



Spectrophotometric study of the interaction of toluidine blue with poly (ammonium acrylate)



Anouar Ben Fradj^a, Ridha lafi^a, Lassad Gzara^b, Ahmed Hichem Hamzaoui^c, Amor Hafiane^{a,*}

^a Laboratory of Wastewater Treatment, CERTe, BP 273, Soliman 8020, Tunisia

^b Center of Excellence in Desalination Technology, King Abdulaziz University, Jeddah, Saudi Arabia

^c Laboratory of Valorisation of Materials, CNRSM, BP 95, Hammam-Lif 2050, Tunisia

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ABSTRACT

The aim of this work is to study the interaction between Toluidine Blue (TB), a cationic dye, and an anionic polyelectrolyte, poly (ammonium acrylate) (PANH₄). The UV–Visible spectroscopy study shows that addition of increasing amounts of poly (ammonium acrylate) induces the formation of a metachromatic complex. The stoichiometry of TB–PANH₄ complex evaluated by the molar ratio method is 1:1 and the large hypsochromic absorption shift (73 nm) obtained is attributed to dye H-aggregates. The effects of sodium chloride concentration, pH and Cetyl pyridinium chloride (CPC) concentration, on metachromasy have also been studied. Thermodynamic parameters of interaction ΔG , ΔH and ΔS at different temperatures have been evaluated to determine the stability constant of the complex.

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1. Introduction

The release of dyes with wide variety of different components from textile activities remains an environmental issue. There are many structural varieties of dyes, such as, azo, diazo, anthraquinone, triphenylmethane and phenothiazine. Most of these dyes are toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [1–4]. The removal of the dye which is considered as pressing task has been done primarily through adsorption using different adsorbents [5–7]. Other techniques involving electrochemical oxidation [8], biological treatment [9], ozonation [10] etc., are also investigated in the literature. In the context of environmental remediation, polyelectrolytes have been widely investigated in coagulation–flocculation [11–14], and polyelectrolyte enhanced ultrafiltration (PEUF) process [15–18]. To remove dyes from aqueous solutions, we use PEUF as hybrid process which combined ultrafiltration and complexation ability of water soluble polymers. But to ensure the efficiency of this method, it is necessary to study in details the nature of the interaction between the dye and the polyelectrolyte [19,20]. On the other hand, it is established that the polyelectrolyte in aqueous solution affects the absorption spectrum of the dye and therefore the accuracy of its analysis. The observed absorption changes have been attributed to binding of the dye [21–23] with a polymer having an opposite charge which enhances dye aggregation at very low concentration. Furthermore the spectral change becomes more

complicated in presence of auxiliary chemicals such as NaCl, HCl, NaOH, and CPC. So in the present work we have focused on the effect physico-chemical parameters on the interaction between Toluidine Blue chosen as model dye and poly (ammonium acrylate) as polyelectrolyte. The study will be done by changing the initial concentration of the polymer, the pH solution, and the NaCl and surfactant concentrations.

2. Materials and methods

2.1. Chemicals

Toluidine blue (C₁₅H₁₆ClN₃S), a cationic phenothiazine dye, was purchased from Fluka. Poly (ammonium acrylate), an anionic polyelectrolyte (PANH₄), with molecular weight Mw 30,000 g·mol⁻¹, was synthesized by radical polymerization of ammonium acrylate monomer. The preparation of this polymer is reported elsewhere [24]. The chemical structures of the two compounds are shown in Fig. 1. Chloride acid, sodium chloride, sodium hydroxide and cationic surfactant cetylpyridinium chloride C₁₆H₃₃Pyr⁺Cl⁻ (CPC), were provided by Sigma-Aldrich. All the chemicals were used without further purification. Distilled water was used for all the experiments.

2.2. UV–visible spectroscopy

The UV–Visible spectra of different TB solutions were acquired by PerkinElmer Lambda 25 spectrophotometer, with a matched pair of cuvetts of 1 cm path length. The temperature was always maintained

* Corresponding author. Tel.: +216 79 325 750; fax: +216 79 325 802.
E-mail address: amor.hafiane@certe.mrt.tn (A. Hafiane).

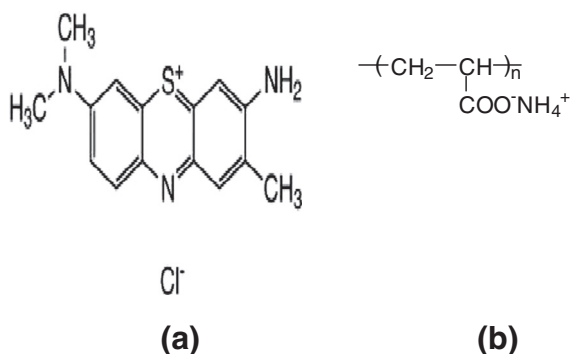


Fig. 1. Molecular structure of a) Toluidine blue and b) Poly (ammonium acrylate).

at 25 ± 0.1 °C. The variation of the polymer/dye ratio (P/D) was determined as follows: An increasing amount of poly (ammonium acrylate) (0.0 ml–6.0 ml, 1×10^{-3} M) is added to a fixed volume of Toluidine Blue (2.0 ml, 1×10^{-4} M) and the total volume is made up to 10 ml in a standard flask.

3. Results and discussion

3.1. Effect of PANH₄ concentration

The absorption spectra of Toluidine Blue in aqueous solution (Fig. 2) showed an absorption band at 623 nm (the value of the molar extinction coefficient of TB (ϵ_0) at 623 nm is $39,515 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 298 K) indicating the presence of a monomeric dye species in the concentration range studied. The absorption peaks were assigned to π – π^* electronic transition between the ground state and the excited state of the chromophore moiety.

