## SPECTROPHOTOMETRIC STUDY ON PINACYANOL CHLORIDE AT DIFFERENT TEMPERATURES.

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Spectral changes of a cyanine dye, pinacyanol chloride, were observed. The aggregation ability of the dye in water, where only the monomer-dimer equilibrium exists, was investigated. The equilibrium constant, $K_a$, and thermodynamic parameters of dimerization were determined. The influence of the dye concentration and temperature variation on the dye aggregation was discussed. The results show that the dimer formation is favoured by negative enthalpy and by increase in entropy.

INTRODUCTION:

Very little work on cyanine dyes has been carried out with regard to their aggregation in aqueous and non aqueous solutions. Cyanines are currently investigated as sensitizers of solar-energy conversion systems through photochemical processes, with special attention being paid to their J-aggregates[1,2].

Cyanine dyes exist in solution in the monomeric form in equilibrium with the dimeric aggregates and/or the poly-

aggregates [2,3]. The concentration of the dyes in solution strongly affects these equilibria:

$$KD \rightarrow m \ [D.D] \rightarrow n \ [DD....D]$$
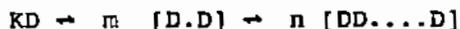
. The monomeric form persists in diluted solution, while the aggregated forms predominate in concentrated solutions. Aggregation of pinacyanol chloride in aqueous $SiO_2$-colloids showed that the aggregation process is a result of high local dye concentration in the vicinity of the colloid owing to the binding of the positively charged dyes to the negatively charged colloidal interface[1].

Absorption spectra of the cyanine dyes are strongly affected by the aggregation[6]. A variety of environmental factors such as hydrophobic dispersions and electrostatic factors affect the dye-dye interactions[3]. It is well known that solutions of cyanine dyes in polar organic solvents at room temperature follow Beer's law over an extended concentration range[6]. The effect of concentration on the aggregation of the Pyronine G dye has been studied using spectrophotometry[7]. It was shown that the dye spectra can be interpreted as being those of the dimerized dye.

In the present investigation we report a study on the effect of concentration, solvents and temperature variations on the aggregation parameters of pinacyanol chloride.

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EXPERIMENTAL:

   Quinaldine Blue, C.I. pinacyanol chloride, was obtained from Sigma Chemical Company, England. It was used as received. Its structure is:
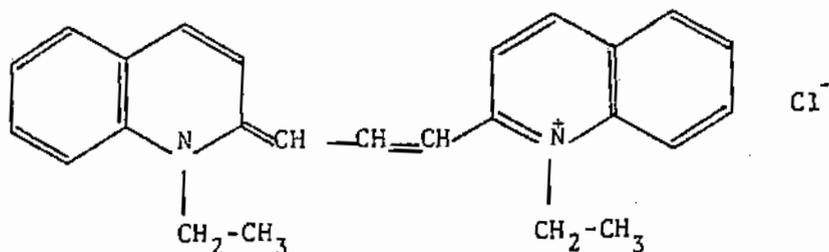


Analar acetone was used. The spectrophotometric measurements were carried out on a Perkin-Elmer Spectrophotometer model 555. Quartz cells of 0.5 and 1.0 cm standard path length were used.

   The dye solutions were prepared in distilled water and in acetone. The dye concentration range extended from 0.04–1.2 X $10^{-4}$ M/dm$^3$ in $H_2O$ and 0.1–3 X $10^{-5}$ M/dm$^3$ in acetone. The same measurements were carried out at different temperatures: 18, 25, 35 and 45°C. The aggregation parameters were calculated using the maximus slope method[8].

RESULTS AND DISCUSSIONS:

   The spectra of pinacyanol chloride have been measured at various concentrations ranging from 0.04 to 1.2 X $10^{-4}$

$M/dm^3$ in distilled water and from 0.1 to 3 $\times 10^{-5}$ $M/dm^3$ in acetone and at 18, 25, 35 and 45°C. The spectra are shown in Fig. (1). It is quite clear that there are two $\lambda_{max}$ for the dye in water at 600 and 547 nm and a shoulder at 520 nm. Pronounced effects of water on the absorption spectra of the dye can be noticed from the figures. The aggregation of the dye with increasing concentration is shown by the reduction in intensity of the molecular maximum at 600 nm and the appearance of a new maximum at 522 nm instead of a shoulder. These spectral changes may be attributed to the decrease of both the delocalization of the $\pi$-electron system and the charge transfer character of the two quinolinium moieties.

There is also a big shift and increase in intensity of the other band which appears in acetone at 560 nm and in water at 547 nm.

