

Effect of chemical parameters on the interaction between cationic dyes and poly(acrylic acid)



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ABSTRACT

Being polymers and electrolytes, polyelectrolytes are widely used in many applications. In perspective of dye removal from textile effluents, they have been used in coagulation–flocculation and to a lesser extent in polyelectrolyte enhanced ultrafiltration. To optimize the abovementioned process we need to study in detail the interaction of dye with polyelectrolyte in conditions near the industry reality. In this context we investigate herein the effect of chemicals additives, NaCl, surfactant, pH on the behavior of two model cationic dyes, methylene blue (MB) and toluidine blue (TB), with polyacrylic acid polymer (PAA). Using spectrophotometric method it was found that the poly(acrylic acid) induced metachromasy in the dyes resulting by the blue shift of the absorbance confirming the formation of dye polymer complexes. The stoichiometry of MB–PAA and TB–PAA complexes determined by the ratio method was found to be 2:1. The stability constant of the complexes at 298 K was found to be 5332 for MB–PAA and 4358 dm³ mol⁻¹ for TB–PAA and the amount of additives inducing total destabilization of the complex were determined.

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1. Introduction

The interaction between dyes and polyelectrolyte in aqueous solutions was largely investigated [1–3]. Studies on binding of dye to different synthetic and natural polymers by absorbance, fluorescence and circular dichroism experiments yielded significant contributions [4–6]. It is known that electrostatic and hydrophobic interactions both contribute to the binding between oppositely charged dyes and polyelectrolytes [7]. The possibility of utilizing electrostatic interactions between anionic polyelectrolytes and cationic dye molecules to foster aggregation has gathered a lot of interest in recent years due to its potential nanomaterial applications [8]. The aggregation of dyes is accompanied by changes in the absorbance and/or fluorescence spectrum compared to the individual monomeric molecules. According to Kasha's exciton theory [9], H-aggregates are spectroscopic entities that are characterized by a blue-shifted absorption with respect to monomer absorption, whereas J aggregates present a red-shifted absorption band. The

H and J-aggregates involve a parallel stacking of dye molecules into well-ordered fashion, in H-aggregate the molecules are aligned in face-to-face arrangement, while in J-aggregate the molecular alignment is edge-to-edge [10]. The strength of such molecular aggregation depends upon both the concentration and structure of the dye, ionic strength, solvent and other factors [11].

On the other hand, polyelectrolytes have been utilized in many applications. In water treatment, polyelectrolytes serve as flocculants to remove particles, colloids and soluble contaminants [12,13]. They may assist the ultrafiltration membrane for the retention of organics of low molecular weight and ions from wastewater in PEUF process [14,15]. In the case of dye effluents treatment the type of interaction between polyelectrolyte and dye will be determinant in the efficiency of those processes. As the effluent is complex the effect of many kind of additive present in wastewater may affect the dye polymer interaction. Furthermore as the UV–vis spectrum of dye is sensitive to its environment it becomes difficult to analyze it with accuracy. For these reason we plan in the present study to investigate the effect of physicochemical parameters on the interaction between two cationic dyes chosen as model cationic dyes and polyacrylic acid (PAA) as anionic polyelectrolyte. TB and MB, two thiazine dyes, have similar chemical structures but differ by their partition coefficients (*P*), the TB coefficient is

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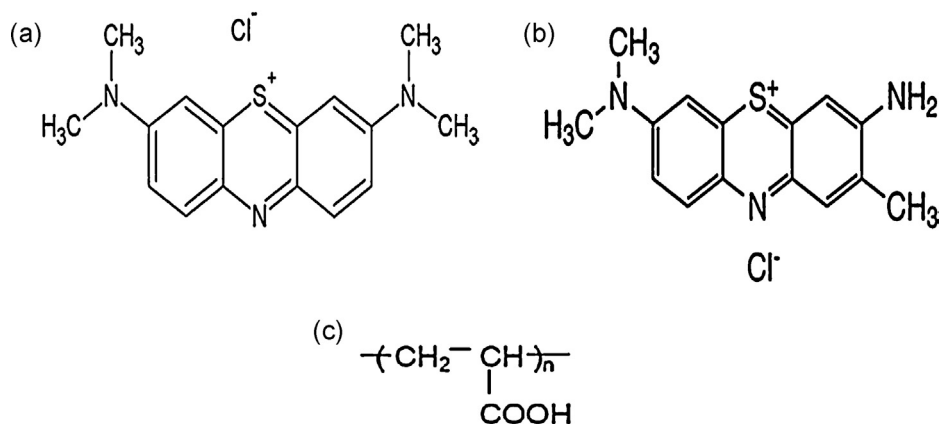


Fig. 1. Molecular structure of (a) methylene blue, (b) toluidine blue and (c) poly(acrylic acid).

almost 3-fold higher than that of MB [16]. The metachromatic effect of polyacrylic on cationic dyes has been demonstrated [17,18], however to our knowledge there is no in the literature an extensive study on the effect of chemical additives on the behavior of the dye–polyelectrolyte system. Therefore, the present experimental study will be done by changing the initial concentration of the poly(acrylic acid), the concentrations of sodium chloride and of cetylpyridinium chloride and pH. Thereafter, thermodynamic parameters of interaction ΔG , ΔH and ΔS and the binding constant of complexes will be evaluated at different temperatures.

