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Molecular Basis of the Binding of Dye to Polycations : Absorption and Emission Spectral Studies[#]

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Abstract — Absorption and emission spectral behaviour of an anionic xanthene dye, eosinY was investigated to perceive the nature and extent of interaction with three different cationic polyelectrolytes. The formation of dye-polymer aggregates was found to be associated with two types of interactive forces : electrostatic and hydrophobic forces. The binding constants and stoichiometry of the dye-polymer aggregates in their ground states were determined by suitably analyzing the absorption spectra by varying the concentration of the polymers. Subsequently, the thermodynamic parameters for the interaction processes were evaluated. The interaction parameters followed the sequence PDMDAAC > JR400 > LM200. The excited state interaction phenomena were studied from the fluorescence data. Change in the excited state lifetime of the fluorophore was insignificant in all the three cases. Consequently, Stern-Volmer quenching constants of the dye-polymer aggregates were calculated using the standard method. Significant information about the changes on the degree of motion of the fluorescent molecule around the polymer matrix was obtained from the anisotropy measurements.

Keywords : *Dye-Polymer interaction, Fluorescence, Interaction constant, Anisotropy.*

INTRODUCTION

Studies on the solution behaviour of biologically relevant macromolecules are considered to be important for their multifarious application potentials which cover almost all segment of human life [1], e.g., food, pharmaceutical technology [2, 3]. Functionalised organic molecules like dye, when added to polyelectrolyte, also find

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many applications, viz., textile, film imaging, drug delivery [4, 5], etc. Towards proper understanding of the behaviour of polymer, studies on their solution behaviour is necessary [6]. In most of the practical applications polymers are mixed with different additives; the most common example involves the use of dye in textile industry [7–9]. Dye molecules find several industrial applications which cover textiles, paper, plastics, cosmetics and leather. In all the cases dyes are used for aesthetic purpose [10]. According to Chatterjee et al. [11], more than 8×10^5 tonnes of textile dyes are used annually, whereby, ten percent of them are discharged as effluents. Presence of these colorants in water is not only aesthetically undesirable but also has serious environmental impact [10]. Most of the textile dyes have additional photostability and chemical inertness for which their removal from waste water becomes difficult [12]. Among different physico-chemical decolourisation processes the flocculation/coagulation technique using oppositely charged polyelectrolytes are considered to be more effective [13]. However, the detailed mechanism involved in this process is still not clear. It is therefore, believed that studies involving oppositely charged dye-polymer aggregates would shed further light in understanding the interaction mechanism.

Eosin Y, a xanthene dye, has multiple applications [14]. Although many studies on the dye-polymer interactions have been done so far [15–17], however, studies on interaction of eosin Y with cationic polymers are not so common.

The cationic polymer poly(diallyldimethyl ammonium) chloride (PDMDAAC) is known to be used as a coagulating agent for waste water treatment. Recently Mukherjee et al. [18] have studied the interaction of PDMDAAC with anionic surfactants using a number of techniques. N,N-dimethyl-N-dodecyl derivative of hydroxyl ethyl cellulose (LM200) and N,N-dimethyl-N-methyl derivative of hydroxyl ethyl cellulose (JR400) are important constituents of the composition for the oxidative dyeing of keratin based fibres [19, 20]. They also find wide applications in the formulation of shampoo as they could intensify the degree of accumulation of shampoos [21, 22]. The present research group is involved in understanding the solution behaviour of anionic polysaccharides isolated from different bacterial strains of gram negative bacteria *Klebsiella* [23–26]. Also there are several reports involving the interactions of cationic dyes with anionic polyelectrolytes [27–29]. However, use of polycation in dye-polymer interaction studies is not so common. It is believed that such studies would be beneficial specially in waste water treatment [30], ink jet inks [31], textile dyeing [32], fluorescence tuning [33]. Besides, such studies are also considered to be important from the fundamental understanding point of view. The

absorption and emission spectroscopic measurements are considered to be the convenient ways in understanding dye polymer aggregates as the dye concentration requirement is usually low. A significant change in the intensity or absorption maxima of dye in the presence of polymer indicates the interaction to take place among the dye and polymer [23]. Formation of a dye-polymer aggregate can be mediated through electrostatic and/or hydrophobic interactions. Different physicochemical parameters, for example, the average mass and charge per repeating unit, stoichiometry of the dye-polymer aggregates and thermodynamic parameters of the binding process can easily be evaluated from such studies. Besides, the tertiary conformation of the macromolecules in solution can also be predicted [23].

