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Research Article

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Polyelectrolyte Induced Metachromasy: Effect of Binding Sites

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ABSTRACT

The interaction of a cationic dye namely, Methylene blue (MB) with anionic polyelectrolytes, namely, sodium carboxymethyl cellulose (NaCMC) and Sodium heparinate has been investigated by spectrophotometric technique. The polymers 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 NaCMC was found to be lesser than that formed between MB and NaHep. This fact was further confirmed by reversal studies using alcohols, urea and electrolytes. The interaction parameters revealed strong binding between MB-Na Hep complexes. The number of binding sites was found to affect metachromatic shift and other interaction parameters. Among the two polyelectrolytes, NaHep has a greater number of binding sites, hence dye aggregation was found to be greater in MB-NaHep complex than in MB-NaCMC complex.

Keywords: Metachromasy; Methyleneblue; Anionic polyelectrolytes; Aggregation; Binding sites

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INTRODUCTION

The term metachromasyrefers 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 [1,2]. Here we briefly report the interaction of methylene blue with various polyelectrolytes. The interaction of methylene blue with sodiumalginate has been reported in the literature [3,4]. Poly (potassium styrenesulfonate) and poly (sodium 4-vinylphenylsulphate) interacted with Methylene Blue to form aggregated polymers [5]. 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 [6]. The structural effect of polyanion on the metachromatic behavior of methylene blue was investigated spectrophotometrically using poly(sodium acrylate), conventional poly(sodium methacrylicacid), 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 [7]. The effect of polyanion on the formation of mixed dimers of methylene blue and trypaflavine, Methyelne blue and Phenosafranin and Methylene blue and Pyronine G was investigated spectrophotometrically [8]. The effect of polyanion poly (potassium vinylsulfate) poly (sodium acrylate) on the alkaline fading reaction of Methylene blue was investigated [9]. The interaction of methylene blue with poly (vinyl alcohol) has been studied [10]. The interaction of Methylene blue with amorphous potassium chondroitin sulphate and crystalline chondroitin sulphate were studied by spectrophotometric method [11]. 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.

MATERIALS AND METHODS

Methylene Blue (Acros Media) were used without further purification. Methanol, ethanol and propanol were obtained from (Merck, India) and were distilled before use. Sodium laurylsulphate and Sodium dodecyl benzene sulphonate (Lobachemie, India) were used as received. Sodiumcarboxymethyl cellulose was obtained from (BDH,UK) and Sodium heparinate was obtained from (Lobachemie, India). 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 NaCMC sample was determined using standard methods and it was found to be 222 g. The equivalent weight of NaHep sample was determined using conductometric titration method and it was found to be 178 g [12-14].

Preparation of Dye and 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 1×10^{-2} 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 0.1 M were made in 100 ml volumetric flasks using distilled water. Appropriate amount of these solutions were used to obtain concentrations in the range $0.01\mathrm{M}^{-1} \times 10^{-8}$ M in various experiments.

Preparation of Urea Solution

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

Preparation of Polymer-Dye Solutions for Studying Reversal of Metachromasy

For the study of reversal of metachromasy, solutions containing polymer and dye in a fixed ratio, which exhibited highest shift, were made. Generally 0.5 ml 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 (0.1 M), urea (9 M), or surfactant (0.1 M) 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 5 ml $\times 10^{-3}$ M) and fixed amount of dye solution (0.5 ml, 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 [15]

$C_D.Cs/ (A-A_0) = 1/(K_cL\ (\varepsilon_{DS}- \varepsilon_D)) + Cs/(L\ (\varepsilon_{DS}- \varepsilon_D))$

Where;

C_D is the the initial molar concentration of the dye.

Cs is the molar concentration of the polymer.

A is the absorbance of the polymer-dye complex at the metachromatic band.

Ao is the absorbance of the pure dye at the metachromatic band.

ε_{DS} is the molar extinction coefficient of the polymer-dye complex.

$\varepsilon_{D}$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 $C_DC_s/A-A_0$ against C_S at each temperature studied.

K_c= Slope/(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, $\Delta G = -RT\ln K_c$; $\ln Kc=-\Delta H/(RT)+C$; and $\Delta G= \Delta H-T\Delta S$.