2. Experimental

2.1. Materials

Methylene blue and toluidine blue, two cationic phenothiazine dyes, were purchased from Fluka. Polyacrylic acid (PAA) ($M_w = 100,000 \text{ g mol}^{-1}$, 35 wt.%) was provided by Sigma–Aldrich. The chemical structures of the three compounds are shown in Fig. 1. Hydrochloric acid, sodium chloride, sodium hydroxide and cetylpyridinium chloride $\text{C}_{16}\text{H}_{33}\text{Pyr}^+\text{Cl}^-$ (CPC), were provided by Sigma–Aldrich. All the chemicals were used without further purification. Distilled water was used for solution preparation.

2.2. UV–vis spectroscopy

The UV–vis spectra were acquired on aqueous MB and TB dyes solutions with a Perkin Elmer Lambda 25 spectrophotometer, with a matched pair of cuvettes of 1 cm path length. The temperature was always maintained at $25 \pm 0.1^\circ\text{C}$ except when we studied the influence of temperature. The stoichiometry of poly(acrylic acid)–dye complex was determined using the ratio method as follows: increasing amounts of polyelectrolyte ($0\text{--}6 \text{ ml}$, $1 \times 10^{-3} \text{ M}$) were added to a fixed volume of dye solution (2 ml , $1 \times 10^{-4} \text{ M}$), dye in different sets of experiments and the total volume was made up to 10 ml by adding distilled water. Absorbance measured at A_m refers to the absorbance of the monomeric band and at A_M refers to the absorbance of metachromatic band. The ratio A_m/A_M was plotted against the poly(acrylic acid) concentration/dye concentration ratio $[P]/[D]$.

3. Results and discussion

3.1. Effect of polymer concentration

In aqueous solution, MB exhibits a band at 665 nm and a shoulder at 612 nm which are assigned to monomeric and dimeric forms, respectively. Toluidine blue presents only one band at 623 nm

indicating the presence of only monomeric form. The addition of increasing amounts of poly(acrylic acid), as shown in Fig. 2a and b, caused the decrease of absorption at maximum wavelength for both dyes followed by the appearance of new band at 598 nm in the case of MB and at 566 nm in the case of TB. This indicates that a new metachromatic complexes were formed between cationic dyes and the anionic polyelectrolyte [17–19]. The large hypsochromic shift for MB (67 nm) and for TB (57 nm) were also attributed to the formation of dye H-aggregates [20,21]. As a consequence of the higher local concentration near the polyanion, the dyes self aggregate by means of aromatic–aromatic interaction forming H-type aggregates at substantially low dye concentrations.

To determine the stoichiometry of poly(acrylic acid)–dye complex, a plot of A_m/A_M versus polymer/dye $[P]/[D]$ ratio was made for MB–PAA. The same procedure was repeated for TB–PAA. According to Fig. 3, the stoichiometry of the two complexes was found to be 2:1 which indicates that the binding takes place on alternate anionic sites [22].

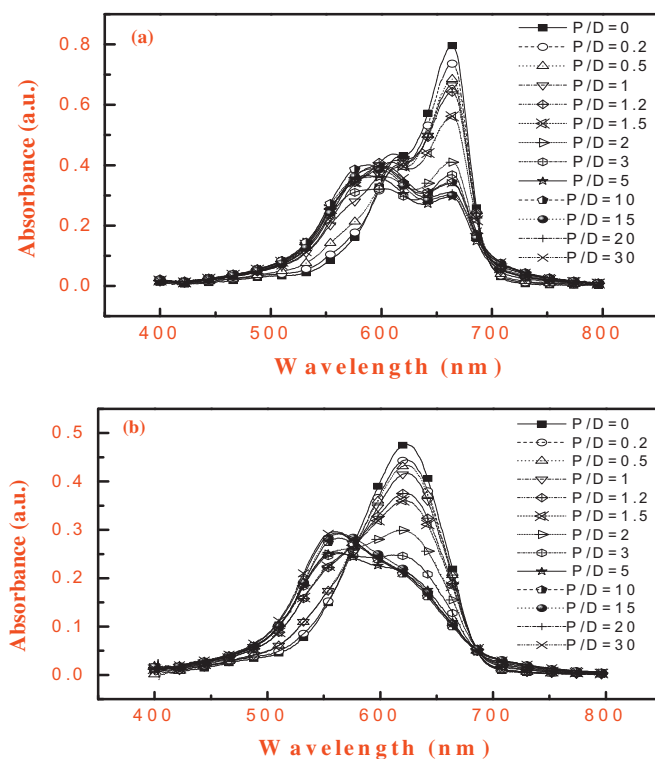


Fig. 2. Absorption spectra of dye in presence of PAA at various P/D ratios: (a) methylene blue and (b) toluidine blue.

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