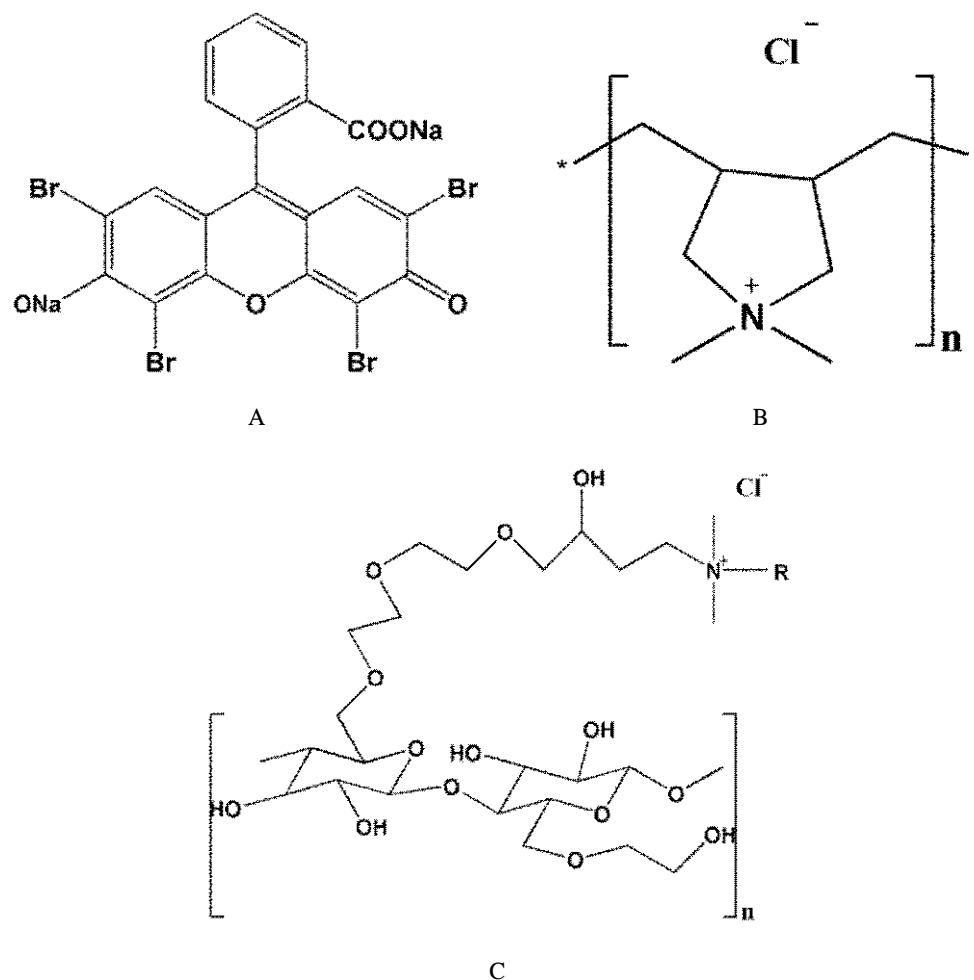
The present study involves the interaction of eosin Y with three different cationic polymers. The choice of these three polymers is intentional. Structure of the dye and three polymers have been shown in Scheme 1. PDMDAAC has an average molar mass of 162 g per repeating unit. It, therefore, can be assumed that the anionic dye eosin Y will prevalently interact with the polymer through electrostatic attraction. And also the degree of motion of the dye molecule bound to the polymer chain is considered to be nearly uniform. However in the case of other two polymers, having structural differences from PDMDAAC as well as among themselves, would definitely interact differently. Beside electrostatic attraction, hydrophobic interactions are also expected to be involved in case of other two polymers.

The absorption spectral studies were endeavoured to determine the binding constants and stoichiometry of the dye-polymer aggregates in the ground state. The excited state dye-polymer binding constants were evaluated from the fluorescence spectra. Anisotropy measurements can furnish significant information about the changes in the degree of motion of the dye molecule around the polymer matrix.