RESULTS AND DISCUSSION

The spectra of pure Methylene blue (MB) dye, shows an absorption maxima at 628 nm. When Sodium carboxy methylcellulose solution is added to the above dye solutions, the spectra shows a blue shift, which occurs at 555 nm in case MB-NaCMC complex and at 528 nm in case of MB-NaHep complex. The reason for the blue shift being, the aggregation of dye molecules on the polymer backbone as reported by [16,17]. The results are shown in Figures 1 and 2

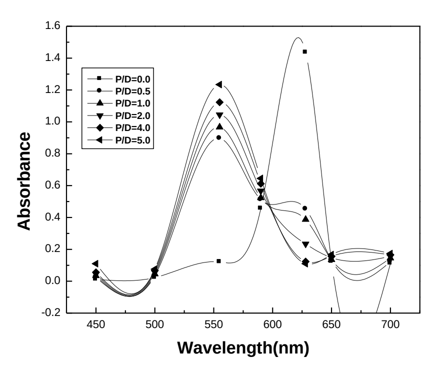

Figure 1: Absorption spectra of MB-NaCMC

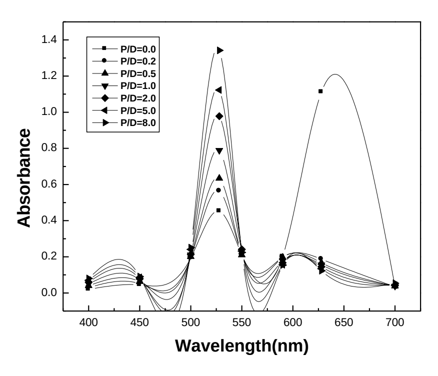

Figure 2: Absorption spectra of MB-NaHep

Stoichiometry

The stoichiometry of MB-NaCMC and MB-NaHep complex were determined as mentioned earlier in the experimental section and were found to be 1:1 and 2:1 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 backbone. These results are in good agreement with those already reported in literature for binding of Pinacyanol chloride with poly (Meth acrylic acid) and poly (Styrenesulfonate) systems by [18,19]. Figure 3 shows the stoichiometry of the complexes.

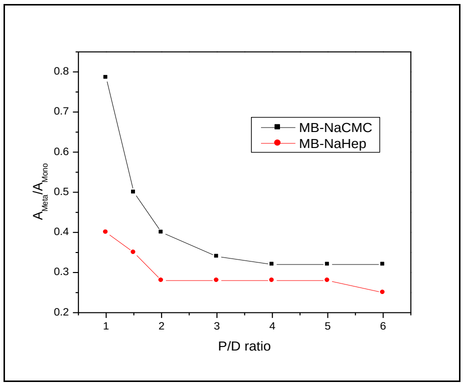

Figure 3: Stoichiometry of polymer-dye complexes

Effect of Alcohols and Urea on Metachromasy

When alcohols such as Methanol, ethanol and 2-propanol were added to case of MB-NaCMC and MB-NaHep 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 [20,21]. The results are shown in Figures 4-6 respectively.

