

Metachromasy Induced by Anionic Polyelectrolyte in Cyanine Dye

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Abstract

*The interaction of a cationic dye namely, Pinacyanol chloride (Pcyn) with anionic polyelectrolyte, namely, sodium alginate (NaAlg) has been investigated by spectrophotometric technique. The polymer induced metachromasy in the dye resulting in the shift of absorption maxima of the dye towards shorter wavelengths. The stability of the complex formed between Pcyn and NaAlg was determined by spectral studies. The thermodynamic parameters of interaction namely, K_C , ΔG , ΔH & ΔS were evaluated. They suggested a **weak** met achromatic complex was formed between Pcyn-NaAlg. This fact was further confirmed by reversal studies using alcohols, urea, electrolytes & surfactants. The reversal studies helps in the determination of the stability of the complex and the nature of binding.*

Keywords: *Metachromasy, Pinacyanol chloride, Aggregation, Binding Sites.*

INTRODUCTION

The interaction of the cyanine dye Pinacyanol chloride (Pcyn) with Klebsiella serotype K20 has been studied 1 by spectral measurements. The K10 polysaccharide is reported to exhibit chromotropic character with respect to induction of metachromasy in pinacyanol

chloride 2. A sharp single banded metachromasy at high P/D ratios and a broad multiple banded metachromasy at low P/D ratios been reported. The authors suggested that the anionic sites of the polysaccharides are not closely packed.

The interaction of pinacyanol chloride with K15 polymer was studied 3 by spectral measurements. The results of stoichiometry suggested stacking conformation. The interaction of K17 with pinacyanol chloride has been investigated 4-6 by spectral measurements and thermodynamic parameters have been evaluated. The interaction of pinacyanol chloride with K03 polysaccharide has been investigated by spectrophotometric method 7. The interaction of K14 with pinacyanol chloride has been studied 8,9 by spectral measurements. The interaction of K16 with pinacyanol chloride has been studied 10 by spectral measurements. The interaction of K10 with pinacyanol chloride has been investigated by spectral measurements 11. The interaction of K20, and K51 with Pinacyanol chloride was studied by absorbance and fluorescence

measurements 12. The interaction of Pinacyanolchloride with Heparin and sodium carragenate has been reported in the literature 13,14. The binding constant, changes in free energy, enthalpy and entropy of the dye polymer complex were also computed from the spectral data at different temperatures to reveal the nature of interaction.

METACHROMATIC STUDIES WITH POLYANIONS

The absorption spectrum of Pinacyanol chloride shows a peak at 600 nm (Fig.1). This band is assigned to the monomeric dye species in the concentration range studied. The intensity of monomeric band was found to decrease progressively upon addition of increasing amounts of polymer solution and the absorption maximum shifts to 493nm (Fig.1).

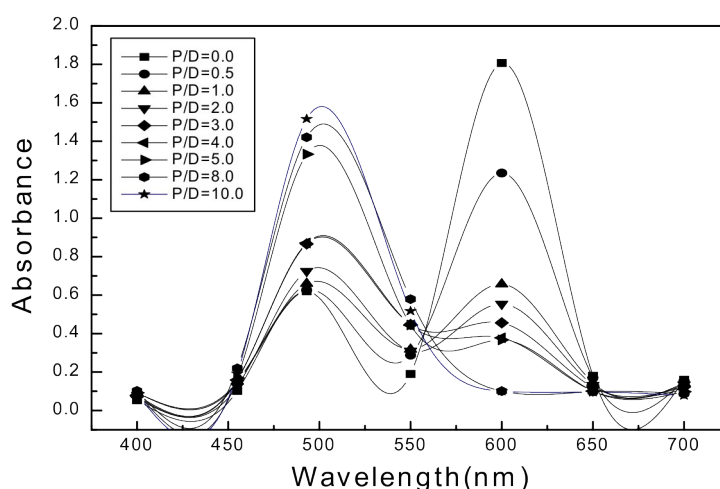


Fig.1 Absorption spectra of Pcyn-NaAlg complex

The blue shifted bands are attributed to the stacking of the dye molecules on the polymer backbone and this reflects high degree of co-operativity in binding 15. Appearance of multiple banded spectra proposed that the polymer might have a random coil structure in solution. Whereas at higher concentration of the polymer almost a single banded spectrum was observed due to possible change of polymer conformation from random coil to helical form 16.

Determination of Stoichiometry of Pcyn-NaAlg complex

To determine the stoichiometry of the polymer-dye complex, a plot of A_{600}/A_{493} versus the polymer/dye ratio was made for NaAlg - Pcyn system. The stoichiometry of NaAlg- Pcyn complex were found to be 1:1 which indicates that the binding is at adjacent anionic sites. This stoichiometry indicates that every potential anionic site of these two polyanions were associated with the dye cation and aggregation of such dye molecules was expected to lead to the formation of a card pack stacking of the individual monomers on the surface of the polyanion¹⁷. The results were in good agreement with the reported values for interaction of similar dyes with polyions¹⁸. This indicates that there is

lesser overcrowding and more aggregation of the bound dyes on the polymer chain in the latter case than in the former case. The result is shown in Fig.2.