EXPERIMENTAL

Materials :

The anionic xanthene dye, 2-(2,4,5,7-tetrabromo-6 oxido-3-oxo-3H-xanthen-9-yl) benzoate, disodium salt (eosin Y, EY) and the cationic polymer poly(diallyldimethyl ammonium) chloride, PDMDAAC, were purchased from Sigma-Aldrich, USA. While the other two cationic polymers N,N-dimethyl-N-dodecyl derivative of hydroxyl ethyl cellulose, LM200 and N,N-dimethyl-N-methyl derivative of hydroxyl ethyl cellulose, JR400 were procured from Amerchol, Union Carbide Chemicals and Plastics Co., USA. The chemicals were stated to be more than 99.5% pure and were used as received. Double distilled water with a conductance of 2–4 $\mu\text{S cm}^{-1}$ was used in preparing the solutions.



Scheme 1. Structures of A, eosinY; B, PDMDAAC and C, JR 400/LM 200 (R = -CH₃ : JR 400, R = -C₁₂H₂₅ : LM 200).

Methods :

1.0 mM aqueous solution of EY and the polymers (PDMDAAC, LM200, and JR400) were prepared using double distilled water. The solutions were then properly diluted as required. The visible absorption spectra were recorded on a UVD-2950 spectrophotometer (Labomed Inc., USA). Spectra were recorded in the range 400–

600 nm using a matched pair of quartz cuvettes of 1 cm path length. Spectra were recorded at five different temperatures (298, 303, 308, 313, and 318 K). The fluorescence spectroscopic studies were carried out in a bench-top spectrofluorometer (Quantamaster-40, Photon Technology International Inc., NJ, USA). EY was excited at 500 nm and the emission spectra were recorded in the range 500–650 nm. Steady state fluorescence anisotropy (r) was determined according to the expression [14] :

$$r = \frac{(I_{VV} - G.I_{VH})}{(I_{VV} + 2G.I_{VH})} \quad (1)$$

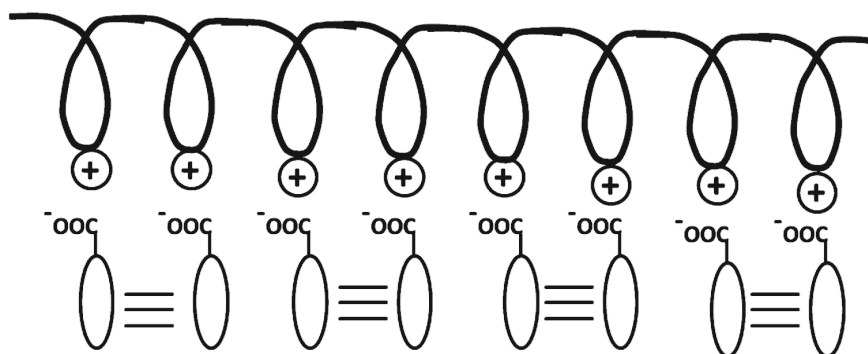
where, $G = I_{HV}/I_{HH}$; I_{VV} corresponds to the intensity obtained when the excitation and the emission polarizers are oriented vertically. I_{VH} is the intensity obtained for vertical excitation polarizer and horizontal emission polarizer. I_{HV} and I_{HH} refer to similar parameters as above for the horizontal positions of the excitation polarizer.

Fluorescence lifetime measurements of EY were recorded with the same fluorometer using a nano LED (Photon Technology International Inc.) of 505 nm wavelength. The emission data were recorded at 535 nm.

RESULTS AND DISCUSSION

Absorption spectral studies :

Aqueous solution of pure EY exhibits a monomeric band at 517 nm and a dimeric band at 496 nm. Results are in conformity with the previously published reports [14, 34]. Effect of polymers in their lower concentration range (0–18 μM) on the visible absorption spectra of 10 μM EY are shown in Fig. 1. With increasing concentration of PDMDAAC solution, intensities of both the bands of EY decrease with the gradual disappearance of the dimeric band (Fig. 1A). Appearance of an isosbestic point at 532 nm indicates the formation of 1 : 1 charge-transfer complex between the dye and polymer [35, 36]. This also reveals the existence of equilibrium in the binding process. Negatively charged dye, after binding stoichiometrically to the positive centres of the polymer, can stack to each other laterally as two dye molecules are in immediate vicinity of each other as shown in Scheme 2. Similar model has been proposed earlier by Yu et al. [37]. The decrease in band intensities is attributed to the electrostatic interaction between the anionic dye and cationic polymer. Attainment of charge neutralization leads to increase in hydrophobicity of the medium around the dye molecule and thus the band shifted to higher wavelength. Decrease in the intensities of the bands were also observed for LM200 (Fig. 1B) and JR400 (Fig. 1C) although to lesser extents. No shifts were observed in the present concentration



Scheme 2. Proposed model for the stacking of dye at the positive charge centres of polymer.

