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Effect of cation exchanged bentonites (CEBs) on the aggregation of a cresol based dye

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Abstract

The effect of raw and cation exchanged bentonite (CEB) samples on the aggregation of a cresol based dye, bromocresol green, was studied by spectrophotometric method. The changes in the absorption spectra were explained in terms of the layer charge of the clay surfaces which controls the stability of the dye aggregates.

Keywords: Bromocresol green; J-aggregate; Clay; Absorption spectra; Cation exchanged bentonite

1. Introduction

It is known that clay minerals possess attractive properties as solid acids [1–3]. Fripiat et al. [4] and Bailey et al. [5] specified that the degree of dissociation of these water molecules in the interlayers of Na^+ and Ca^{2+} montmorillonite is small and is some orders of magnitude higher than in the bulk solution. The reactivities of Si–OH and Al–OH groups, exhibiting amphoteric properties based on their affinity for protons [6–8], which are located at the broken edges and basal spaces, are also affected by isomorphic substitutions [9–11]

J-aggregation of pigments and dyes plays an important role in many technical applications, such as photography, optoelectronics, solar cells, photobiology and as supra-molecular fibres. Several types of aggregates have been described with respect to their spectral behaviour. These spectral changes may be reflected by a monomer (one molecule), dimer (two molecules), H- or J-aggregates. When a monomer or dimer is formed, the absorption shifts slightly to higher energy (lower wavelength) and the absorption spectrum narrows slightly. The absorption spectrum of an H-aggregate shifts to higher energy and broadens as compared to the monomer. A J-aggregate is formed when the dye molecules arrange into a slanted stack. The absorption spectrum of a J-aggregated dye will shift to lower energy [12].

Earlier investigations have shown that dye/clay interactions affect the optical properties of adsorbed dyes [13,14], adsorption kinetics [15], irreversibility of the process [16], basal spacing of clay [17] and stability of J-aggregate [18]. When a solution of dye is mixed with a clay dispersion, dye aggregates may occur as a consequence of the dye accumulation at the interface and this is likely to be enhanced by the presence of inorganic ion at the clay surfaces [19]. Clay surfaces significantly affect the aggregation of dye species either by stabilizing or leading to decomposition of the aggregates [20–22].

Our focus in this study is to gain more insight into the influence of the nature of clay surface on the features of J-aggregates of bromocresol green at different pH values.

2. Experimental

2.1. Materials

The bentonite sample (from Unye, Turkey) was ground and washed in deionized water several times at a 1:10

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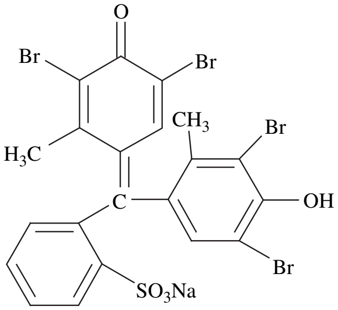
clay/water ratio. The mixture was stirred for 3 h and then kept undisturbed overnight. After the clear liquid was decanted off the top, the solid was exposed to slow evaporation to dryness, and then ground and sieved to 78–120 µm size. The clay samples were rehydrated with deionized water and 10 g metal chloride of corresponding salts was added to homoionic form. The resulting mixtures were stirred for 24 h and centrifuged at 3000 rpm for 5 min until attaining chloride-ion-free form ($AgNO_3$ test). Bromocresol green was obtained from Merck. The structure of the dye is shown below:



Bromocresol green

2.2. Electronic spectroscopy

A 50 mg sample was mixed with a 50 ml dye solution of known concentration in the polyethylene bottle. Supernatants were separated by centrifuge 3000 rpm for 5 min and the electronic spectra of dye were obtained with a Unicam UV2-100 Spectrophotometer in the 200–800 nm range. The spectra were recorded 5 h following the preparation of the dye–clay suspension. The pH values were adjusted by adding a few drops of dilute NaOH or HCl and were measured by a Jenway 3040 model pH-meter. Buffer solutions with pH = 4.0 and 9.0 were used for calibration.