The adsorption spectra of TB at different ratio of $[\text{PANH}_4]/[\text{TB}]$ ranging from 0 to 30 are shown in Fig. 3. From $P/D = 0$ to 1, the maximum absorbance of monomer band decreases but no changes are observed in the shape of the absorption band. From $P/D = 1$ to 30, the absorption band at 623 nm vanishes and new absorption band centered at 550 nm appears, which indicates that a new metachromatic complex was formed. On the other hand, the large hypsochromic absorption shift obtained is attributed to the formation of dye H-aggregates [25,26]. In fact, according to Kasha's exciton theory [27], H-aggregates are spectroscopic entities that are characterized by a blue-shifted adsorption with respect to monomer absorption, whereas J-aggregates present a red-shifted adsorption band. The H-aggregates and J-aggregates involve a parallel stacking of dye molecules into well-ordered fashion, in H-aggregates

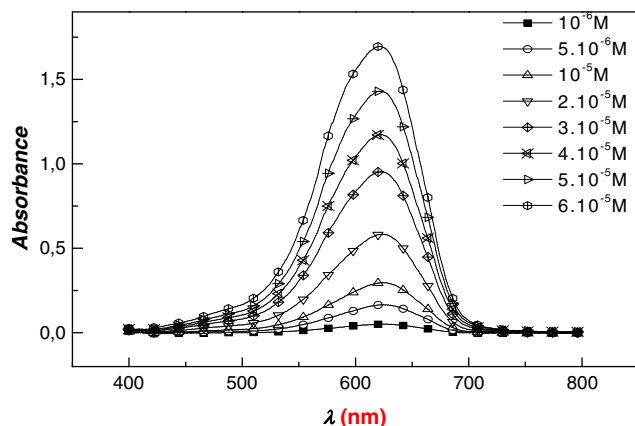


Fig. 2. Absorption spectra of toluidine blue at various concentrations.

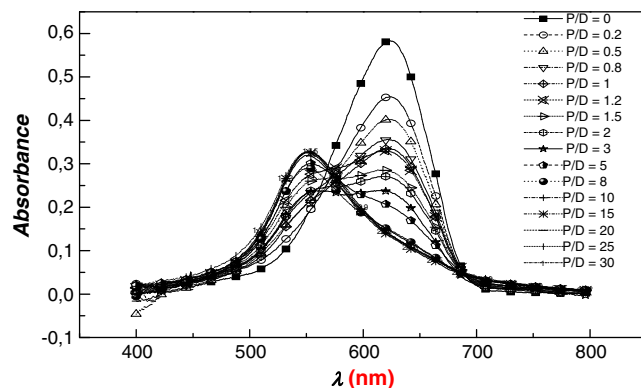


Fig. 3. Absorption spectra of TB in presence of PANH₄ at various P/D ratios.

the molecules are aligned in face-to-face arrangement, while in J-aggregates the molecular alignment is edge-to-edge.

The decrease in λ max and absorbance values can be assumed to some sort of association or complex formation between cationic dye and polyelectrolyte [28]. As a consequence of the higher local concentration near the polyanion, the dyes may self-aggregate by means of aromatic–aromatic interaction forming H-aggregates at substantially lower dye concentrations.

To determine the stoichiometry of the polyelectrolytes–dyes complexes using the ratio method, a plot of A_{623}/A_{550} versus the polyelectrolyte/dye ratio was made. According to Fig. 4, A_{623}/A_{550} ratio decreased with the increase of P/D and the value of P/D corresponding to the stoichiometry of TB–PANH₄ complex was about 1:1. This result indicated that every potential anionic site of the polyanion was associated with the corresponding cationic site. Similar results were reported in the case of Toluidine Blue O/Cyclodextrin [29] and for the interaction of pinacyanol chloride on poly (methacrylic acid) systems [30].

3.2. Effect of NaCl

The effect of added electrolyte on dye aggregation has been well investigated [31]. It has been recognized that the self-association of ionic dyes in aqueous solutions can be enhanced by the addition of inorganic salt. This behavior has been linked to the increase of the screening factor or to the increase of effective dielectric constant. The effect of NaCl concentration on the absorption spectra of TB in absence and presence of polyelectrolyte was studied at fixed dye concentration equal to $2 \cdot 10^{-5}$ M with NaCl concentration ranged from 10^{-5} to 4 M.

In absence of polyelectrolyte, Fig. 5a shows that the absorbance increases upon increasing of NaCl concentration up to 2 M without change of spectral shape. For NaCl concentration larger than 2 M a

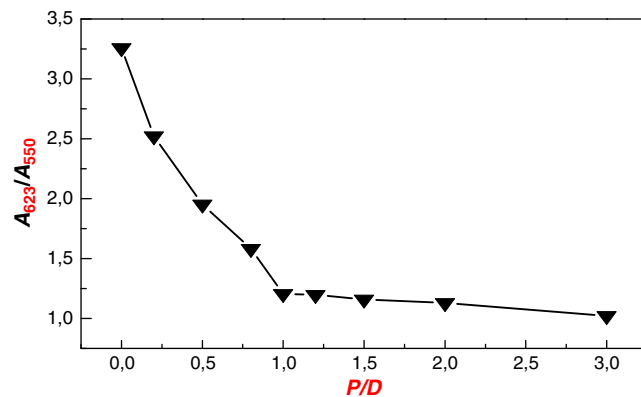


Fig. 4. Stoichiometry of TB–PANH₄ complex.

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