Metachromasy in clay dye systems: the adsorption of acridine orange by Na-beidellite

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(Received 4 February 1998; revised 24 June 1998)

ABSTRACT: The adsorption of the metachromic dye acridine orange (AO) by Na-beidellite was investigated by visible spectroscopy. Different types of clay-AO association were identified from the appearance and location of absorption bands $\alpha$ or $\beta$. The colloidal properties were determined from curves of the absorbance vs. the degree of saturation. Three regions were identified in the absorbance curve. In the first region beidellite is peptized with small amounts of AO and the dye penetrates into the interlayer space where it undergoes metachromasy due to $\pi$ interactions between the aromatic entity and the oxygen plane of the clay. With larger amounts of AO (second region), the clay flocculates due to the aggregation of the dye cations in the interparticle space of the flocs. In excess AO (third region), beidellite is gradually peptized, forming small tactoids with monomeric AO in the interlayer space and at the same time adsorbing dimeric and polymeric AO cationic species at the solid-liquid interface. Compared with the other smectites, AO shows the greatest tendency to undergo metachromasy in the presence of beidellite.

The visible absorption spectrum of the metachromic dye acridine-orange [AO, 3,6-bis (dimethylamine) acridine hydrochloride] has been used recently in the determination of surface basicity of inner surface O planes of several Na-smectites (beidellite, montmorillonite, saponite and Laponite) and of Na-vermiculite. In that study the dye was added to an aqueous clay suspension and adsorbed by the minerals. The spectra of the suspensions recorded with small loadings were dependent on the ability of the oxygens from the inner surface O planes to donate electrons to the $\pi$ system of AO cations (Garfinkel-Shweky & Yariv, 1997a). The adsorption of AO by montmorillonite, Laponite and saponite and the colloidal properties of aqueous AO-clay suspensions have been widely investigated by visible spectroscopy (Cohen & Yariv, 1984; Garfinkel-Shweky & Yariv, 1995, 1997b) supplemented by thermal analysis (Yariv et al., 1989). This process occurs primarily via a cation exchange mechanism resulting from the electrostatic attraction between the organic cation and the negative clay particle. In addition to the long range electrostatic forces, different types of short range interactions may occur between the dye cation and active sites on the surface of the minerals. These interactions depend on: (1) the nature of the mineral; (2) its colloidal state; and (3) the degree of saturation of the clay.

In our previous publication (Garfinkel-Shweky & Yariv, 1997b), different types of AO-saponite association were identified by visible spectroscopy and possible models for these associations were shown in Fig. 4 of that publication. Similar associations were identified in systems containing montmorillonite or Laponite with AO (Cohen & Yariv, 1984; Garfinkel-Shweky & Yariv, 1995). The identification of the different associations was based on the appearance of bands $\alpha$, $\beta$ and $\gamma$ and on the locations of these bands. Monomeric cations are adsorbed either on the surface of the TOT platelets or of small tactoids (at the water-solid interface) or inside the interlayer space. Monomeric AO in the water-solid interface (association type $A_1$) absorbs...
visible light at $\leq 490$ nm (band $\alpha$). In the interlayer space monomeric AO cations can be H-bonded to acidic interlayer water, absorbing visible light at $>490$ nm (association types $B_1$, $C_2$ and $C_3$), and/or $\pi$-bonded to the inner-surface O planes by accepting lone pair electrons into the antibonding $\pi$ orbitals of the aromatic rings (Yariv, 1988, 1992), giving rise to a metachromic band $\beta$ at 450–470 nm (association types $B_2$ and $C_3$). The exact location of this band depends on the surface basicity of the O plane of the smectite (Garfinkel-Shweky & Yariv, 1997a).

Dimeric cations are adsorbed either on the surfaces of the TOT platelets or of small tactoids (association type $A_2$) or in the interparticle space of flocs in flocculated systems (types $C_1$, $C_2$ or $C_3$). The former absorbs visible light at 473–475 nm, whereas the latter absorbs at lower frequencies which depend on the degree of flocculation of the clay. With increasing flocculation and floc size the hydrophobicity of the interparticle space increases and the aggregation of AO becomes very strong. This leads to a blue shift of band $\beta$. Consequently, for highly flocculated smectites, band $\beta$ can be located at 450 nm and shifts to higher wavelengths with decreasing size of flocs (Garfinkel-Shweky & Yariv, 1995). Polymeric cations are adsorbed to a very small extent either on the surfaces of the TOT platelets (association type $A_3$) or in the interparticle space of the flocs (type $D$), absorbing visible light below 450 nm. This association was identified only by comparative spectroscopy.