The dye solutions in acetone follow Beer's law at the concentration range 0.04 $\times 10^{-4}$ to 1.2 $\times 10^{-4}$ $M/dm^3$. The shape of the spectrum in acetone is typical for the molecular spectrum of cyanine dyes[5]. In aqueous medium, however, on increasing the dye concentrations, a peak corresponding to an isobestic point appears at shorter wavelength. According to the well known properties of the isobestic point, two coloured species are in equilibrium, the monomer form and the dimer form of the dye[6].

In Fig.(1), the position of the peak at 600 nm is generally similar in water and in acetone either on increasing the dye concentration or the temperature. This indicates the predominance of the monomeric species of the dyes under these conditions. From the above results, the following monomer/dimer equilibrium can be assumed $2M \rightleftharpoons D$.

Hence, the monomer and the dimer concentrations ($C_M$ and $C_D$ respectively) change according to the law of mass action as follows:

$$K_a = C_D/C^2_M,$$

where $K_a$ is the equilibrium constant for dimer formation. Plots of log $C_D$ against log $C_m$ at different temperatures and various concentrations are shown in Fig. (2). It is clear from the results that, for pinacyanol chloride, the slopes at 18 and 25°C have a value of 1.8. This value decreases on increasing the temperature to 45°C. These results are comparable with those obtained by other authors[1,2].

In the present study, the aggregation constant, $K_a$ and the aggregation number, n, were determined using the maximum slope method according to the equation:

$$\log C \, (\epsilon_1 - \epsilon) = n \log C \, (\epsilon - \bar{\epsilon}_{ao}) + \log nK_a \, (\epsilon_1 - \bar{\epsilon}_{ao})^{1.9}$$

(210)

Where $\epsilon$ = experimentally measured molar absorptivity for dye solution.

$\epsilon_1$ = monomer molar absorptivity.

$\epsilon_n$ = polymer molar absorptivity.

$\bar{\epsilon}_{no} = \epsilon_{n/n}$

This maximum slope method is described in detail elsewhere[6]. $K_a$, and n were calculated from the intercept and slope of the plots of log C $(\epsilon_1 - \epsilon)$ against log C $(\epsilon - \bar{\epsilon}_{no})$ Fig. (3). The results are shown in Table (1).

. The standard free-energy change for the dimer formation, $\Delta G$, and the change of entropy, $\Delta S$, have been calculated using the standard equations:

$$\Delta G = - RT \ln K_a$$

and $$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The values of $\Delta H$ were calculated by using the slope obtained from linear regression analysis.

The results in Table (1) showed that the dye dimerizes in aqueous solutions at 18°C. The increase of temperature causes the aggregation constant, $K_a$, to decrease significantly. This may be due to disaggregation on increasing the temperature which agrees with the results

obtained by other authors[9]. This can also be explained on the basis of the disruption of hydrogen bonds since the aggregation of the pinacyanol chloride is believed to be due to hydrogen bonding[1].

The calculated $K_o$ (9.8 X $10^4$) for the pinacyanol chloride dye is found to be consistent with those for cyanine dyes[1,6,10]. For cyanine and thiocarbocyanine dyes the value of K were vary from $10^3$ to $10^6$.

The importance of London-Van der Waal's forces and the contribution of dispersion forces associated with delocalized electrons to the self association of dyes[10,11] is well recognized. The influence of hydrophobic forces may be included. Water molecules at the hydrocarbon portion of the dissolved dyes have been considered to form structured region of low entropy, the so-called icebergs. The hydrocarbon-hydrocarbon interactions would displace this water and causes the system to gain entropy, leading to dye association[2].

It is clear from this study that the dye is almost molecularly dispersed at all temperatures in the non-aqueous medium using acetone. However, in aqueous media it has been

suggested that the aggregation of dyes may involve sandwiched water molecules as intermediates[12]. So acetone may prevent aggregation by making such intermediates water molecules unavailable. The effect of acetone on icebergs around the dye ions should, on the other hand, affect both monomers and the aggregated species.

The thermodynamic parameters of aggregation of the dyes in aqueous and non aqueous solutions at different temperatures are given in Table (2). The results show that dimer formation is accompanied by positive entropy change. The most likely candidate for the source of this positive entropy change is the Frank and Evance type of icebergs or structured regions of water around non polar solute[13]. Addition of solvents to the dimeric systems causes disaggregation and makes the entropy more negative. Thus, there is less negative free energy change of formation corresponding to disaggregation.

