

Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

METACHROMASY IN CLAY MINERAL SYSTEMS

Spectrophotometric and calorimetric study of the adsorption of crystal-violet and ethyl violet by Na-montmorillonit and by Na-kaolinite

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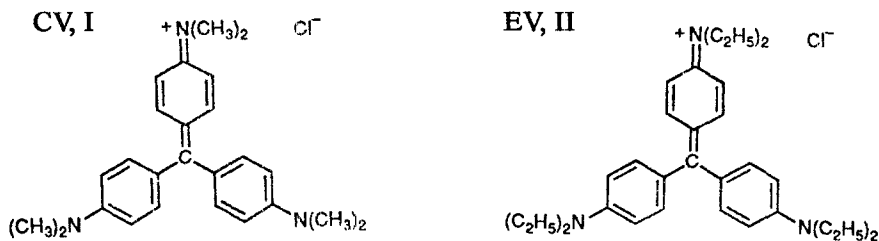
Adsorption of the metachromic (colour depends on concentration) cationic dyes crystal violet (CV) and ethyl violet (EV) by Na-kaolinite and Na-montmorillonite has been studied by visible spectroscopy and titration calorimetry. In the kaolinite system, metachromasy stems from association of the dye cations on the external surface of the clay. Enthalpies of adsorption at small dye/clay ratios are -3.5 and -3.8 kJ/mol for CV and EV, respectively. In the montmorillonite system, which has been studied more thoroughly, metachromasy stems from the π electron interactions between the dyes and the oxygen plane of the alumino-silicate. Enthalpies of adsorption (more exothermic than for kaolinite) depend on the dye/clay ratio in ways that are consistent with the spectra and the derived picture of dye/clay interactions.

Some dyes, including those investigated in this research, are called metachromic because their colours in solution depend on concentration. Previous investigations, several of which are cited below, have provided information about the state of aggregation of dissolved dyes and thence some understanding of the effects of concentration on colour. These and other investigations, cited below, have also shown how investigations of clay + water + dye systems can lead to information about adsorption of organic ions by clays.

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Adsorption of the metachromic dye crystal violet (CV, I) by montmorillonite [1, 2] and laponite [3] has been investigated by visible (electronic) spectroscopy, X-ray diffraction, and simultaneous DTA-EGA. Cation exchange [4-7] is the principal mechanism for adsorption of this cationic dye. Although adsorption by both of these smectites results in metachromasy, different types of bonding in the two clays have been inferred from the experimental results. In montmorillonite, metachromasy results from π interactions [7-12] between the adsorbed aromatic dye and the oxygen plane of the aluminosilicate. For laponite, on the other hand, metachromasy is observed under conditions where the clay is flocculated, but is not observed when the clay is peptized [3, 11, 12], which lead to the suggestion that the observed metachromasy is due to dimerization of adsorbed CV in the interparticle spaces of flocs.

Recently we have carried out spectroscopic investigations [14] of the adsorption (from water and from organic solvents) of CV and its homologue ethyl violet (EV, II) by kaolinite. The adsorbed dyes (CV more than EV) exhibit metachromasy. The "broken bonds" surfaces of kaolinite behave like polyelectrolytes and metachromasy results from dimerization and polymerization of the cationic dyes adsorbed on the external surfaces of the mineral, with π interactions between parallel adsorbed aromatic species.



In a previous publication [2] on the simultaneous DTA-EGA investigation of the Na-montmorillonite + CV system, some representative spectra were presented, along with the derived models of four kinds of bonding between clay and dye. In the present paper, we report results of further investigation of the visible spectra of this system and also the Na-montmorillonite + EV system.

In a previous paper [15], we reported the results of calorimetric investigations of adsorption of CV on M^{n+} -montmorillonite (M^{n+} = various inorganic cations) and showed that the molar enthalpy of adsorption ΔH depended on the dye/clay ratio. This concentration dependence of observed ΔH on amount adsorbed was explained with the idea that different types of clay-dye interactions (already suggested by results of spectroscopic inves-

tigations) that occur at different dye/clay ratios have different molar ΔH values. Now, in this paper, we report the results of further calorimetric measurements that have been designed to test and supplement the models that have been derived from results of spectroscopic investigations.

Experimental

Materials

Wyoming bentonite (Na-montmorillonite) from Wards Natural Science Establishment was ground to 80 mesh. Non-clayey material was separated by sedimentation from 4 wt% aqueous suspension. Well-crystallized kaolinite from Washington County, Georgia, USA, obtained from the Source Clay Repository, Department of Geology, University of Missouri, Columbia, USA, was treated as described [14] previously.