3. Results and discussions

3.1. The electronic absorption spectra of dye

3.1.1. Effect of dye concentration

The electronic absorption spectra at different dye concentrations in aqueous solutions are shown in Fig. 1. Inspection of Fig. 1 reveals that absorption maximum in the presence of 2×10^{-5} mol l^{-1} dye concentration shifts from 399 to 442 nm with increasing the concentration from 4×10^{-5} to 1.2×10^{-4} mol l^{-1}. But the intensities of absorption bands at 442 and 615 nm do not linearly increase in this concentration range (Fig. 2). These spectral behaviours show that the electronic absorption band at 399 nm can be attributed to the monomeric form of dye. Shifting of the absorption band to higher wavelengths arises from the increasing of the interactions between the hydrophobic molecular planes of heteroaromatic groups of dye molecules with dye concentration, and thus J-aggregate takes places between the dye molecules.

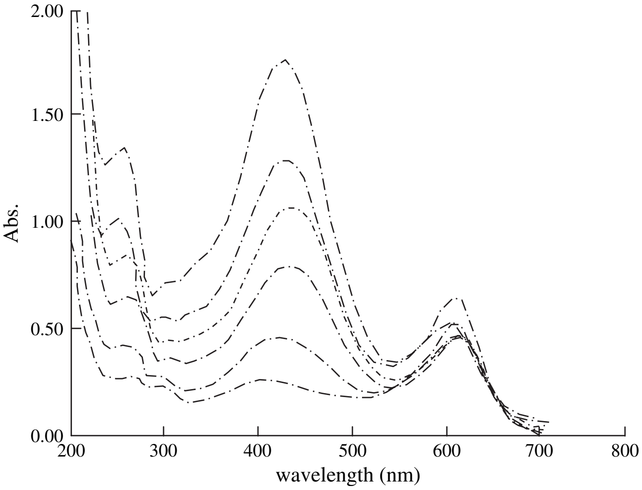


Fig. 1. The electronic absorption spectra of dye in the concentration range of ca. 1×10^{-5}–1.2×10^{-4} mol l^{-1}.

3.1.2. Effect of pH

The electronic absorption spectra of 1×10^{-4} mol l^{-1} dye solution within the pH range from 2.7 to 8.7 were recorded in deionized water. As shown in Fig. 3, molecular form of dye (HA) is shown by the band at $\lambda = 442$ nm, which is attributed to J-aggregate form, formed as a consequence of interactions between dye molecules and polar water molecules [23] at the pH value below 5.5.

At the pH values above 5.5, acidic form dissociates into monomer in the anionic form [24], which is shown by the adsorption band with a maximum at $\lambda = 615$ nm. Therefore,

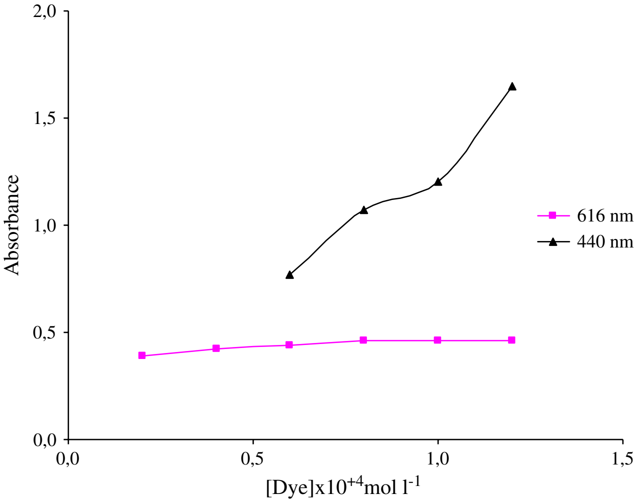


Fig. 2. The absorbance–concentration plots at different wavelengths in the concentration ranges of 2×10^{-5}–1.2×10^{-4} mol l^{-1}.

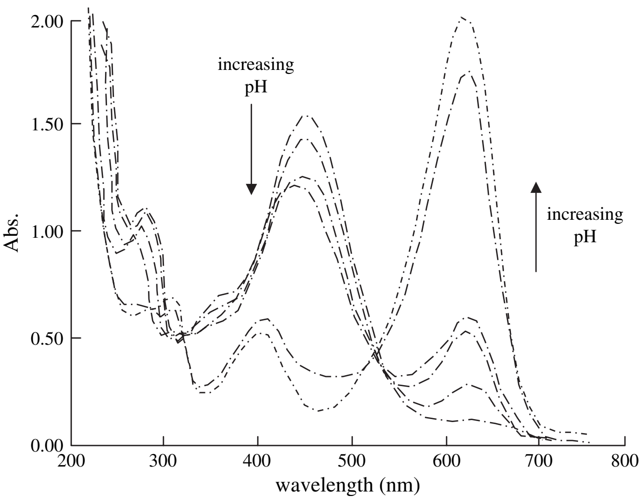


Fig. 3. The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye at pH 2.7–8.7 range.

