  $A_0$  which are the absorbance of PIN in the presence and absence of surfactants, respectively,  $\epsilon_m$  is the molar extinction coefficient of the dye fully bound to micelles determined in large excess of the micelles.  $C_m$  is the concentration of the micellized surfactant ( $C_m = [\text{total surfactant concentration} - \text{CMC}] / n$ ).

The plot of  $\frac{D_T}{\Delta A}$  versus  $\frac{1}{C_m}$  was found to be linear in all cases showing 1:1 complex. The  $K_C$  values derived from the slope and intercept of the straight line are presented in **Table 1**. Free energy changes were calculated from the relation  $\Delta G^0 = -RT \ln K_C$ . The negative sign of  $\Delta G^0$  indicates the spontaneity of the binding of PIN with sodium alkyl sulfate. The dye-micelle complexes have different degrees of affinity following the order: SHS > STS > SDS which follows reverse order with CMC values. Since  $K_C$  varies inversely with the CMC, a good correlation can be observed by plotting  $\log K_C$  vs  $\log \text{CMC}$  as shown in **Fig. 3** and can be fitted as

$$\log K_C = \log A - \phi \log \text{CMC} \quad (2)$$

where  $A$  and  $\phi$  are appropriate constants. The values of  $\log A$  and  $\phi$  calculated from the plots in Fig. 3. It is observed that the larger the non-polar tail in the sodium alkyl sulfate, the stronger the complex, indicating a direct correlation of complexation with hydrophobicity.

**Inset of fig. 3** shows the relationship between the logarithm of the CMC and the alkyl chain length. This Fig. shows that the relationship between the logarithm of the CMC and the alkyl chain length is linear.

The binding constant ( $K_C'$ ) at pre-micellar stage was calculated using Rose-Drago equation [22] at different temperatures.

$$\frac{C_D \cdot C_S}{A - A_0} = \frac{1}{K_C' \cdot L(\epsilon_{DS} - \epsilon_D)} + \frac{C_S}{L(\epsilon_{DS} - \epsilon_D)} \quad (3)$$

Where,  $C_D$  = Initial concentration of the dye,  $C_S$  = Initial concentration of the surfactant,  $A_0$  = Absorbance of the pure dye solution at  $\lambda_{max}$ ,  $A$  = Absorbance of the dye-surfactant solution at  $\lambda_{max}$ ,  $K_C'$  = Binding constant between the dye and surfactant,  $\epsilon_D$  = molar absorption coefficient of the dye,  $\epsilon_{DS}$  = molar absorption coefficient of the dye-surfactant complex,  $L$  = Length of the light path.

Plot of  $(C_D \cdot C_S)/(A - A_0)$  versus  $C_S$  at 298 K shows a linear relationship. From the slope and intercept of the straight lines, the interaction constant ( $K_C'$ ) values were calculated. All thermodynamic properties calculated from this method are summarized in Table 2. The value of binding constant between dye-surfactant systems for pre-micellar stage is not appreciable as in post-micellar stage because both hydrophobic and electrostatic interaction takes place in post-micellar stage.

#### 4. Conclusion

PIN-sodium alkyl sulfate interaction was basically electrostatic in origin. When the effect of the length of the alkyl chain of surfactants and cyanine dye were investigated, the results indicated that hydrophobicity of alkyl chain plays an important role in the complex formation. Therefore, for the interaction between anionic surfactant and ionic dye both electrostatic and hydrophobic forces were important. Interaction of PIN with micellar systems depends on the hydrocarbon chain. It can be predicted from the above table that, the value of maximal absorbance is related to the number of methyl groups. In this way, SHS with a chain of 16 methyl gave the highest value, whereas the least corresponds to SDS with 12 methyl. That means that the more hydrophobic the molecule, the higher the hyperchromic effect produced. Dye-micelle binding constant values at higher concentration indicate 1:1 stoichiometry. The negative values of free energy change indicate the process to be spontaneous. The longer the alkyl chain of surfactant, higher is the  $K_C$  values.  $K_C$  varies inversely with the CMC. The  $K_C$  values of the complexes formed are linearly related to the CMCs of the sodium alkyl sulfate.

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**Table 1:** Spectroscopic and thermodynamic parameters of PIN in micellar medium at 298 K

Surfactants	CMC <sup>a</sup> mM	K <sub>C</sub> <sup>b</sup> (10 <sup>-6</sup> ) (mol dm <sup>-3</sup> )	K <sub>C</sub> <sup>'d</sup> (10 <sup>3</sup> ) (mol dm <sup>-3</sup> )	-ΔG <sup>Oe</sup> (kJ/mol)	λ <sub>mic</sub> <sup>*</sup> /nm
SHS	0.5	1.332	0.732	34.29	610.5
STS	2.1	1.025	0.678	34.20	608.3
SDS	8.0	0.921	0.654	34.15	607

CMC<sup>a</sup> is the critical micellar concentration of the surfactants taken from refs. [18]

K<sub>C</sub><sup>b</sup> is the dye-surfactant binding constant at post-micellar stage