The low values for $\Delta H$ indicate weakly bonded species[10]. The $\Delta H$ value may arise from the combination of several types of interactions, particularly dispersive interaction of London type and hydrogen bonding. Hence,the results obtained are comparable with those reported for the dye pyronine G[7] ($\Delta G = -18.9$ KJ/mol, $\Delta H = -21$ KJ/mol) and with the results obtained using other techniques[9].

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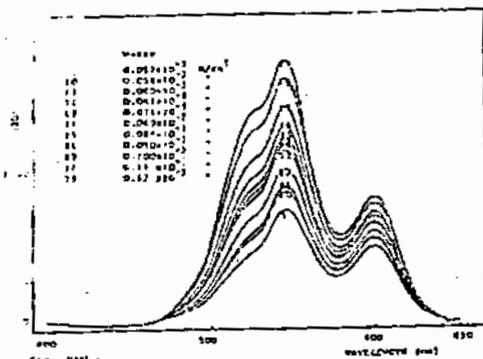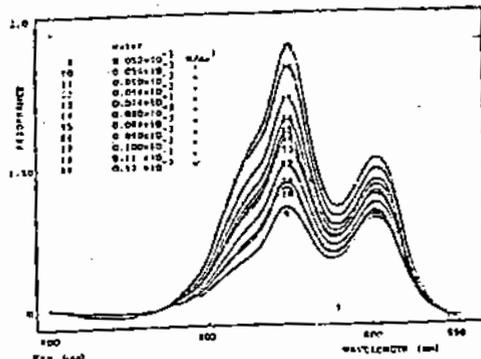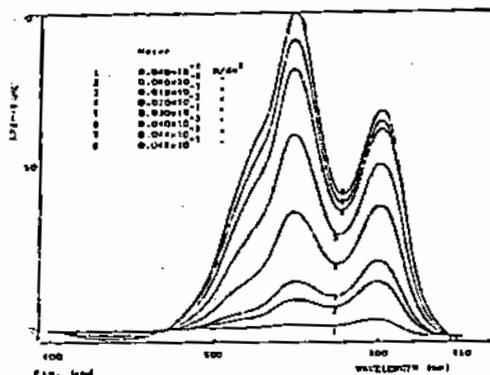at 18°C                                    at 25°C

Fig. (1)  Absorption spectra  of pinacyarol chloride at different
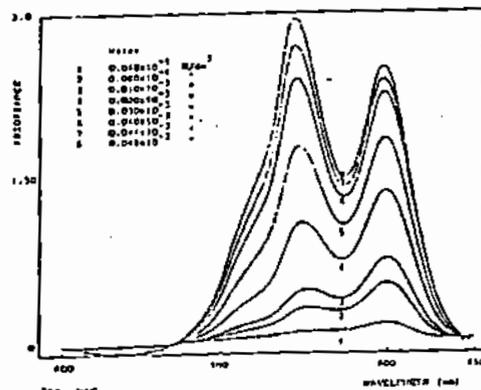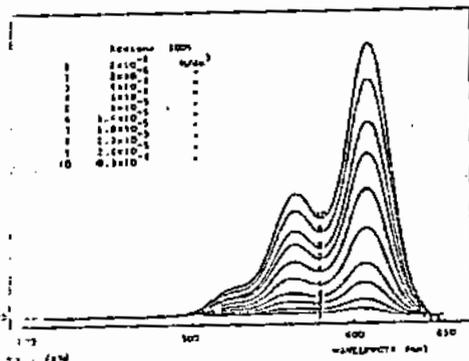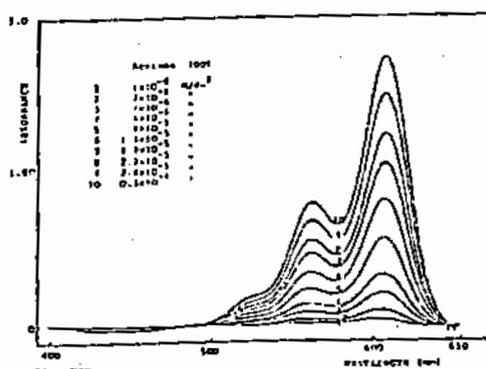temperature

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at 35°C                           at 45 °C

Fig. (1)  Continued. Absorption Spectra  of  pinacyanol Chloride at
         different  temperatures
                        (216)