The organic dyes were supplied by B. D. H. as the chloride salts.

Spectrophotometric measurements

Spectra of aqueous suspensions of Na-montmorillonite in the concentration range 0.0002 to 0.040 wt% in the presence of 4.0×10^{-6} or 16.0×10^{-6} molar CV or EV were recorded at room temperature, using a Cary double-beam spectrophotometer (Model 219), in the 700–400 nm range. The optical path was 10 mm. Each suspension was subjected to ultrasound for 7 minutes immediately after its preparation. Each spectrum was recorded within three hours after preparation of the suspension.

Calorimetric measurements

Our "home made" solution calorimeter consisted of a glass vessel (90–95 cm³ capacity) suspended in a brass can that was immersed in a constant temperature bath maintained at $25.00 \pm 0.01^\circ$ and held constant during each calorimetric measurement to 0.001° . Titrant solution was delivered to the calorimeter by a motor driven buret-titrator. Small temperature changes in the calorimeter were measured with high sensitivity (better than $1 \times 10^{-4}^\circ$) with a thermistor combined with a Current Comparator Bridge (Model 9975, Guildline Instruments, Smith Falls, Ontario Canada). The calorimeter was calibrated electrically after each calorimetric titration measurement.

We have checked the accuracy of this calorimetric system by way of measurements of the enthalpy of solution of KCl(cr) in distilled water, the

enthalpy of solution of 4-aminopyridine in excess perchloric acid [16], and the enthalpy of neutralization of aqueous tris(hydroxymethyl)aminoethane ("THAM" or "tris") by excess aqueous acid. Results of these test measurements, as reported elsewhere [17] along with a more detailed description of the calorimeter, agreed to within 0.5%, 0.04%, and 0.02% with the "best" values from the literature.

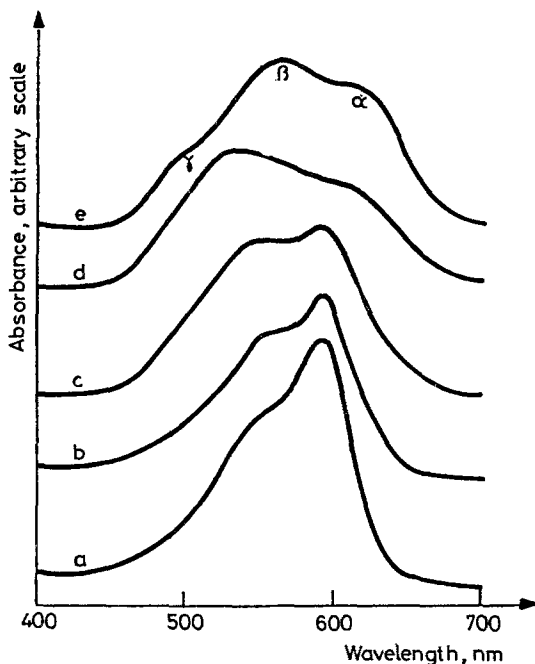


Fig. 1 Absorption spectra of (a) an aqueous solution of CV ($4 \times 10^{-6} M$) and of the same solution containing (b) 0.0002%, (c) 0.0003%, (d) 0.0005%, and (e) 0.002% Na-montmorillonite. Dye/clay ratios for (b-e) are 200, 135, 80, and 20 mmol CV/100 g clay, respectively

For most of the calorimetric measurements reported here, 0.20 g of bentonite or 4.00 g of kaolinite were suspended in 84 g of distilled water. A known amount of dye solution of known concentration (≈ 0.01 molar) was titrated into the calorimeter after passing through a coil in the constant temperature bath. Reaction (ion exchange, adsorption) of the dye with the clay was complete within 3-4 min, as judged by the observed temperature-time curve following addition of the solution of dye to the suspension of clay.

Results

Spectra of dye solutions and dye-clay suspensions

Spectra [14] of dilute aqueous solutions of CV and EV are shown in Figs 1a and 2a. Band α , due to monomeric species, is the principal absorption band in the spectra of these dilute solutions of CV and EV. Band β , at shorter wavelengths, due to dimeric species, appears only as a shoulder in the spectra of dilute solutions. Band β becomes more prominent in more concentrated solutions of the dyes. Band γ at still shorter wavelengths, due to polymeric species, is found in the spectra of still more concentrated solutions.