Beidellite is a dioctahedral smectite with tetrahedral substitutions of Al for Si. Since this mineral is rare compared to montmorillonite, very little work has been reported on the adsorption of organic matter by this mineral. In order to obtain information on the different types of beidellite-AO associations the adsorption of AO by beidellite was studied in more detail in the present investigation. The visible spectra of the AO-clay suspensions, recorded at different dye loadings, were used to study the different species which were obtained in peptized or flocculated systems.

**EXPERIMENTAL**

**Materials**

Beidellite (California SBCa-1) was obtained from the Source Clay Repository of the Clay Minerals Society. The natural sample contains 3, 10 and 79 mEq exchangeable Na$^+$, K$^+$ and Ca$^{2+}$ per 100 g clay, respectively (Newman & Brown, 1987). One hundred ml of 1% clay suspension was first saturated with 20 ml LiCl solution (0.1 M). After washing the excess LiCl from the clay, it was saturated with 20 ml NaCl solution (0.1 M) and 48 h later, the excess salt was washed out with distilled water by centrifugation. A 0.4% clay suspension (particle size $<2$ $\mu$m) was used as a stock solution from which the large particles were separated by sedimentation. The AO was purchased from BDH and used as supplied. The dye content was determined by C, H and N analyses.

**Methods**

The experimental procedures (electronic spectroscopy, X-ray diffraction and cation exchange study, i.e. release of Na, K and Ca and adsorption of AO) and the instruments were as described previously (Garfinkel-Shweky & Yariv, 1997b). Visible spectra were recorded against: (1) water in the reference beam (normal spectroscopy); (2) the supernatant liquid in the reference beam (comparative clay-dye/supernatant spectroscopy). The former was applied for all degrees of saturation and the latter was applied when the dye was in excess (loading $>80$ mmol AO/100 g clay). A few spectra of well peptized systems (loading $<20$ mmol AO/100 g clay) were recorded against a clay suspension in the reference beam (comparative clay-dye/clay spectroscopy).

Two series of clay-dye suspensions were investigated by visible spectroscopy. In one series increasing amounts of AO (2.4 $\times$ 10$^{-5}$ or 2.4 $\times$ 10$^{-4}$ M) were added to aqueous clay suspensions. The total clay concentration in each system was 0.0016 or 0.016%. In another series a constant amount of dye solution was added to increasing amounts of clay suspensions (0.04 wt%). The total dye concentration in each system was 4 $\times$ 10$^{-2}$ M. At this concentration the aqueous dye solution contains mainly monomers.

**RESULTS**

**Cation exchange**

AO was adsorbed by beidellite and metallic cations were released from the clay into the aqueous solution. Exchangeable Na, K and Ca were determined by atomic absorption, using
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Table 1. Quantity of metallic cations (in mEq/100 g beidellite) released into the equilibrium suspensions of Na-beidellite treated with AO for one week and of adsorbed AO (in mmol AO/100 g beidellite). The total clay concentration in the system was 0.016 wt%. Initial concentration of AO in the equilibrium suspensions (in mol l⁻¹) and total dye in the system (in mmol AO/100 g clay).

<table>
<thead>
<tr>
<th>mol/l</th>
<th>6 x 10⁻⁵</th>
<th>8 x 10⁻⁵</th>
<th>1 x 10⁻⁴</th>
<th>2 x 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmol/100 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Released Na</td>
<td>36</td>
<td>48</td>
<td>62</td>
<td>120</td>
</tr>
<tr>
<td>cations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ca</td>
<td>–</td>
<td>8</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>adsorbed AO</td>
<td>36</td>
<td>48</td>
<td>62</td>
<td>109</td>
</tr>
</tbody>
</table>

calibration curves which contain AO (Table 1). The table shows that dye adsorption takes place largely by a cation exchange mechanism.

The supernatant solutions, which were separated from the clay suspensions three months after the preparation of the samples, were completely colourless up to 80 mmol AO/100 g clay, indicating that up to this degree of saturation, the dye was completely adsorbed by the clay. The adsorbed amounts in suspensions containing >80 mmol AO/100 g clay are given in Table 2. The table shows that quantities of AO above the CEC of the clay were adsorbed by the clay. The excess adsorption of the dye is due to hydrophobic interactions.