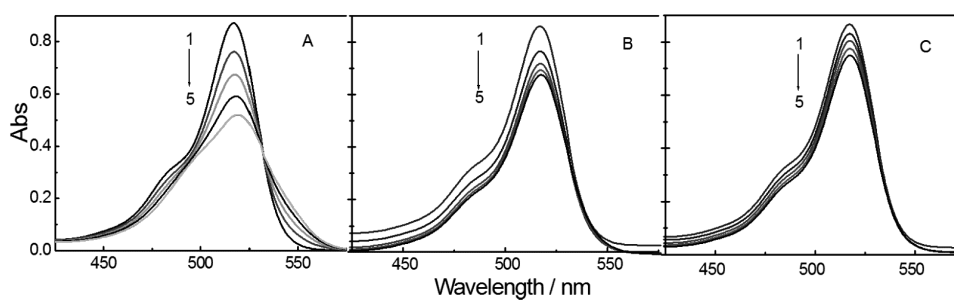


Fig. 1. Absorption spectra of 10 μM EY in presence of polymers at different polymer/dye ([P]/[D]) molar ratio. (A) PDMDAAC, (B) LM 200 and (C) JR 400. [P]/[D] values : (A) 1, 0; 2, 0.2; 3, 0.4; 4, 0.7 and 5, 0.9. For (B) and (C) 1, 0; 2, 0.4; 3, 1.1; 4, 1.4 and 5, 1.8. Temperature : 298 K.

range in both the cases.

Effect of polymers on the absorption spectra of EY in higher polymer concentration range was further investigated. Results are summarized in Fig. 2. In all the three cases there occurred bathochromic shift in the absorption spectra of EY upon the addition of polymers. After the attainment of a certain polymer/dye ratio, no further spectral shift was observed. Such shifts in the peak position are due to encaging of dye into the polymer matrix involving both electrostatic and hydrophobic interactions [38]. However, in case of PDMDAAC the absorbance value increases gradually with the increasing polymer/dye ratio at shifted wavelength (Fig. 2A) contrary to LM200 (Fig. 2B) and JR400 (Fig. 2C), where the absorbance decreases

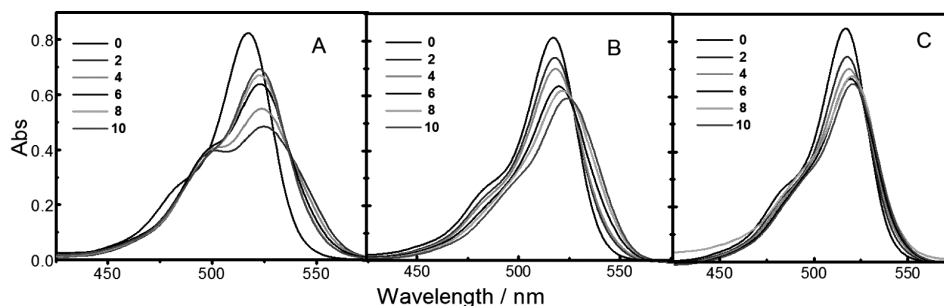


Fig. 2. Absorption spectra of 10 μ M EY in presence of polymers at different polymer/dye ([P]/[D]) molar ratio in the higher range. (A) PDMDAAC (B) LM 200 (C) JR 400. [P]/[D] values are mentioned in the figure. Temperature : 298 K.

with the increasing polymer concentration in the studied range. This is due to higher charge density of PDMDAAC in comparison to LM200 and JR400. Between LM200 and JR400 the former seems to exhibit stronger shift in the band position than the latter due to higher hydrophobicity. It was established in our previously published reports [14] that the absorption maximum shifts to higher wavelength with increasing hydrophobicity of the medium. In the present case due to charge neutralization, the dye molecule experiences less polarity (localized) in the surrounding medium.

