

A Study of effect of dye structure on polyelectrolyte Induced metachromasy

Nandini R*

Department of Chemistry, MITE, Moodbidri

*Corresponding author: E-Mail: hodche@mite.ac.in, Telephone: 9964412316

ABSTRACT

The interaction of a cationic dyes namely, Methylene blue (MB) and Crystal violet (CV) with AN anionic polyelectrolyte, namely, sodium carrageenate (NaCar) 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 MB and NaCar was found to be greater than that formed between CV and NaCar. This fact was further confirmed by reversal studies using alcohols, urea and electrolytes. The interaction parameters revealed weaker binding between CV-NaCar complexes. The structure of dye was found to affect metachromatic shift and other interaction parameters. Among the two dyes Crystal violet, a triphenylmethanedye has a larger structure interacts less strongly with sodium carrageenate than Methylene Blue a planar cationic dye.

KEY WORDS: Metachromasy, Methylene blue, Crystal violet, Aggregation, Binding Sites.

1. INTRODUCTION

The term metachromasy refers to the change in the visible absorption spectra of the dye, on interaction with a polymer/polyelectrolyte. It occurs due to aggregation of dye molecules on the polymer backbone (Mitra, 1997). (Mitra, 2006). Here we briefly report the interaction of Methylene blue & Crystal violet with various polyelectrolytes. The interaction Crystal violet with sodium polyphosphate, polyacrylate, poly (ethylene sulfonate), sodium and potassium (p-styrene sulfonate), native and denatured calf thymus DNA has been reported by Yamaoka & Takatsuki (1978). The interaction of crystal violet with lecithin water and disodium chromoglycate-water lyotropic liquid crystals as hosts was studied (Kobayashi, 1990).

The interaction of Methylene blue with sodium alginate has been reported in the literature (Seely, 1983). Poly (potassium styrenesulfonate) and poly (sodium 4-vinylphenylsulphate) interacted with Methylene Blue to form aggregated polymers (Shirai & Nagatsuka, 1977). The effect of alkali metal chlorides and 1-substituted 3-carbomylpyridinium bromides on the metachromatic behavior of methylene blue induced by poly (potassium styrenesulfonate) and poly (potassium vinyl sulfate) was investigated spectrophotometrically (Shirai, 1977). The structural effect of polyanion on the metachromatic behavior of methylene blue was investigated spectrophotometrically using poly (sodium acrylate), conventional poly (sodium methacrylic acid), isotactic poly (sodium methacrylate) and the copolymer poly (sodium maleate-covinyl alcohol). The metachromatic behavior was followed by the changes in the molar absorption coefficient of methylene blue and in the wavelength of the metachromatic band. (Shirai, 1977). The effect of polyanion on the formation of mixed dimers of methylene blue and tryptaflavine, Methylene blue and Phenosafranin and Methylene blue and Pyronine G was investigated spectrophotometrically (Shirai, 1978). The effect of polyanion poly (potassium vinylsulfate) poly (sodium acrylate) on the alkaline fading reaction of Methylene blue was investigated (Shirai, 1978). The interaction of methylene blue with poly (vinyl alcohol) has been studied. (Otsuki & Adachi, 1993) The interaction of Methylene Blue with amorphous potassium chondroitin sulphate and crystalline chondroitin sulphate were studied by spectrophotometric method (Ghosh & Moulik, 1981) Hence the main objective underlying the current study is to investigate the extent to which the number of binding sites affects the metachromatic behavior The reversal of metachromasy on addition of alcohols, urea, NaCl, KCl, and oppositely charged surfactants, temperature and the thermodynamic parameters of interaction will also be reported.

2. MATERIALS & METHODS

Methylene Blue & Crystal violet (Acros Media) were used without further purification. Methanol, Ethanol and Propanol were obtained from (Merck, India) and were distilled before use. Sodium lauryl sulphate and Sodium dodecyl benzene sulphonate (Lobachemie, India) were used as received. Sodium carrageenate was obtained from (BDH, UK) the spectral studies were carried out using Shimadzu UV-2550 spectrophotometer.