K<sub>C</sub><sup>'d</sup> is the dye-surfactant binding constant at pre-micellar stage

ΔG<sup>Oe</sup> is the free energy change for post-micellar stage; λ<sub>mic</sub><sup>\*</sup>/nm is the absorption maxima of PIN at different surfactant

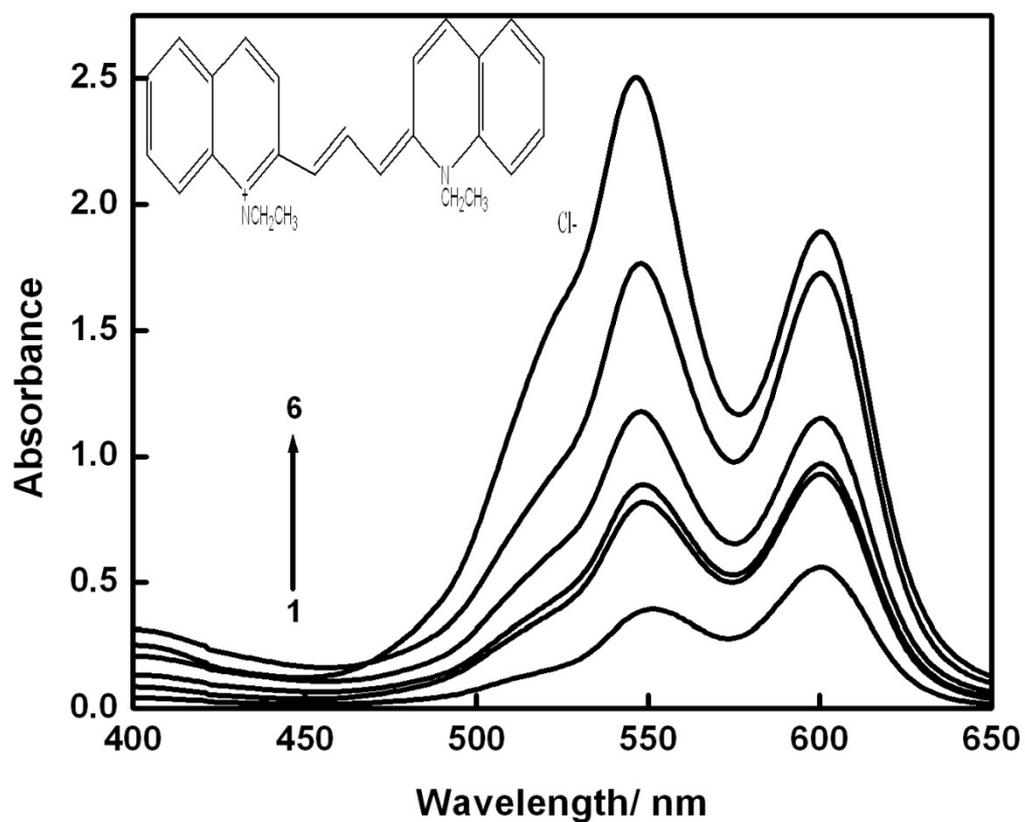


Fig 1: Visible absorption spectrum of PIN in various concentration of water; Inset: chemical structure of PIN

Concentration of PIN ( $\text{mol dm}^{-3}$ ) in water: 1,  $1 \times 10^{-6}$ ; 2,  $5 \times 10^{-6}$ ; 3,  $1 \times 10^{-5}$ ; 4,  $1.5 \times 10^{-5}$ ; 5,  $2.0 \times 10^{-5}$ ; 6,  $2.5 \times 10^{-5}$ .