The spectral data with a fixed concentration of EY and varying concentrations of the polycations were suitably processed in determining the interaction constant between the dye and the polymers. For polymer-EY aggregates, binding constant values were derived using the Benesi-Hildebrand formalism [39] :

$$\frac{C_D}{A - A_0} = \frac{1}{\epsilon_m - \epsilon_0} + \frac{1}{K_b (\epsilon_m - \epsilon_0) C_p} \quad (2)$$

where, C_D = concentration of dye, C_p = concentration of polymer, A_0 = absorbance of dye in absence of polymer. A = absorbance of dye in presence of polymer. ϵ_0 = molar absorption coefficient of the dye in absence of polymer, ϵ_m = molar absorption coefficient of dye-polymer aggregates.

While determining the K_b values comprising LM200 and JR400, the absolute values of the slopes were used for the calculation [40]. Representative plots of $C_D/(A_0 - A)$ vs. $1/C_p$ have been shown in Fig. 3 for PDMDAAC, LM200 and JR400. From the ratio of intercept and slope the binding constants were calculated. The K_b values show that JR400 undergoes stronger binding with EY than LM200. This was

as expected; although the stacking of dye was higher in case of LM200 due to higher hydrophobicity, however, the electrostatic interaction was strong in case of JR400 due to less steric hindrance of smaller hydrocarbon tail. In the present case the electrostatic interaction precedes over hydrophobic forces. In case of PDMDAAC, there was bathochromic shift in the spectra of EY in the higher polymer concentration range which then underwent gradual increase in the absorbance with increasing polymer concentration. However, in the cases of LM200 and JR400, the reverse phenomena happened. Straight lines were obtained (Fig. 3A) from $C_D/(A_0-A)$ vs. $1/C_P$ plots and from the ratio of intercept and slope the interaction constants, K_b were calculated. From the K_b values, the thermodynamic parameters like the changes in the standard

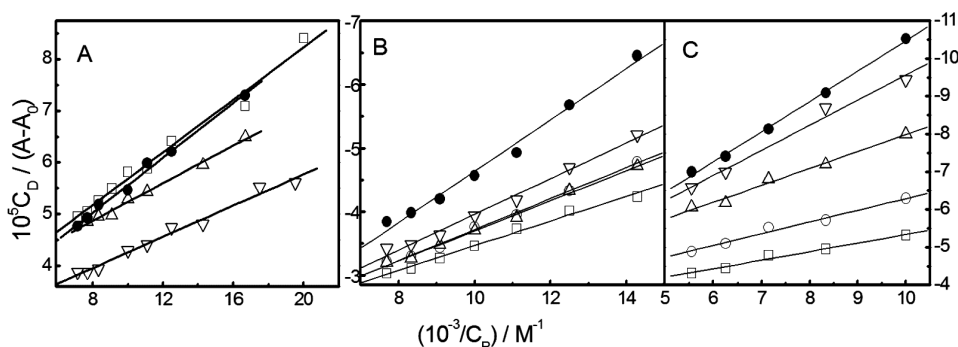


Fig. 3. Plot of $C_D/(A_0-A)$ vs. $1/C_P$ according to Benesi-Hildebrand formalism to determine the interaction constant of EY (10 μ M) - polymer aggregates. Polymers : (A) PDMDAAC, (B) LM 200, and (C) JR 400. Temp (in K) : \square , 298; \circ , 303; Δ , 308; ∇ , 313 and \bullet , 318.

Gibbs free energy (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) for the dye-polymer aggregate were determined using the following thermodynamic expressions [41] :

$$\Delta G^\circ = -RT \ln K_b \quad (3)$$

Changes in the standard enthalpy (ΔH°) were evaluated by the van't Hoff equation [14] :

$$\left[\frac{\partial(\Delta G^\circ/T)}{\partial(1/T)} \right] = \Delta H^\circ \quad (4)$$

In the present study, ΔG° vs. T profile was found to follow a 2^o polynomial equation

as [42] :

$$\Delta G^\circ = a + bT + cT^2 \quad (5)$$

where, a, b and c are the polynomial coefficients.