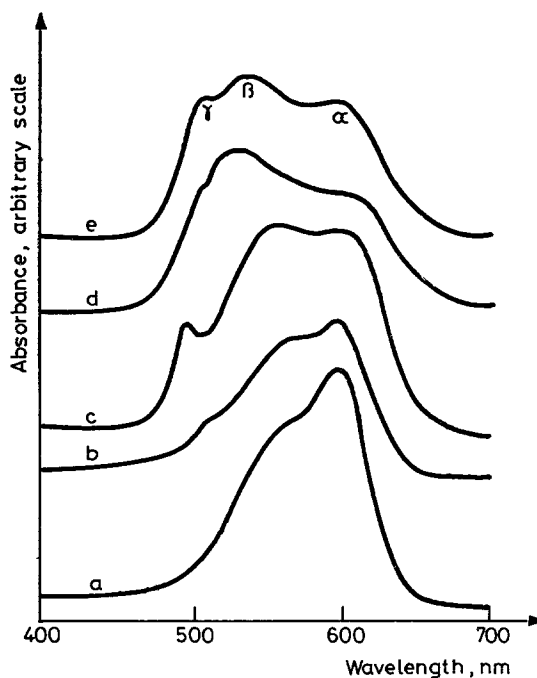


Fig. 2 Absorption spectra of (a) an aqueous solution of EV ($4.0 \times 10^{-6} M$) and of the same solution containing (b) 0.0002%, (c) 0.0003%, (d) 0.0006%, and (e) 0.002% Na-montmorillonite. Dye/clay ratios for (b-e) are 200, 135, 67, and 20 mmol EV/100 g clay, respectively.

The spectra of aqueous solutions of CV and EV to which different amounts of Na-montmorillonite have been added are also shown in Figs 1 and 2. When the concentration of suspended clay is very small, the spectrum

is very similar to that of the corresponding aqueous solution of dye. As the concentration of suspended clay increases, metachromic band β becomes more prominent. Ratios of intensities of bands α and β are shown in Figs 3 and 4. Wavelengths of the absorption maxima of bands α and β depend on the dye/clay ratio as also shown in Figs 3 and 4. Spectra of solutions of CV containing high concentration of clay show band γ at still shorter wavelengths, as shown in Fig. 1e. Spectra of solutions of EV containing clays at several concentrations show band γ , as illustrated in Figs 2b, c, d, e.

Enthalpies of adsorption

Molar enthalpies of adsorption of CV by Na-montmorillonite are summarized in Fig. 3, and molar enthalpies of adsorption of EV by Na-montmorillonite are summarized in Fig. 4.

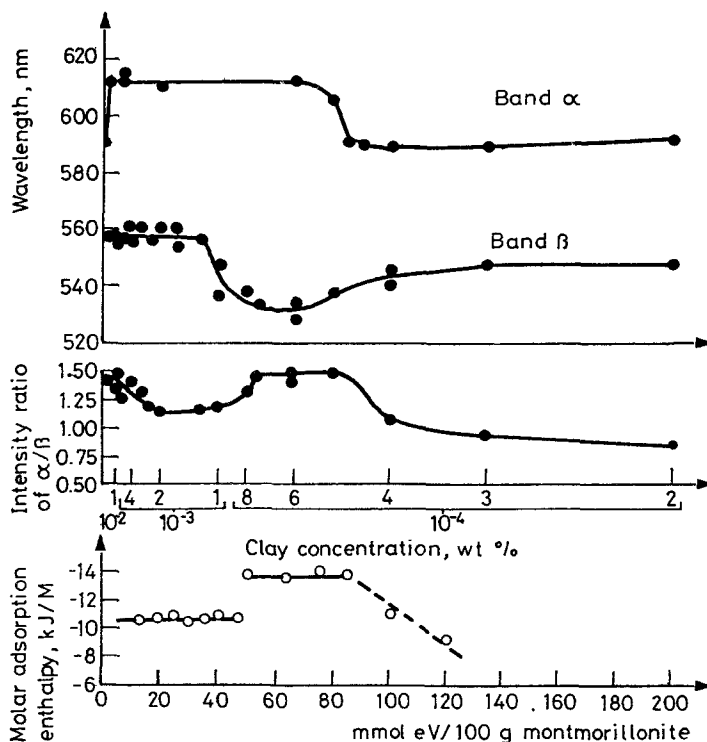


Fig. 3 Effect of clay concentration on the wavelength (top) of the maximum of bands α and β and on the ratio of intensities (middle) of bands α and β , the effect of clay/dye ratio on molar enthalpy of adsorption (bottom) of CV on Na-montmorillonite (0.20 g clay in 84 g of water)