X-ray diffraction

Most of the XRD study of AO-beidellite associations has been described previously (Garfinkel-Shweky & Yariv, 1997a). Samples were examined at room temperature (equilibrated at 40% humidity) and after dehydration at 100 and 300°C under vacuum. At the latter temperature Na-beidellite is collapsed to 1.0 nm. The AO beidellite samples did not collapse under the same thermal treatment, indicating that the dye was located in the interlayer space. That study has been enlarged and oriented samples containing 360, 615 and 840 mmol AO/100 g clay were prepared without washing out the excess dye. They showed basal spacings of 1.33, 1.60 and 1.61 nm, respectively, after heating at 100°C. These spacings indicated that there were no polymeric cations in the interlayer space.

Visible spectroscopy

A dilute aqueous solution of AO absorbs at 490 nm (band α), whereas a concentrated solution shows a metachromic band at 470 nm (band β), characterizing monomeric and dimeric species, respectively (Cohen & Yariv, 1984, Garfinkel-Shweky & Yariv, 1995).

Effect of Na-beidellite on the absorption spectrum of acridine orange

Normal absorption spectroscopy. Representative absorption spectra of AO solutions, to which different amounts of Na-beidellite have been added (clay-dye suspensions), are shown in Fig. 1. The adsorption of AO by beidellite was accom-

Table 2. Adsorption of AO by Na-beidellite (in mmol AO/100 g clay) in the presence of excess dye (third region in the absorbance curve) after three months’ ageing of the equilibrium suspension. The total clay concentration in the system was 0.0016 wt%.

<table>
<thead>
<tr>
<th>Total dye in the system (mmol AO/100 g clay)</th>
<th>Adsorbed dye (mmol AO/100 g clay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>82</td>
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<tr>
<td>120</td>
<td>109</td>
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<tr>
<td>240</td>
<td>140</td>
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<tr>
<td>360</td>
<td>228</td>
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<tr>
<td>615</td>
<td>300</td>
</tr>
<tr>
<td>840</td>
<td>270</td>
</tr>
</tbody>
</table>
Fig. 1. Electronic spectra of aqueous suspensions of Na-beidellite (0.0166%) treated with different amounts of AO. Degrees of saturation: (a) 3.6; (b) 8.4; (c) 24.0; (d) 61.5; (e) 120.0; and (f) 360.0 mmol AO/100 g clay. Spectra were recorded against water in the reference beam.

panied by metachromasy, that is the disappearance of band $\alpha$ and the appearance of band $\beta$ at a shorter wavelength.

The colloidal behaviour of AO-treated beidellite was studied by observing (with the naked eye) the effect of the degree of saturation on the flocculation of the clay. With $<15$ mmol AO/100 g clay, the suspension was clear. With higher saturations it flocculated. Maximum flocculation was observed with 35–60 mmol dye. With $>100$ mmol AO/100 g clay the system was re-peptized.

It has previously been shown that flocculation resulted in a decrease of absorbance, whereas with peptization the reverse was the result (Grauer et al., 1984, 1987a,b; Yariv et al., 1990). The absorbance of band $\beta$, as a function of the loading of beidellite (absorbance curve) for a constant beidellite concentration, is shown in Fig. 2. This absorbance curve can be divided into three distinct regions. In the first region, up to 15 mmol AO/100 g clay, the clay was peptized and there was a linear increase in absorbance with increasing saturation. This is in agreement with Beer’s Law. In the second region, up to 46 mmol AO/100 g clay, absorbance decreased with increasing saturation as a result of flocculation. In the third region, it increased with increasing saturation, with an approximate log dependence, because of re-peptization of the clay.

The absorbance of band $\beta$ as a function of the degree of saturation for a constant dye concentration, is shown in Fig. 3. Since a constant dye concentration was used for this series, any change in absorbance resulted from a change in the colloidal state of the clay. This curve could be divided into three distinct regions which were equivalent to the three regions of Fig. 2. In the first region, there was almost no change in the absorbance, indicating that the suspensions were stable. In the second and third regions, absorbance decreased and increased, respectively, with flocculation and peptization of the clay.

Several investigators have shown that the spectra of dye-smectite associations change with time (Schoonheydt & Fleughebaert, 1992; Breen & Rock, 1994; Breen & Loughlin, 1994; Gessner et al., 1994; Tapia Estévez et al., 1994; López Arbeloa et al., 1995). In the present study, after two months, the absorbance of band $\beta$ in the first region had not changed, but it had increased drastically, by $>100\%$, in the spectra of samples from the second region, indicating that some of the flocculated clay was peptized. Samples belonging to
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**Na-beidellite**

![Graph](image)

**FIG. 2.** The absorbance (in absorbance units) of bands $\alpha (\blacklozenge)$ and $\beta (\blacktriangle)$ vs. the loading of AO (in mmol/100 g clay) for a constant Na-beidellite concentration (0.0166% or 0.00166% with saturations < or > 100 mmol AO/100 g clay, respectively). Spectra were recorded 2 h after the preparation of the sample. Absorbance of samples with $\geq$ 100 mmol AO/100 g clay is multiplied by 10.