Determination of stoichiometry and interaction parameters of Polymer-dye complexes: The equivalent weight of NaCar sample was determined using Alcian Blue as per the standard method (Ramus, 1977) and it was found to be 327g.

Preparation of dyes & polymer solutions: The stock solutions of the various dyes were made in 100 ml volumetric flasks using distilled water. The stock solutions of polymers of concentration $1 \times 10^{-2} \text{M}$ was made in 100 ml volumetric flask considering the equivalent weights of the polymer.

Preparation of electrolyte and surfactant solutions: The stock solutions of concentration 0.1M were made in 100 ml volumetric flasks using distilled water. Appropriate amount of these solutions were used to obtain concentrations in the range 0.01M- 1×10^{-8} M in various experiments.

Preparation of urea solution: The stock solution of concentration 9M was made in 100 ml volumetric flasks using distilled water. Appropriate amount of this stock solution were used to obtain concentrations in the range 1-8M in various experiments.

Preparation of solutions containing polymer & dye in different amounts: The stock solution of concentration 9M was made in 100 ml volumetric flasks using distilled water. Appropriate amount of this stock solution were used to obtain concentrations in the range 1-8M in various experiments.

Preparation of polymer-dye solutions for studying reversal of metachromasy: For the study of reversal of metachromasy, solutions containing polymer & dye in a fixed ratio, which exhibited highest shift, were made. Generally 0.5ml of 1×10^{-3} M dye solution and appropriate amount of polymer solution (0.0-0.9 ml of 1×10^{-2} M) solution were mixed in 10 ml volumetric flask and appropriate amounts of alcohols, NaCl (0.1M), urea (9M), or surfactant (0.1M) were added and the solution was made up to 10 ml with distilled water.

Determination of thermodynamic parameters: The thermodynamic parameters of interaction are determined as follows: Solutions containing different amounts of polymer samples (1, 2, 4 and 5ml $\times 10^{-3}$ M) and fixed amount of dye solution (0.5ml, 1×10^{-3} M) were made up to 10 ml in different volumetric flasks and the solutions were equilibrated and the readings were measured at 4 different temperatures, 36°C, 42°C, 48°C and 54°C. The absorbances were measured at both monomeric and metachromatic band. Absorbance results were treated using Rose-Drago equation:

$$C_D \cdot C_S / (A - A_0) = 1 / (K_c L (\epsilon_{DS} - \epsilon_D)) + C_S / (L (\epsilon_{DS} - \epsilon_D))$$

Where, C_D is the initial molar concentration of the dye; C_S is the molar concentration of the polymer; A is the absorbance of the polymer-dye complex at the metachromatic band; A_0 is the absorbance of the pure dye at the metachromatic band; ϵ_{DS} is the molar extinction coefficient of the polymer-dye complex; ϵ_D is the molar extinction coefficient of the dye.

At each temperature the value of K_c was obtained from the slope and intercept of the plot of $C_D C_S / A - A_0$ against C_S at each temperature studied.

$K_c = \text{Slope}/(\text{Intercept})$: The free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) associated with complex formation between dye and the polymer were calculated using the standard expressions,

$$\Delta G = -RT \ln K_c; \ln K_c = -\Delta H / (RT) + C; \text{ and } \Delta G = \Delta H - T \Delta S$$

3. RESULTS AND DISCUSSION

The spectra of pure Methylene blue (MB) dye & Crystal violet, shows an absorption maxima at 628nm & 589nm respectively. When Sodium carrageenane solution is added to each of the above dye solutions, the spectra shows a blue shift, which occurs at 538 nm in case MB-NaCar complex and at 536nm in case of CV-NaCar complex. The reason for the blue shift being, the aggregation of dye molecules on the polymer backbone as reported by (Basu, 1982; Pal, 1961). The results are shown in Fig.1 & Fig.2.