The polynomial coefficients thus helped in determining the ΔH° values according to the following expression [42] :

$$\left[\frac{d(\Delta G^\circ/T)}{d(1/T)} \right] = a - cT^2 = \Delta H^\circ \quad (6)$$

The standard entropy change (ΔS°) for the dye-polymer complex formation was then evaluated according to the following expression [14] :

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (7)$$

Thermodynamic parameters for the formation of the dye-polymer aggregate have been summarized in Table 1. The results show that with increasing temperature, the binding constant (K_b) values decrease except for PDMDAAC, where systematic interactions does not occur with increasing temperature. For this particular system, K_b value passes through a maximum at 308 K. This is similar to biologically relevant processes where optimum interaction among the different components occurs at 310 K. For LM200 and JR400, the results imply that with the rise in temperature the dye-polymer aggregates become unstable. Increase in the negative values of enthalpy change with increasing temperature proves the exothermicity of the binding process. The involvement of dual interactions (hydrophobic and electrostatic) is also supported by the higher values of the free energy change. The values of the thermodynamic parameters are found to be comparable with those of reversible biological processes [23].

Fluorescence spectral studies :

Aqueous solution of EY, when excited at 500 nm, emits at 535 nm. Fig. 4 shows that at lower polymer/dye ratio, the fluorescence intensity of the dye is quenched with the gradual addition of polymers. However, quenching efficiency is dependent on the type of polymer. Quenching is more significant in case of PDMDAAC (Fig. 4A) compared to LM200 (Fig. 4B) and JR400 (Fig. 4C). Results reveal that the electrostatic binding is stronger in case of PDMDAAC compared to the other two as the electrostatic binding subjects the probe molecule to the bulk aqueous phase and thus aids the interaction with the quencher [35]. The presence of hydrocarbon tail especially in LM200 renders more hydrophobic forces compared to electrostatic forces. The excited state lifetime of the fluorophore does not change

significantly (in the studied concentration range) in all the three cases and the Stern-Volmer quenching constants were calculated using the following method [43].

$$\frac{F_0}{F} = 1 + K_{sv} [Q] \quad (8)$$

where F_0 and F are the fluorescence intensities of EY in the absence and presence of quencher, Q ; $[Q]$ = Quencher concentration (herein the polymers). Here K_{sv} refers to the static quenching and can be expressed as :

$$K_{sv} = K_q \tau_0 \quad (9)$$

TABLE 1.

Thermodynamic parameters for the interaction of EY with different polymers

Polymer*	T/K	$K_b \times 10^{-3}/M^{-1}$	$(-\Delta G^\circ)/kJmol^{-1}$	$(-\Delta H^\circ)/kJmol^{-1}$	$(-\Delta S^\circ)/JK^{-1}mol^{-1}$
PDMDAAC ^a	298	12.33	23.41	-75.06	-330.43
	308	18.78	25.28	4.88	-66.24
	313	17.59	25.52	45.83	64.9
	318	10.98	24.67	87.45	197.39
	LM 200 ^b	298	7.80	22.27	-20.32
LM 200 ^b	303	5.29	21.66	18.18	-142.94
	308	5.66	22.19	57.32	114.04
	313	4.12	21.73	97.11	240.83
	318	1.49	19.38	137.53	371.55
	JR 400 ^b	298	13.50	23.64	35.82
303		10.27	23.34	48.41	82.74
308		7.82	23.03	61.21	123.99
313		4.34	21.86	74.23	167.30
318		3.03	21.26	87.45	208.14