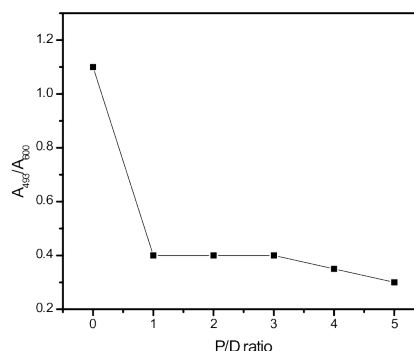


Fig.2. Stoichiometry of Pcyn-NaAlg complex

Reversal of metachromasy using various additives

The metachromatic effect is presumably due to the association of the dye ion with the polyelectrolyte resulting in extended interaction. The destruction of metachromasy by alcohol and urea is attributed to the involvement of hydrophobic bond in the induction of metachromasy. The fact that urea weakens hydrophobic bonding has already been established. This has¹⁹⁻²² been ascribed for breaking up of hydrogen bonds in water and thus destroying the icebergs which presumably are associated with fairly large scale cooperative structures stabilized by water-water hydrogen bonding. Thus urea increases the surface

tension of water slightly and reduces the dielectric constant appreciably. The efficiency of alcohols in disrupting metachromasy was found to be in the order methanol<ethanol< 2-propanol indicating that reversal becomes quicker with increasing hydrophobic character of the alcohols. For Pcyn-NaCar system, the percentage of alcohols needed for complete reversal of metachromasy was found to be 50% MeOH, 40% EtOH, and

30% PrOH. The result is shown in Fig.3. The molar concentration of urea needed for complete reversal of metachromasy was found to be 5M. The result is shown in Fig.4. This agrees with the results of other polyelectrolyte systems. Similar reports 23-25 are available in literature for reversal of metachromasy in anionic polyelectrolyte/cationic dye systems addition of alcohols or urea .

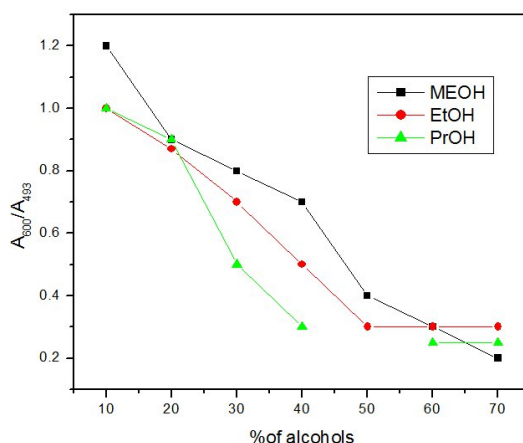


Fig.3: Effect of alcohols on Pcyn-NaAlg complex

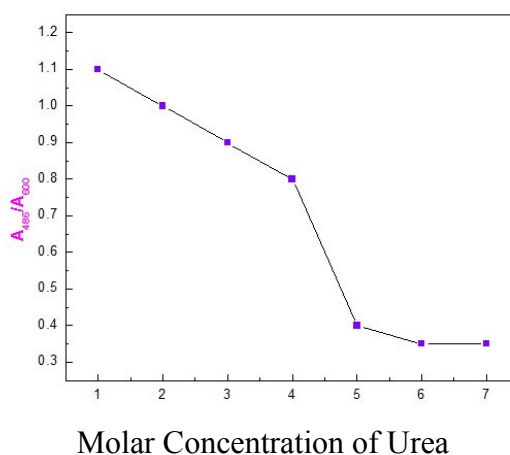


Fig.4. Effect of urea on Pcyn-NaAlg complex

Tan et al 26 have reported the disruption of metachromatic band with the variation of ionic strength. In aqueous solutions the charged polymer molecule will be in the extended conformation due to the repulsion between the charged groups. On adding the dye the conformation of the poly cation changes to a compact coil owing to dye binding, resulting from electrostatic interaction thus giving rise to metachromatic band. On addition of electrolytes, the reverse process is expected to occur releasing the bound dye resulting in the appearance of monomer dye band. In the present studies sodium chloride and potassium chloride of varied ionic strengths were added to Pcyn-NaCar complex and the absorbances were

measured in the range 350-700 nm. The molar concentration of sodium chloride needed for complete reversal of metachromasy was found to be $1 \times 10^{-2} \text{M}$. The result is shown in Fig.5. Similar results are obtained with potassium chloride also.

The strength and nature of interaction between water soluble polyelectrolyte and oppositely charged surfactants depend on the characteristic features of both the polyelectrolyte and the surfactant. The charge density, flexibility of the polyelectrolyte and the hydrophobicity of the non-polar part and the bulkiness of the polar part also play a vital role in the case of polymer-surfactant interaction 27.