(a) at 10 C

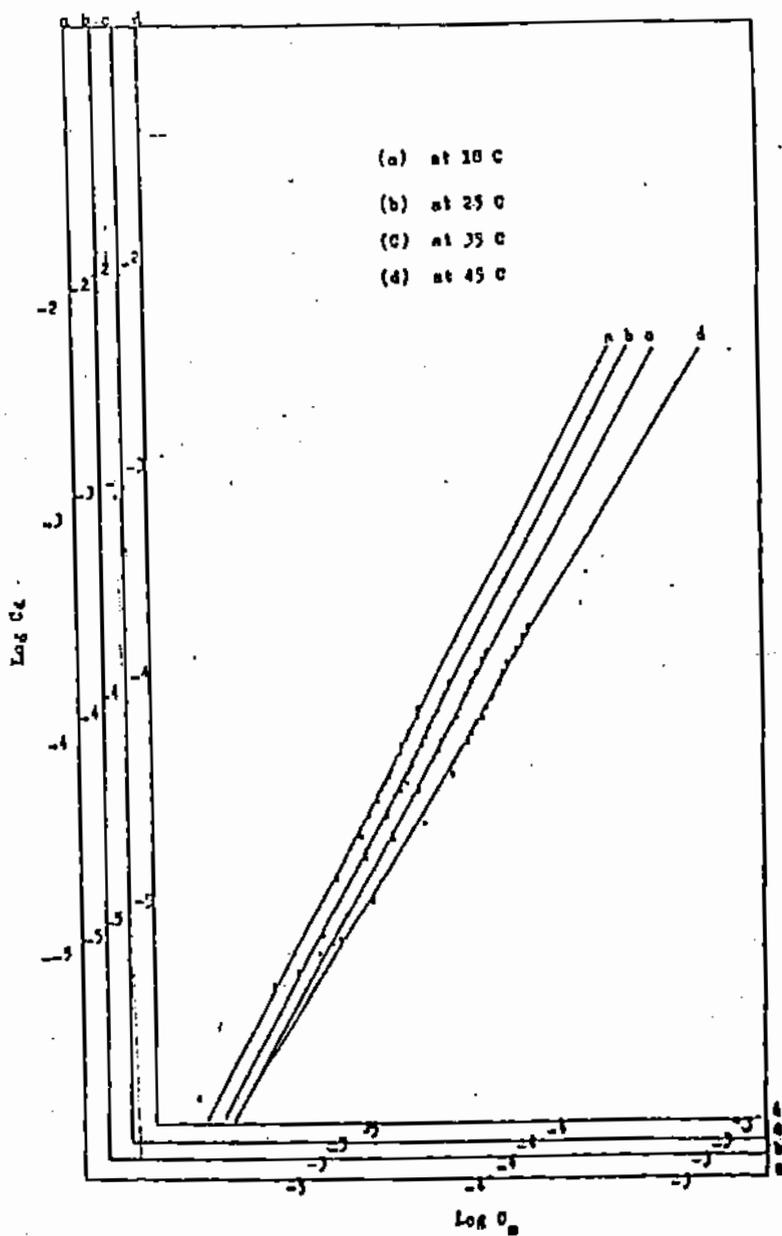(b) at 25 C

(C) at 35 C

(d) at 45 C

Log Cd

Log C_m

Fig.(2): Log θ_d Vs. Log C_m for Pinacyanol chloride
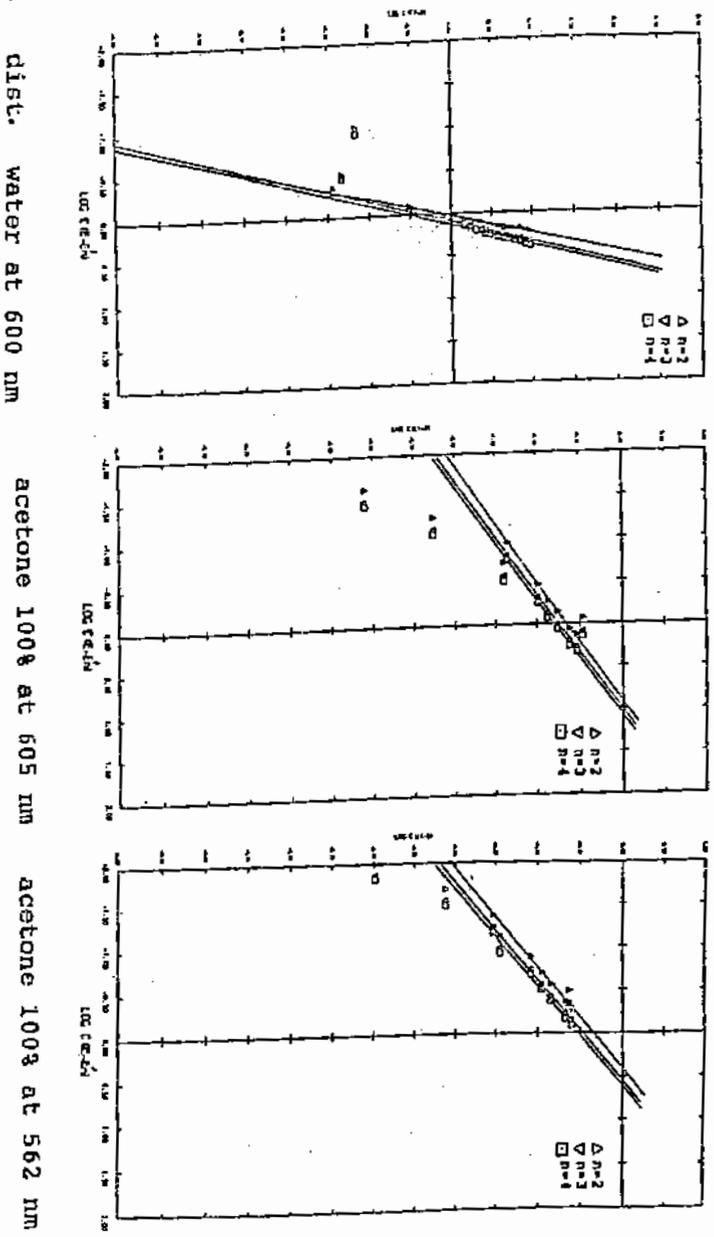in distilled water at different temperatures.