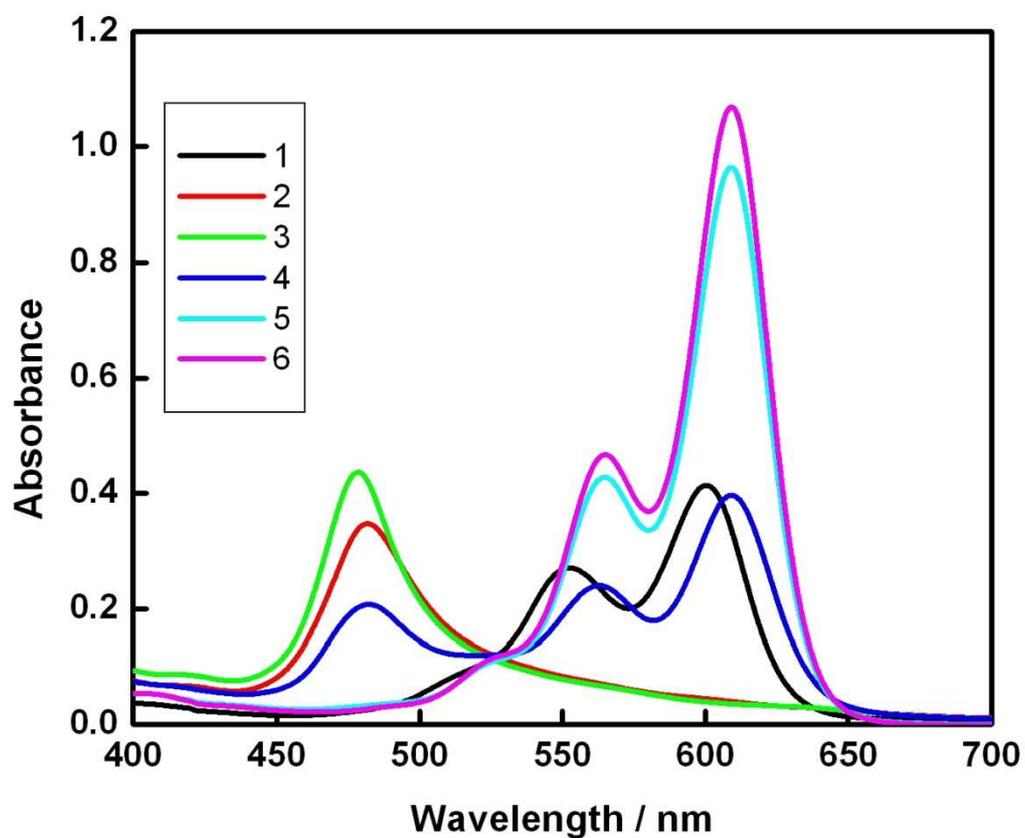


Fig 2: Visible absorption spectra of PIN ( $10^{-5}$  mol  $\text{dm}^{-3}$ ) in presence of varying concentration of STS in aqueous medium at 298 K. Concentration of STS ( $\text{mmol dm}^{-3}$ ): 1, 0; 2, 0.3; 3, 0.9; 4, 1.5; 5, 3.0; 6, 3.5.

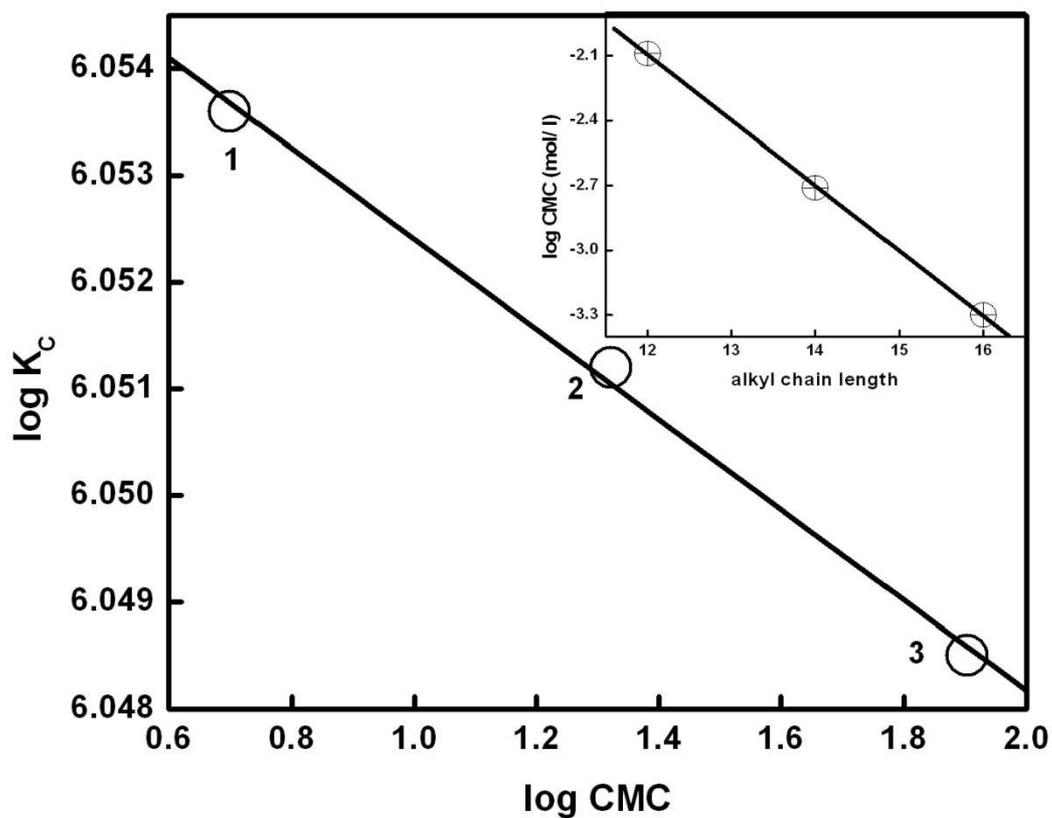


Fig 3: Variation in the dye-surfactant binding constant ( $K_C$ ) with the CMC of surfactants at 298 K. Inset: Dependence of critical micellar concentration (CMC) on the hydrocarbon chain length of surfactants. A  $10^{-5}$  mol  $\text{dm}^{-3}$  PIN was used in water. Surfactants used are: 1, SDS; 2, STS; 3, SHS.

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