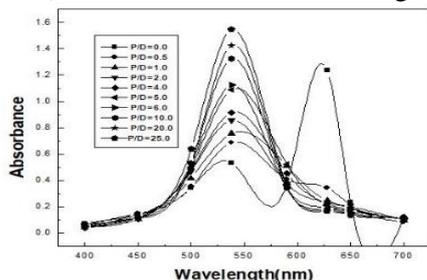


Figure.1. Absorption spectra of MB-NaCar

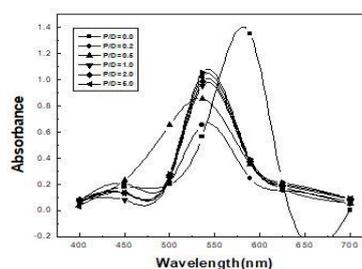


Figure.2. Absorption spectra of CV-NaCar

Stoichiometry: The stoichiometry of MB-NaCar & CV-NaCar complex were determined as mentioned earlier in the experimental section and were found to be 2:1 and 1:1 respectively. A 2:1 stoichiometry suggests that dye binding occurs at alternative site of the polyelectrolyte while in case of 1:1 stoichiometry binding of the dye molecule occurs at adjacent anionic sites resulting in a card pack stacking of the dye molecules on the polymer. These results are in good agreement with those already reported in literature for binding of Pinacyanol chloride with Poly (Meth acrylic acid) and Poly (Styrene sulfonate) systems by (Pal & Ghosh, 1979, 1980). Fig.3, shows the stoichiometry of the complexes.

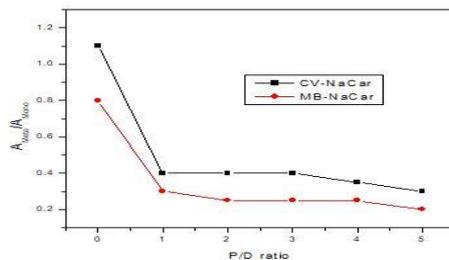


Figure.3. Stoichiometry of Polymer-dye complexes

Effect of alcohols and urea on metachromasy: When alcohols such as Methanol, ethanol and 2-propanol were added to case of MB-NaCar & CV-NaCar complexes the metachromatic bands disappeared and the bands of the pure dyes reappeared. This is due to breaking of the polymer-dye complex and release of pure dye in the solution. These observations indicated the involvement of hydrophobic forces in the polymer-dye complex formation. Further it was also observed that as the hydrophobic chain length of alcohols increases the reversal becomes quicker. Our observations matches well with that reported in the literature. (Frank & Quist, 1961; Rabinowitch & Epstein, 1941). The results are shown in fig.4, fig.5 & fig.6, respectively.

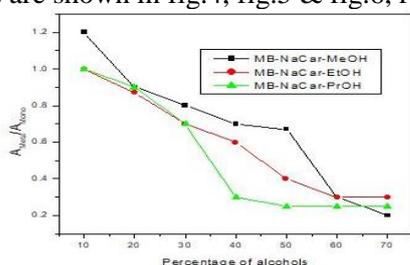


Figure.4. Effect of alcohols on MB-NaCar system

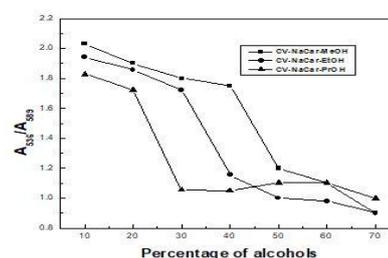


Figure.5. Effect of alcohols on CV-NaCar system

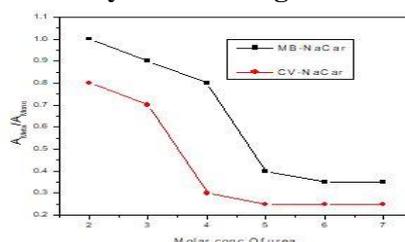


Figure.6. Effect of urea on Polymer-dye systems

Effect of electrolytes: On adding the electrolytes NaCl/KCl to the MB-NaCar & CV-NaCar complexes, the metachromatic band disappears and the original monomeric band reappears. The reason behind this being, the change in conformation of polymer from extended conformation before adding dye to compact coil conformation on binding with the dye. The reversal of metachromasy on addition of electrolytes indicate the involvement of electrostatic forces in polymer-dye interaction. These observations have been supported by literature reports of (Tan & Schneider, 1975). The results are depicted in fig.7 & fig.8.