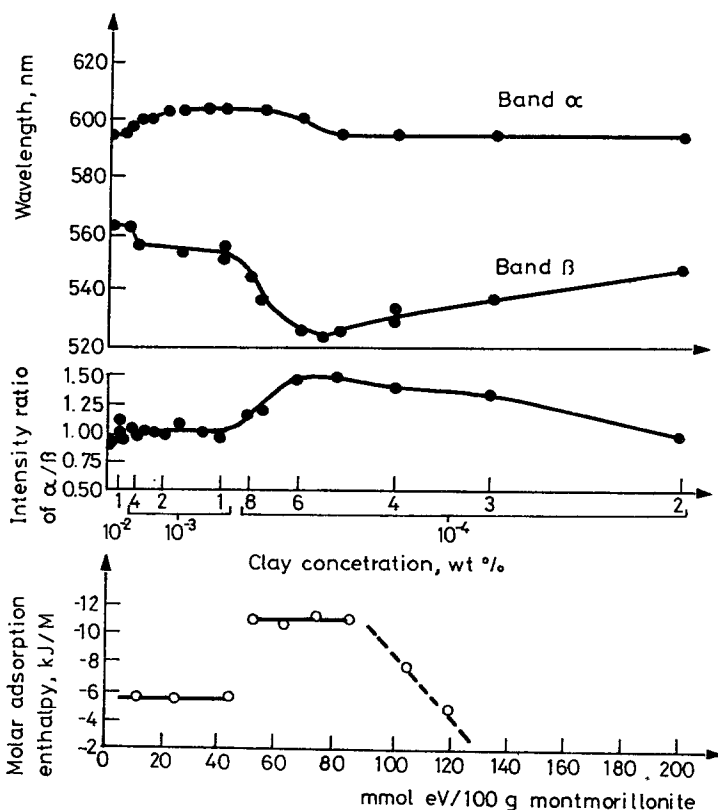


Fig. 4 Effect of clay concentration on the wavelength (top) of the maximum of bands α and β and on the ratio of intensities (middle) of bands α and β , and effect of clay/dye ratio on molar enthalpy of adsorption (bottom) of EV on Na-montmorillonite (0.20 g clay in 84 g of water)

A smaller number of calorimetric measurements has led to $\Delta H = -3.5 \pm 0.7$ kJ/mol for adsorption of CV by Na-kaolinite and to $\Delta H = -3.8 \pm 1.0$ kJ/mol for adsorption of EV by Na-kaolinite. In both systems the dye/clay ratio was in the range 0.5 to 1.0 mmol dye/100 g clay. The possible dependence of ΔH on dye/clay ratio has not yet been thoroughly investigated for kaolinite.

Discussion

Previous spectroscopic investigations [2] of aqueous CV and aqueous CV + Na-montmorillonite and simultaneous DTA-EGA study of the solids have led to evidence that there are four kinds of clay-dye interactions or

bondings. Now we summarize these earlier results and conclusions and relate them to the results of present investigations as follows.

Band α

When the concentration of suspended clay is small (large dye/clay ratios) so that the clay is peptized, band α is located at 590 and 595 nm in the spectra of CV + clay and EV + clay, respectively. Because these maxima are at nearly the same wavelengths as for the same dyes in very dilute aqueous solution (no clay), it is inferred that the adsorbed monomeric dye cations are in environments in which the polarity is similar to that of bulk water. This environment is probably at the water-clay interface, outside the "inter-layer space". This kind of adsorption or interaction has been labelled "type A".

With larger concentrations of clay or smaller dye/clay ratios, band α is shifted bathochromically to wavelengths longer than 590 and 595 nm in the spectra of systems containing CV and EV, respectively. The adsorption of CV or EV that is responsible for this shift is labelled "type B". Since this kind of bathochromic shift is often due to an increase in environmental acidity and interlayer water has been reported [18] to be much more acidic than bulk liquid water, we attribute type B adsorption to monomeric dye cations located inside the "interlayer space" of the clay, with electrostatic interaction of the positively charged dye ions with the negatively charged clay [11, 12] being the principal binding force. This kind of adsorption occurs when the suspended clay is composed of tactoids with parallel alumino-silicate layers. The bathochromic shift is much smaller for EV and than for CV, probably due to steric effects on the nitrogen that are related to the difference in size of ethyl and methyl groups.