It can be concluded that the ionisation to A^- passes through the formation of the monomer intermediate, HA [Eq. (1)]

$$\underset{442\ \text{nm}}{(HA)_2} \xrightarrow{\text{below pH 5.5}} \underset{399\ \text{nm}}{2HA} \xrightarrow{\text{above pH 5.5}} \underset{615\ \text{nm}}{2A^-} + 2H^+ \quad (1)$$

3.2. Interactions with CEBs

3.2.1. Influence of J-aggregates on absorption spectra

As shown in Table 1, pure dye is mainly J-aggregate form in the experimental conditions. When metal-exchanged bentonite particles were introduced into dye solution, shifting of the absorption band was observed. These spectral shifts depend on geometric and steric aspects of an intermolecular association and the number of interacting dye molecules. Hence, the intensities and positions of the absorption bands assigned to the J-aggregates reflected qualitatively the amount and size of the J-aggregates and the degree of the aggregation [12].

Fe–EB and Cr–EB surfaces showed acidic properties, which is in fact due to extensive hydrolysis of water molecules as a consequence of the polarization power of these cations. If the acidification of dye proceeds on these clay surfaces, an interaction would occur as a result of the hydrolysis of hydrated Fe and Cr cations. Acidic properties of these surfaces may stabilize ordered J-aggregates of dye, thus absorption maxima shifted to higher wavelengths than that of the pure dye either at pH 5.5 or 3.5.

In the other CEBs (Al–EB, Zn–EB, Cu–EB, Ca–EB, Ni–EB, Co–EB, Pb–EB, raw, Ba–EB) dye absorption maxima shifted below the pure dye absorption maximum either at pH 5.5 or 3.5. This behaviour can be explained by the protonation of the surfaces through binding of H^+ to oxygen containing surface groups. The distortions in the electrical potential at the basal surface caused by the isomorphic substitutions resulting in a stronger reactivity of oxygen containing

Table 1
Wavelengths and intensities of 1.0×10^{-4} mol l^{-1} pure dye and in different clay suspensions

Sample		Al–	Pure dye	Fe–	Cr–	Zn–	Cu–	Ca–	Ni–	Co–	Pb–	Raw	Ba–
pH 5.5	λ; A of first peak	430; 0.621	438; 1.201	439; 1.296	441; 1.358	399; 0.825	399; 0.806	403; 0.837	404; 0.887	406; 0.880	407; 0.925	408; 0.890	411; 0.930
	λ; A of second peak	616; 1.197	616; 0.594	617; 0.479	614; 0.218	614; 2.917	614; 2.963	616; 2.514	615; 2.335	616; 2.245	616; 2.229	616; 2.182	616; 1.928
pH 3.5	λ; A of first peak	437; 1.275	442; 1.436	443; 1.589	442; 1.453	411; 1.127	424; 1.204	436; 1.312	436; 1.123	434; 1.113	440; 1.214	443; 1.463	442; 1.564
	λ; A of second peak	616; 0.802	615; 0.260	613; 0.136	615; 0.194	616; 1.958	616; 1.444	616; 0.939	616; 0.885	616; 0.827	615; 0.519	615; 0.507	616; 0.630

Table 2
Visible absorption bands position of 1.0×10^{-5} mol l^{-1} in the different clay suspensions

Sample		Pure dye	Raw	Cu–	Ca–	Ni–	Ba–	Pb–	Zn–	Co–	Al–	Cr–	Fe–
pH 5.5	λ of first peak	399	–	–	–	–	–	–	–	399	425	442	428
	λ of second peak	616	614	614	616	614	616	615	614	614	613	–	–
pH 3.5	λ of first peak	399	437	431	402	403	401	427	409	407	440	443	444
	λ of second peak	–	617	614	615	615	615	615	615	615	615	611	–

surface groups support this. Different intensities and positions of the absorption bands arise from the different layer charge which controls the distribution of the dye molecules on the clay surface and in this way affects both the extent and the type of dye molecular aggregation [19].