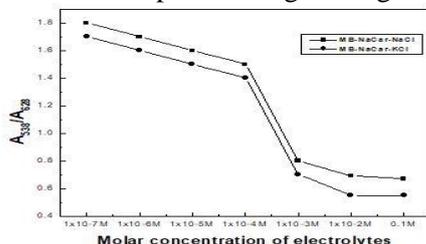


Figure.7. Effect of electrolytes on MB-NaCar system

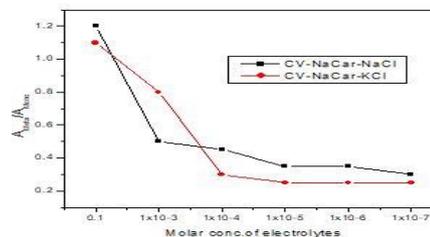


Figure.8. Effect of electrolytes CV-NaCar system

Effect of surfactants: On adding surfactants to MB-NaCar & CV-NaCar complexes the polymer interacts with the oppositely charged surfactant molecules and releases the free dye into the solution, as a result the monomeric band of the dye reappears. This is due to the interaction between anionic sites of the polymer with the surfactant thereby releasing the free dye into the solution, which indirectly indicates the involvement of electrostatic forces involved in polymer-dye binding. Moreover as the chain length of the surfactant increases, the reversal became quicker, thus indicating that hydrophobic forces also play a vital role in polymer-surfactant interaction. These facts were also supported by reports from (Konradi & Ruhe, 2005; Villetti, 2004; Romani, 2005). The fig.9 & fig.10, shows the effect of surfactants.

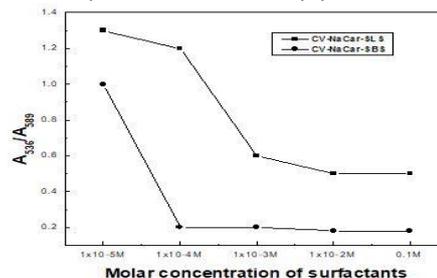
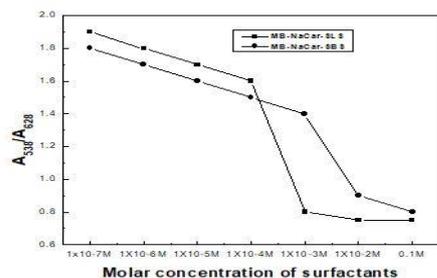


Figure.9. Effect of surfactants MB-NaCar system

Figure.10. Effect of surfactants CV-NaCar system

Determination of interaction parameters: The interaction between the polymer-dye were studied at various temperatures ranging from 309K-327K and the interaction constant K_e and other thermodynamic parameters namely, ΔG , ΔH & ΔS were evaluated as mentioned earlier. The negative values of ΔH indicates the exothermic nature of polymer-dye interaction. Also the negative value of ΔS indicates an orderly arrangement of ions. The results are given in table.1.