*Polymer concentration range (μM) : PDMDAAC = 50 – 150

LM200 = 70 – 150

JR400 = 100 – 200

A 10 μM EY was used in each study

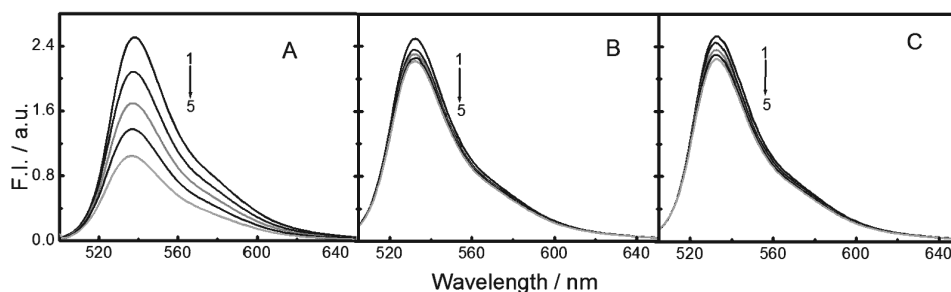


Fig. 4. Fluorescence spectra of 10 μ M EY in presence of polymers at different polymer/dye ([P]/[D]) molar ratio. A, PDMDAAC; B, LM 200 and C, JR 400. [P]/[D] values : (A) 1, 0; 2, 0.2; 3, 0.4; 4, 0.7 and 5, 0.9 (B) and (C) 1, 0; 2, 0.4; 3, 1.1; 4, 1.4 and 5, 1.8. Temperature : 298K. λ_{ex} = 500 nm.

where, K_q is the quenching constant and τ_0 is the unquenched fluorescence lifetime of the fluorophore.

The product of probe-quencher interaction constant (K_q) and fluorescence lifetime (τ_0) remained constant, i.e., K_{SV} could easily be calculated from the slope of F_0/F

TABLE 2.

Excited state interaction constant of 10 μ MEY-polymer aggregates at 298K

Polymer	$K_{\text{SV}}^{(a)} \times 10^{-4}/\text{M}^{-1}$	$K^{(b)} \times 10^{-5}/\text{M}^{-1}$
PDMDAAC	11.1	8.5
LM 200	1.3	–
JR 400	1.3	–

(a) Values were determined from Stern-Volmer plot⁴³.
 (b) Values were determined from Benesi-Hildebrand formalism⁴⁴.

vs. [Q] plot which produced a straight line with unit intercept (figure not shown) proving that the quenching is a static one. The Stern-Volmer quenching constant (K_{SV}) values are represented in Table 2.

Similar to the absorption spectroscopic studies, fluorescence spectroscopic studies were also carried out at higher polymer/dye ratio (Fig. 5). But unlike the absorption spectra, no significant spectral shifts were observed suggesting the fact that

the excited state dye-polymer aggregates do not lead to significant change in polarity. In presence of PDMDAAC (Fig. 5A) the fluorescence intensities of EY increases with the increasing polymer/dye ratio. Excited state dye-polymer interaction constant (K) was calculated from the fluorescence spectra using the Benesi-Hildebrand equation [44] :

$$\frac{F_{\infty} - F_0}{F_x - F_0} = 1 + (K[L])^{-1} \quad (10)$$

where, F_0 = fluorescence intensity of the dye in absence of polymer, F_x = fluorescence intensity at an intermediate polymer concentration, F_{∞} = fluorescence intensity at a polymer concentration where the interaction is complete, L = total polymer concentration. Results are summarized in Table 2. However, in the presence of LM200 (Fig. 5B) and JR400 (Fig. 5C) no systematic changes were observed. This shows that the process of dye-polymer binding for LM200 and JR400 in the excited

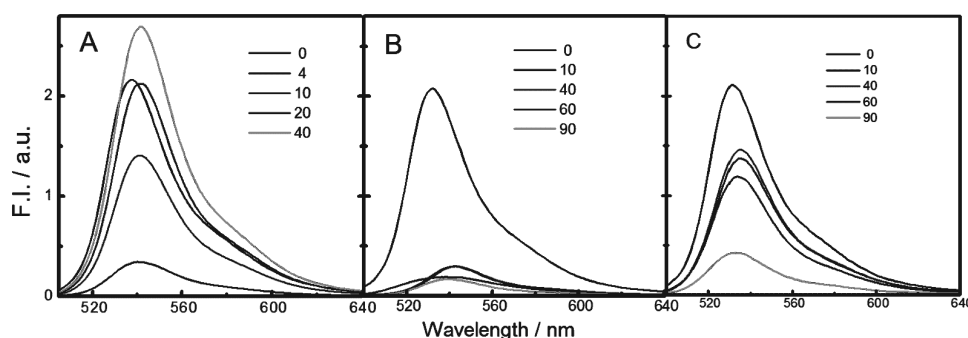


Fig. 5. Fluorescence spectra of 10 μ M EY in presence of polymers at different polymer/dye ($[P]/[D]$) molar ratio in the higher range. (A) PDMDAAC (B) LM 200 (C) JR 400. $[P]/[D]$ values are mentioned in the figure. Temperature : 298K. λ_{ex} = 500 nm.

state is unfavourable at higher polymer/dye ratio. When the fluorescence data were recorded the background was corrected with respect to the individual polymers. It is worthwhile to mention that in the present study polymers did not exhibit significant absorption in the studied range.