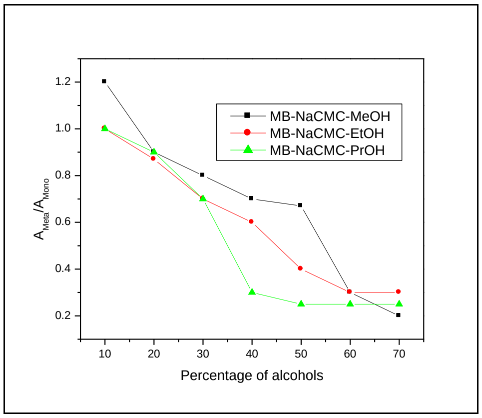

Figure 4: Effect of alcohols on MB-NaCMC system

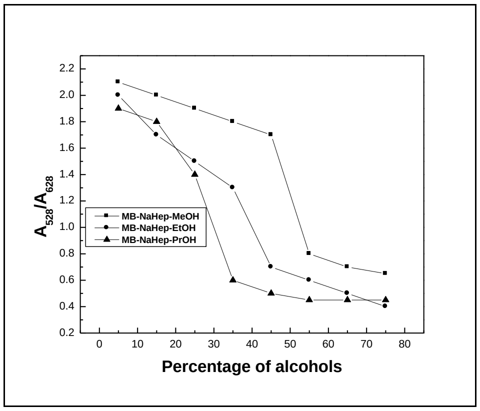

Figure 5: Effect of alcohols on MB-NaHep system

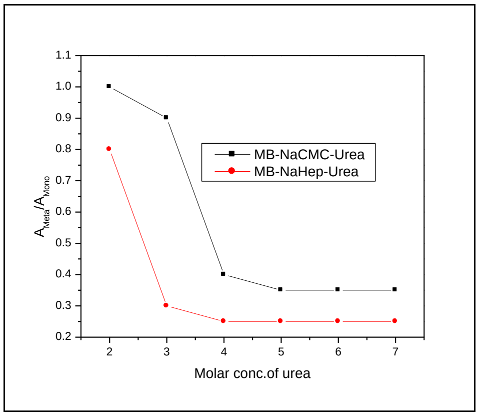

Figure 6: Effect of urea on Polymer-dye systems

Effect of Electrolytes

On adding the electrolytes NaCl/KCl to the MB-NaCMC and MB-NaHep complexes them etachromatic 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 indicates the involvement of electrostatic forces in polymer-dye interaction. These observations have been supported by literature reports of [22]. The results are depicted in Figures 7 and 8.

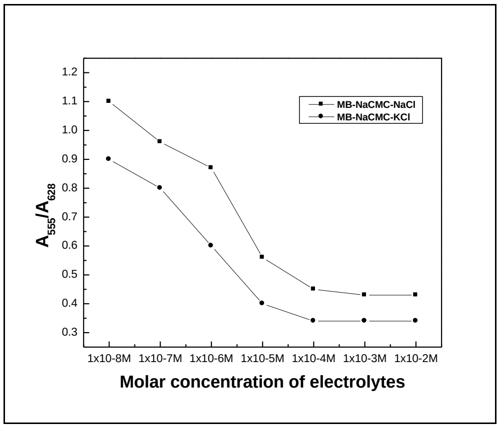

Figure 7: Effect of electrolytes on MB-NaCMC system

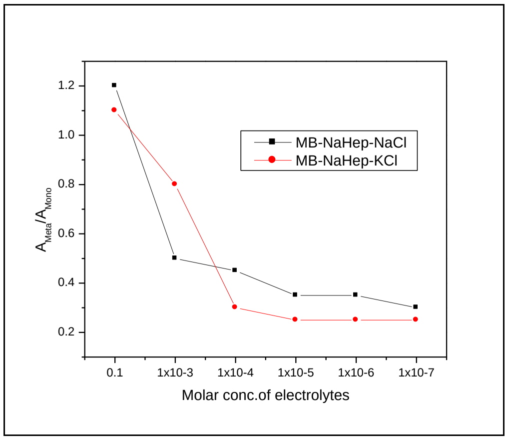

Figure 8: Effect of electrolytes MB-NaHep system

Effect of Surfactants

On adding surfactants to MB-NaCMC and MB-NaHep 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. Morover 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 [23-25]. Figures 9 and 10 shows the effect of surfactants.