Table.1. Thermodynamic parameters of Polymer-dye systems

System	Temp (K)	$K_e(\text{dm}^3\text{mol}^{-1})$	$\Delta G(\text{kJ. mol}^{-1})$	$\Delta H(\text{kJ. mol}^{-1})$	$\Delta S(\text{J. mol}^{-1}\text{K}^{-1})$
CV-NaCar	309	4150	-21.4		
	315	3750	-21.7	-20.9	-18.7
	321	2185	-20.3		
	327	1986	-20.6		
MB-NaCar	309	7015	-22.7	-20.2	-38.3
	315	6154	-22.8		
	321	5215	-22.6		
	327	4528	-22.9		

Effect of dye structure: The structures of Methylene blue and Crystal violet are given below:

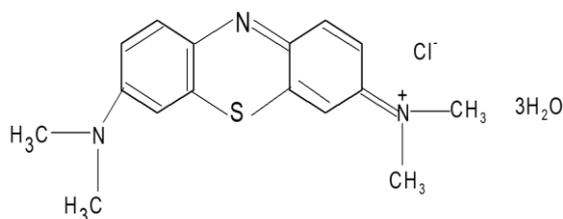


Figure.11. Structure of Methylene blue

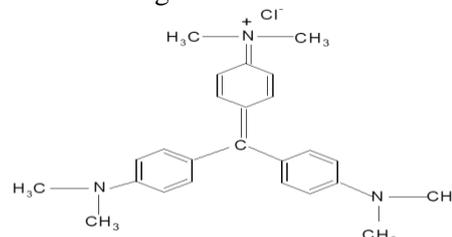


Figure.12. Structure of Crystal violet

On comparing the above structures, it is evident that Crystal violet is a large Triphenyl methane dye with bulky methyl groups which offers steric hindrance for interaction with the anionic polyelectrolyte, sodium carrageenane than Methylene blue which is comparatively a smaller dye hence it interacts more strongly with sodium carrageenane. These facts are further confirmed by interaction parameters which is greater for MB-NaCar complex than for CV-NaCar complex.

4. CONCLUSIONS

From the present investigation it can be concluded that anionic polyelectrolytes Viz. NaCar induced metachromasy in the dye Methylene Blue and Crystal violet. The extent of metachromasy induced by Sodium carrageenane in Methylene Blue was greater than in Crystal violet. This is evident in the extent of blue shift which is 90nm in case of MB-NaCar complex and 53nm in case of CV-NaCar complex. The above fact is also confirmed by the interaction constants which are higher for MB-NaCar complex than that for CV-NaCar complex. Further it was also found that the dye structure also influences metachromasy.

REFERENCES

- Basu S, Gupta AK, Rohatgi-Mukherjee KK, Concentration depolarization, energy-transfer and kinetics of concentration quenching of fluorescence of anthracene sulfonates, J. Indian Chem. Soc., 59, 1982, 578-582.
- Frank HS, Quist AS, Pauling's Model and the Thermodynamic Properties of Water, J. Chem. Phys., 1961, 34, 604.
- Ghosh S, Moulik S.P, Can. Spectrophotometric investigation on the interaction of acridine orange with methylene blue, phenosafranin, and disulphine blue in aqueous medium, Ind. J. Chem., 59, 1981, 2449-2556.

Gummow B.D and Roberts G.A.F, Studies on chitosan-induced metachromasy, Some correlations between dye structure and metachromatic behaviour *Makromol. Chem.*, 187, 1985, 995-1004.

Kobayashi M, Matsumoto H, Hoshi T, Metachromasy Bands of Disk-Like Guests in the Host Lyotropic Liquid Crystal Disodium Chromoglycate-Water, *Molecular Crystals and liquid crystals*, 1808, 1990, 252.

Konradi R, Ruhe Binding of Oppositely Charged Surfactants to Poly (methacrylic acid) Brushes, *J. Macromolecules*, 38, 2005, 6140–6151.

Mitra A, Chakraborty A.K, A comparative study on the physico-chemical properties of bacterial capsular polysaccharides from different serotypes of *Klebsiella*, *J. Photochem. Photobiol. A: Chem.*, 178, 2006, 98-105.

Mitra A, Nath R.K, Biswas S, Chakraborty A.K, Panda A.K, Mitra A, Interaction of cationic dyes with *Klebsiella* K14J, *Photochem. Photobiol. A: Chem.*, 111, 1997, 157-168.