Steady-state fluorescence anisotropy :

Fluorescence anisotropy measurements were carried for all the three systems. Such studies are believed to enlighten ideas on the micro-viscosity of the medium around

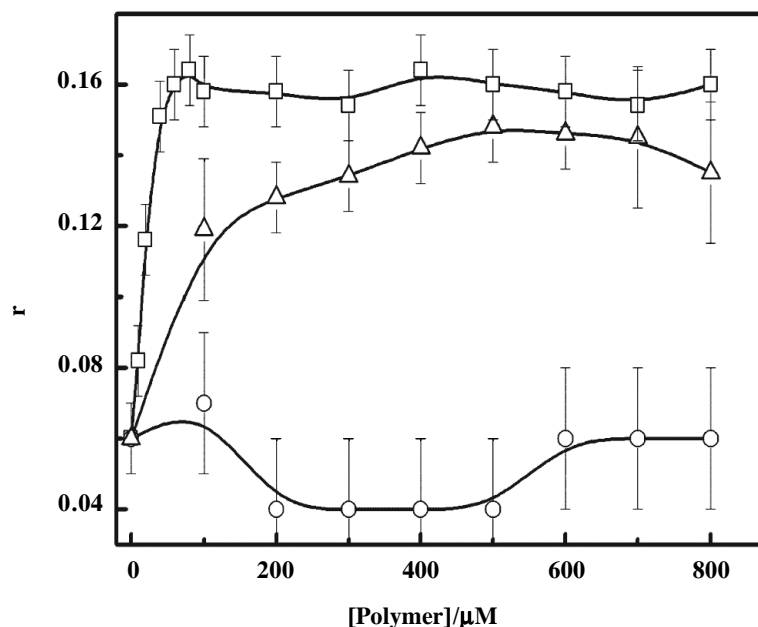


Fig. 6. Variation in the fluorescence anisotropy (r) of 10 μM EY with polymer concentration ([P]) in aqueous medium at 298K. Polymers : \square , PDMDAAC; Δ , JR 400 and \circ , LM 200. $\lambda_{\text{ex}} = 500 \text{ nm}$ and $\lambda_{\text{em}} = 535 \text{ nm}$.

a fluorophore. Variation of fluorescence anisotropy with the polymer concentration has been shown in Fig. 6. The anisotropy value of pure EY in water is 0.0614, which increases with the increasing polymer concentration and then attain constancy. The increase in the anisotropy value attributes to the increase in the rigidity of the environment surrounding the dye molecule [35] leading to its decrease in the degree of freedom and when all the dye molecules are entrapped within the polymer matrix, the anisotropy values become constant. In case of PDMDAAC, a sharp increase is observed upto polymer/dye ratio value of 10 and after which it did not change significantly, i.e., the rigidity of the environment becomes unchangeable after 100 μM PDMDAAC. For JR400, the increase is low in comparison to PDMDAAC and no significant changes in the anisotropy value with the increasing concentration of LM200 are observed. This again proves that the electrostatic interaction of the dye with LM200 is weak in comparison to JR400.

CONCLUSIONS

The present work reports comprehensive studies on the interaction of three cationic polymers with an anionic xanthenes dye eosin Y. The dye molecules are held around the polymer matrix both by way of electrostatic and hydrophobic forces. Interaction of EY with PDMDAAC is stronger compared to JR400 and LM200 and also an equilibrium exists in the binding process. In case of JR400, electrostatic interaction precedes over hydrophobic forces, compared to LM200, as evidenced from the binding constant values. The binding processes are exothermic in nature and the stability of the systems is hindered with the rise in temperature. Fluorescence spectral studies suggest that the excited state dye-polymer aggregates do not lead to significant change in polarity. Also, in the excited state, the binding of EY with LM200 and JR400 is unfavourable at higher polymer/dye ratio. The anisotropy results propose the entrapment of the dye within the polymer matrix. However, in order to confirm the complete entrapment of dye molecules further studies are required, which is considered as the future perspective.

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