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Fig. (3): Relation between log C $(\varepsilon_1 - \varepsilon)$ and log C $(\varepsilon - \varepsilon_\infty)$ in dist. water and acetone for pinacyanol chloride at 25 °C.

dist. water at 600 nm    acetone 100% at 605 nm    acetone 100% at 562 nm

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Table (1) The aggregation Constants and Aggregation Numbers for Pinacyanol Chloride From The Maximum Slope Method.

**18°C.**

| Solv.Conc.(1V/V) | Agg.Cons.($K_n$) | Agg.Number (n) |
|---|---|---|
| Water | $7.5?0 \times 10^3$ | 2.4 |
| Acetone 100($\lambda$=605 nm) | $0.0062 \times 10^2$ | 1.1 |
| Acetone 100($\lambda$=562 nm) | $0.0053 \times 10^2$ | 0.9 |

**25°C.**

| Solv.Conc.(1V/V) | Agg.Cons.($K_n$) | Agg.Number (n) |
|---|---|---|
| Water | $5.98 \times 10^4$ | 2.2 |
| Acetone 100($\lambda$=605 nm) | $0.0052 \times 10^2$ | 1.0 |
| Acetone 100($\lambda$=562 nm) | $0.005 \times 10^2$ | 0.73 |

**35°C**

| Solv.Conc.(1V/V) | Agg.Cons.($K_n$) | Agg.Number (n) |
|---|---|---|
| Water | $4.64? \times 10^3$ | 2.0 |
| Acetone 100($\lambda$=605 nm) | $0.0050 \times 10^2$ | 0.9 |
| Acetone 100($\lambda$=562 nm) | $0.0040 \times 10^2$ | 0.7 |

**45°C**

| Solv.Conc.(1V/V) | Agg.Cons.($K_n$) | Agg.Number (n) |
|---|---|---|
| Water | $3.980 \times 10^3$ | 2.0 |
| Acetone 100($\lambda$=605 nm) | $0.0040 \times 10^2$ | 0.9 |
| Acetone 100($\lambda$=562 nm) | $0.0030 \times 10^2$ | 0.7 |

Table (2) Thermodynamic parameters for pinacyanol chloride.

| Solvent (% v/v) | T= 291°C | | T= 298°C | | T=303°C | | T=318°C | | ΔH KJ/mole |
|---|---|---|---|---|---|---|---|---|---|
| | ΔG KJ/mole | ΔS J/deg/mole | ΔG KJ/mole | ΔS J/deg/mole | ΔG KJ/mole | ΔS J/deg/mole | ΔG KJ/mole | ΔS J/deg/mole | |
| H₂O | -27.19 | +30.94 | -27.21 | +30.28 | -27.52 | +30.29 | -28.00 | +30.85 | -18.19 |
| Acetone At 605nm. | -1.16 | -37.44 | -1.52 | -36.58 | -1.78 | -25.39 | -2.42 | -34.40 | 12.64 |
| At=552 | -1.54 | 31.89 | -1.72 | 31.14 | -2.15 | -30.13 | -3.18 | -29.18 | -11.49 |