Because the interactions between the anionic dye and CEBs do not bring about any ion-exchange process, metal cations may not be found in the solutions. Thus, both direct and indirect effects of the cations to absorption spectra were not taken into account. This phenomenon supports the tendency of the more aggregated form in the raw bentonite suspension than the tendency of Zn–EB, Cu–EB, Ca–EB, Ni–EB, Co–EB, Pb–EB suspensions (Table 1).

3.2.2. *Influence of monomer on absorption spectra*

The dye–bentonite suspensions were prepared at pH 3.5 and 5.5. The visible spectra of pure dye solution show an absorption band maxima at 399 and 615 nm, due to the molecular and ionic forms of dye in the 2×10^{-5} M dye concentration, respectively, at pH 3.5 and 5.5 values (Table 2). Comparison of absorption maxima of dye in clay suspensions with pure dye absorption maxima (Table 2) leads to the finding that dye aggregation was strongly affected by the exchangeable cation. At pH 5.5, first visible absorption band of the dye was observed, of which intensities and positions reflect qualitatively the amount, size and degree of the J-aggregate in the Al^{3+}, Cr^{3+}, Fe^{3+} exchanged bentonite suspensions. The second visible absorption band belongs to the anionic form of dye, and likely arises from proton binding of dye to negative charge on bentonite surfaces. At pH 3.5, all bentonite suspensions showed the first visible absorption maximum at different wavelengths, of which positions correlated with degree of the dyes J-aggregate. Although second visible absorption band is not observed in the pure dye solution, it is observed in other bentonite suspensions except from Fe–EB suspensions. This is due to the negative charge at broken edges which is still effective on these CEB surfaces at pH 3.5. Fe–EB–dye suspension does not show second visible absorption band. This behaviour can be explained by the highest surface acidity in the presence of the Fe^{3+} cations.

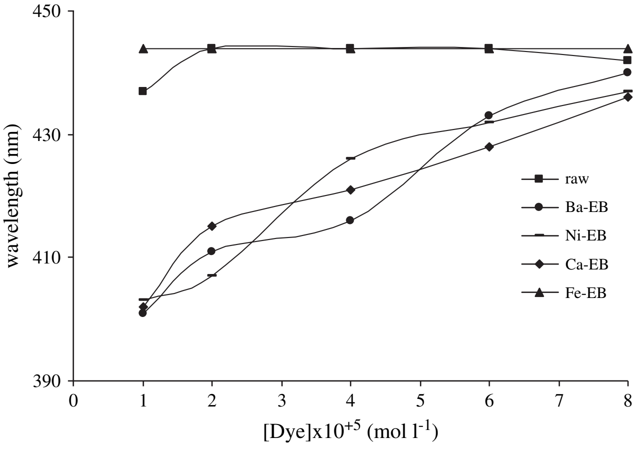


Fig. 4. Effect of bentonite type and dye concentration to absorption band position.

3.2.3. *Effect of surface type and dye concentration*

Absorption band maximum positions as a function of the added amount of dye is plotted in Fig. 4. Different $\Delta\lambda$ values of a number of bentonite suspension show that formation of J-aggregates is largely dependent on the CEBs surface features, and concentration effect is less important in the dye specification in the experimental conditions.

4. Conclusions

The aggregation of bromocresol green in bentonite suspensions is highly affected by the bentonite surface features. The observed experimental results may be concluded as following:

- Formation of aggregates appears as changes in the absorption spectra.
- A change in the intensities and positions of absorption bands that correlated with aggregate size and volume, which may be affected by CEB suspensions.
- Decomposition of J-aggregates is increased depending on the type of clay surfaces. This change is due to the attraction of H^+ ions to the surface edge sites of clay.
- Different absorption band intensities and positions observed are mainly related to acidic properties of clay surfaces. This interpretation is based on the observation that dye absorbs light at same wavelength in acidic or basic solutions.
- Intensities and positions of the absorption bands in the clay suspensions can be concluded with the fact that the ionisation step from $(HA)_2$ to A^- passes through the formation of the monomer form HA. This behaviour can be explained by the fact that isomorphic substitution increases negative charges, thus clay surface can form strong affinity for protons.

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