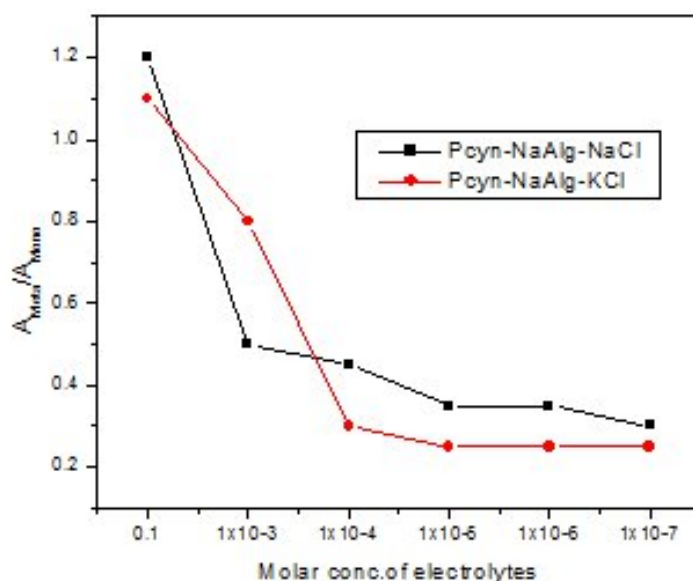


Fig.5. Effect electrolytes on Pcyn-NaAlg complex

The reversal of dye binding may also occur on addition of surfactants to P-D complex. The molar concentrations of SLS and SBS needed to because reversal was found to be $1 \times 10^{-3} \text{M}$ and $1 \times 10^{-2} \text{M}$ respectively. The results agree with those reported earlier in literature 28. Thus the surfactant molecules interacted with the polymer by replacing the cationic dye.

The release of dye molecules from the dye-polymer complex in presence of surfactants revealed that surfactants interacted electrostatically 29 with the anionic site of the polymer and thus the dye becomes free. The ease of reversal of metachromasy can be correlated with its chain length 30. The result is shown in Fig.6.

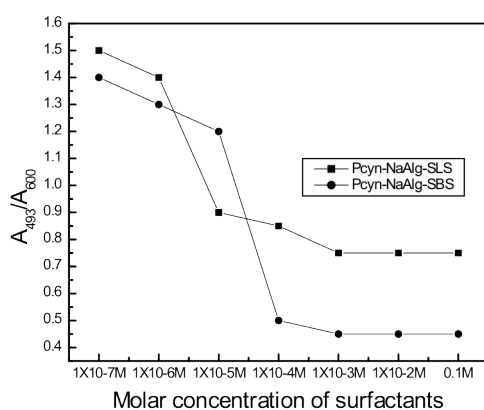


Fig.6 Effect of surfactants on PcyN-NaAlg complex

Evaluation of thermodynamic parameters Determination of K_c & thermodynamic parameters

The value of K_c was obtained from the slope and intercept of the plot of $CD_{CS}/(A-AO)$ against C_s (Fig.7.) using the expression $K_c = \text{slope} / (\text{intercept})$ also the thermodynamic parameters of interaction ΔH and ΔS were evaluated from the plots displayed in (Fig. 8.)

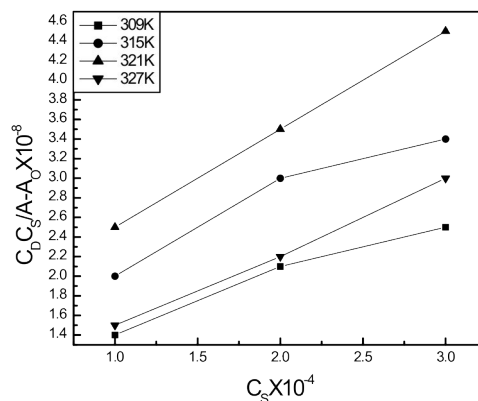


Fig.7 Effect of temperature on PcyN-NaAlg system

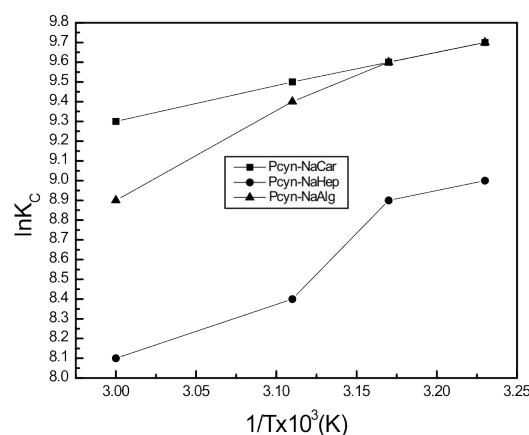


Fig.8 Van'thoff plot for PcyN-polymer systems

System	Temp (K)	K_C ($\text{dm}^3\text{mol}^{-1}$)	ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$)
Pcyn-NaCar	309	21607	-25.7	-23.5	-14.7
	315	20000	-25.9		
	321	17037	-26.0		
	327	13421	-25.8		

CONCLUSION

The polyelectrolyte sodium alginate induces metachromasy in the dye pinacyanol chloride. The blue shift of 107nm indicates a fairly strong metachromatic behavior. The reversal parameters indicate involvement of both electrostatic and hydrophobic forces in bonding. The value of interaction constant decreases with rise in temperature suggesting exothermic nature of the reactions and a low value of ΔG suggested a non-chemical type of interaction. The negative value of ΔS indicated a more ordered state of ion due to its aggregation.

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