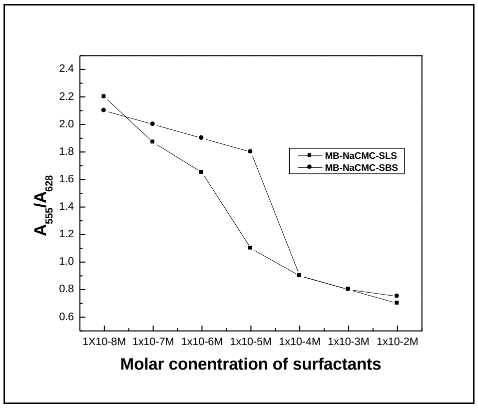

Figure 9: Effect of surfactantsMB-NaCMC system

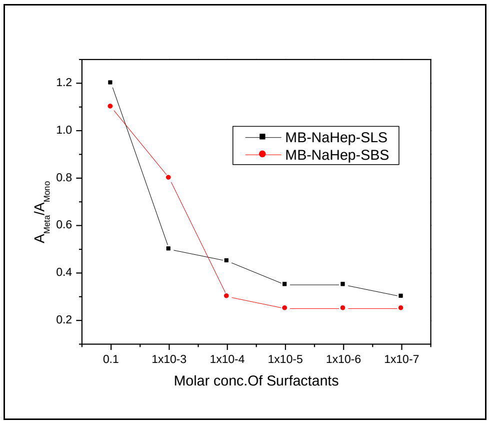

Figure 10: Effect of surfactantsMB-NaHep system

Determination of Interaction Parameters

The interaction between the polymer-dye were studied at various temperatures ranging from 309K-327K and the interaction constant K_c and other thermodynamic parameters namely, ΔG, ΔH and ΔS were evaluated as mentioned earlier. The negative value 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_C(dm^{3}mol^{-1})	ΔG(kJ.mol^{-1})	ΔH(kJ.mol^{-1})	ΔΣ(J.mol^{-1}K^{-1})
MB-NaCMC	**309**	6218	-22.4		
	315	5415	-22.6	-23.5	-33.3
	321	4321	-22.3		
	327	3785	-23.7		
	309	7315	-22.8	-20.2	-38.3
MB-NaHep	**315**	6512	-23		
	321	5423	-23.5		
	327	4751	-23.8		

Effect of Binding Sites

The structures of sodium carboxymethyl cellulose and Sodium heparinate are given below:

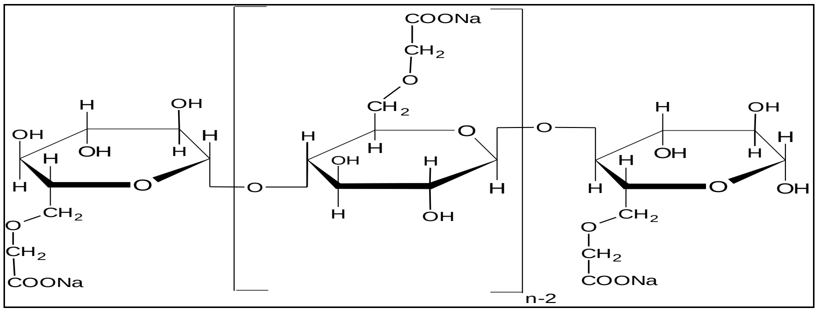

Figure 11: Structure of NaCMC

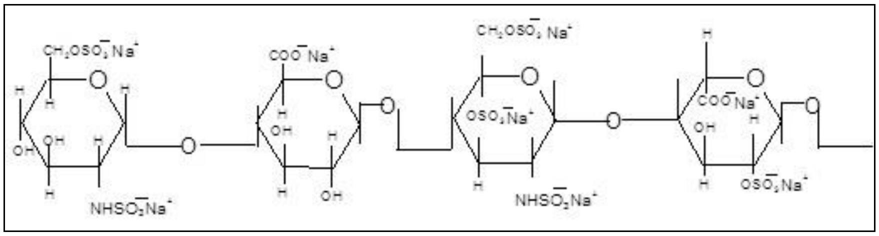

Figure 12: Structure of NaHep

On comparing the above structures, it is evident that for heparin there are two binding sites (Figures 11 and 12), namely carboxylate and sulphate groups, whilst sodium carboxy methyl cellulose contains only carboxylate groups. Hence, binding between heparin Methylene Blue and is stronger than in the case of Methylene Blue and sodium carboxymethyl cellulose. These facts are further confirmed by the interactions constants and other interaction parameters.

CONCLUSION

From the present investigation it can be concluded that both the anionic polyelectrolytes, namely, NaCMC and NaHepinduced metachromasy in the dye Methylene Blue. The extent of metachromasy induced by in Sodiumheparinate was greater than that by Sodium carboxymethyl cellulose. Thisis evident in the extent of blue shift which is 100 nm in case of MB-NaHep complex and 73 nm in case of MB-NaCMC complex. The above fact is also confirmed by the interaction constants which are higher for MB-NaHep complex than that for MB-NaCMC complex. Further it was also found that the number of bindingsites also influences metachromasy.

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