During a titration of Na-montmorillonite with CV and EV during which the dye/clay ratio is increased, band α first shifts to longer and then to shorter wavelengths. We define a "transition point" during such a titration as the dye/clay ratio at which the location of band α is the same as that of a dilute aqueous solution of the dye (no clay). These transition points are 85 and 75 mmol dye/100 g clay for CV and EV, respectively.

Band β

Band β in the spectra of dye + clay systems has been described [8–10, 13] as due to "type C" adsorption in which dye cations located in the interlayer space are bound to the clay by π electron interactions.

The *c*-spacing of CV + montmorillonite has been measured [2] by X-ray diffraction. There is a correlation between the location of band β and the *c*-spacing as follows. For dye/clay ratios smaller than 40 mmol dye/100 g clay, the *c*-spacing was shorter than 1.45 nm, which implies a monolayer of CV in the interlayer space, with the aromatic rings of the dye parallel to the silicate layers. In this range of dye/clay ratios, the maximum in band β was located at 556–558 nm. For larger dye/clay ratios, band β was shifted to shorter wavelengths and the *c*-spacing was increased to 1.65 nm, which implies formation of a bilayer of CV in the interlayer space or the tilting of the plane of the dye cation relative to the plane of the silicate layer "type B". For still larger dye/clay ratios (larger than the defined transition point), band β was shifted back to longer wavelengths and the *c*-spacing expanded to 2.06 nm with the subsequent occurrence of type A adsorption.

Band γ

Previous investigations [3, 11] of metachromasy of smectite + dye systems have led to the conclusion that this metachromic band γ is due to polymeric dye cations adsorbed ("type D") in the interparticle spaces of flocs of clay. From the intensities of band γ it appears that EV shows a greater tendency to type D adsorption than does CV. This observation is consistent with the accumulated evidence that cation-cation association is stronger for large aqueous alkyl ammonium cations than for smaller cations of similar type.

Enthalpies

Results of our earlier investigations [15] of enthalpies of adsorption of CV by M^{n+} -montmorillonite (M^{n+} = inorganic cations) were consistent with the generalization that the enthalpies of adsorption of type C are most exothermic, with those of type B being less exothermic, and those of type A being least exothermic. Conditions of the earlier and present calorimetric measurements were such that interactions of type D occurred to a negligible extent.

Figures 3 and 4 show striking correlations between the enthalpies of adsorption and the spectroscopic results, especially the intensity ratios α/β . Thus the present results provide support for the generalizations above about the relative exothermicity of the various kinds of montmorillonite-dye interactions. Also, these calorimetric results are consistent with the spectroscopic results which show that the metachromic effect is larger for CV than for EV in dye + montmorillonite systems.

Because our only calorimetric results for Na-kaolinite + dye-systems are for conditions under which type C interactions are dominant, we can only suggest that the enthalpies of adsorption for dyes on kaolinite for small dye/clay ratios are less endothermic than for adsorption of dyes on montmorillonite at similarly small dye/clay ratios because of the lesser strength of π interactions in the dye + kaolinite systems as compared with the dye + montmorillonite systems.

* * *

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Zusammenfassung — Mittels Spektroskopie im sichtbaren Bereich und Titrationskalorimetrie wurde die Adsorption der metachromen (Farbe ist konzentrations-abhängig) Kationenfarben Kristallviolett (CV) und Ethylviolett (EV) durch Na-Kaolinit und Na-Montmorillonit untersucht. In den Kaolinit-Systemen rührt die Metachromasie von der Assoziation der farbigen Kationen an der externen Oberfläche der Tonerde her. Die Adsorptionenthalpien für kleine Farbstoff/Tonerde Quotienten betragen für CV und EV – 3.5 bzw. –3.8 kJ/mol. In den umfassender untersuchten Montmorillonit-Systemen rührt die Metachromasie von den π -Elektronenwechselwirkungen zwischen den Farbstoffen und der Sauerstoffebene des Aluminosilikates her. Die Adsorptionenthalpien (exothermer als bei Kaolinit) hängen vom Farbstoff/Tonerde-Quotienten ab, wie es in Übereinstimmung mit den Spektren und den Vorstellungen über die Farbstoff-Tonerde-Wechselwirkungen steht.