Otsuki S, Adachi K, Metachromasy in Polymer Films, Changes in the Absorption Spectrum of Methylene Blue in Nafion Films by Hydration Polymer, *Journal*, 25, 1993, 1107-1112.

Pal MK, Ghosh BK, Metachromasia of pinacyanol chloride induced by synthetic polyanions, *Macromol. Chem.*, 180, 1979, 959-967.

Pal MK, Ghosh BK, Not all polyanions induce a J-band in the dye pseudoisocyanine, *Macromol. Chem.*, 181, 1980, 1459-1467.

Pal MK, Schubert M, Specific adsorption of metachromatic compounds of Chondroitin sulfate by insoluble calcium salts, *J. Histochem. Cytochem.*, 9, 1961, 673-680.

Rabinowitch E, Epstein LF, Polymerization of Dyestuffs in Solution, Thionine and Methylene Blue, *J. Am. Chem. Soc.*, 63, 1941, 6938.

Romani A.P, Gehlen M.H and Itri R, Surfactant–Polymer Aggregates Formed by Sodium Dodecyl Sulfate, Poly(N-vinyl-2-pyrrolidone), and Poly(ethylene glycol), *Langmuir*, 21, 2005, 127-133.

Rose N.J, Drago R.S, Molecular Addition Compounds of Iodine. I. An Absolute Method for the Spectroscopic Determination of Equilibrium Constants, *J. Am. Chem. Soc.*, 81, 1959, 6138-6141.

Seely G.R, Knots R.R, Binding of methylene blue to alginate: Effect of acid treatment on metachromasy, *Carbohydrate Polymers*, 3, 1983, 109-127.

Shirai M, Murakami Y, Tanaka M, Interaction between dyes and polyelectrolytes, Metachromatic behavior of methylene blue induced by poly (sodium acrylate) and its homologues, *Makromol. Chem.*, 178, 1977, 2141-2147.

Shirai M, Nagaoka Y, Tanaka M, Interaction between dyes and polyelectrolytes, Effect of organic and inorganic salts on metachromasy of methylene blue, *Makromol. Chem.*, 178, 1977, 1633-1639.

Shirai M, Nagatsuka T, Tanaka M, Interaction between dyes and polyelectrolytes, Metachromatic behavior of methylene blue induced by potassium poly(vinyl sulfate) and its homologs, *J. Polym. Sci: Polym. Chem. Ed.*, 5, 1977, 2083-2095.

Shirai M, Nagatsuka T, Tanaka M, Interaction between dyes and polyelectrolytes, Structural effect of polyanions on the methylene blue binding, *Makromol. Chem.*, 178, 1977, 37-46.

Shirai M, Nagatsuka T, Tanaka M, Interaction between dyes and polyelectrolytes, Effect of polyanions on the mixed dimer formation of cationic dyes, *Makromol. Chem.*, 179, 1978, 173.

Shirai M, Yamashita M, Tanaka M, Interaction between dyes and polyelectrolytes, Effect of polyanions on alkaline fading reaction of methylene blue, *Makromol. Chem.*, 179, 1978, 747-753.

Tan J.S, and Schneider R.L, Dye binding and its relation to polyelectrolyte conformation, *J. Phys. Chem.*, 79, 1975, 1380-1386.

Villetti MA, Borsali R, Crespo JS, Soldi V, Fukada K, Static and Dynamic Light Scattering of Polyelectrolyte/Surfactant Solutions: the Na-Hyaluronate/(C10TAB) System, *Macromol. Chem. Phys.*, 205, 2004, 907-917.

Yamaoka K, Takatsuki M, Metachromasy, The Simultaneous Determination of the Bound Dye Spectra and the Equilibrium Constants between Metachromatic Dyes and Various Polyelectrolytes by the Extended Principal Component Analysis Method, *Bulletin of the Chemical society of Japan*, 51, 1978, 3182-3192.