Moreover, the transition between the second and third regions (maximum flocculation) shifted to a higher degree of saturation (from 46 to 54 mmol AO/100 g clay). These changes became more

**Na-beidellite**

![Graph](image)

**FIG. 3.** Absorbance curve of aqueous suspensions of Na-beidellite (different concentrations) treated with AO ($4 \times 10^{-5}$ M). The absorbance of bands $\alpha (\blacklozenge)$ and $\beta (\blacktriangle)$ are given vs. the loading of AO (in mmol/100 g clay) for a constant AO concentration ($4 \times 10^{-5}$ M). Spectra were recorded 2 h after the preparation of the samples.
pronounced after one year of ageing. With higher saturations there were no changes in absorbance even after one year of ageing.

Band $\beta$ appeared in the spectrum even when the degree of saturation was as low as 1 mmol AO/100 g clay, as was expected for a dioctahedral smectite with tetrahedral substitutions (Yariv, 1988). This is in contrast to Laponite which did not show metachromasy below a dye content of 25 mmol AO/100 g clay even though it is similar to montmorillonite and saponite. The location of band $\beta$ in the spectra of samples with low loadings of AO (first region) was 450–454 nm. After an ageing period of two months this band shifted slightly to 455–458 nm. Note that in our previous study of the surface basicity of the O plane of beidellite (Garfinkel-Shweky & Yariv, 1997a), the location of band $\beta$ in spectra at low AO loadings was determined by comparative clay-dye/clay spectra. Because of the strong light scattering of the beidellite suspensions, differences of ~4 nm between maxima of band $\beta$ in the comparative clay-dye/clay spectroscopy and normal spectroscopy were observed.

Band $\alpha$ was not observed provided the degree of saturation was <200 mmol AO/100 g clay. With 120 mmol AO/100 g clay a weak shoulder was observed (Fig. 1c). Above 200 mmol AO/100 g clay band $\alpha$ clearly appeared at $\leq$490 nm, and was similar in appearance to that in the spectra of the other smectites in the presence of excess dye. This band is characteristic of the presence of non-adsorbed dye in the solution. It should be noted that in the spectra of montmorillonite and saponite with small loadings of AO, band $\alpha$ appears as a shoulder or as a distinct weak band at wavelengths >490 nm, and is considered to be characteristic of the presence of association B$_1$.

Comparative clay-dye/supernatant absorption spectroscopy. When the degree of saturation was >80 mmol AO/100 g clay, the supernatant solutions were coloured and their spectra were similar to those obtained during the study of the adsorption of AO by saponite (Garfinkel-Shweky & Yariv, 1997b). Comparative spectra were recorded of samples in which the supernatant contained non-adsorbed dye (Fig. 4). When the degree of saturation was <400 mmol AO/100 g clay, only band $\beta$ was observed at 460–464 nm, characteristic of the presence of dimers in the interparticle space of very small flocs. Between 600–800 mmol AO/100 g clay, the comparative spectra showed bands $\alpha$, $\beta$ and $\gamma$ at 500, 476 and 448 nm, respectively. At this stage the deflocculation of the beidellite was probably complete.

From the location of band $\alpha$ in the comparative spectra, it was obvious that in systems containing excess dye (>400 mmol AO/100 g clay), beidellite formed small tactoids (type B$_1$). In this respect beidellite behaves like montmorillonite and saponite but not like Laponite which is dispersed as single platelets. The appearance of bands $\beta$ and $\gamma$ in these comparative spectra indicated that in the case of large excess of dye, the particles adsorb dimeric and polymeric positively charged species. According to the X-ray diffraction patterns of these samples, recorded in the presence of excess dye, the adsorbed polymeric cations were not located inside an interlayer space, but in the solid-liquid interface of the dispersed beidellite tactoids (associations A$_2$ and A$_3$). Above 800 mmol AO/100 g clay band $\beta$ almost disappeared, whereas band $\gamma$ increased. This observation indicates that with increasing dye concentration adsorbed dimers were replaced by polymeric cations.

DISCUSSION AND CONCLUSIONS

Thermal treatment of Na-beidellite at 300°C resulted in dehydration as indicated by a basal spacing of 1.00 nm. Larger basal spacings (1.26–1.38 nm) were recorded after a similar thermal treatment of beidellite samples with different loadings of AO (Garfinkel-Shweky & Yariv, 1997a). This is due to the fact that charcoal was formed inside the interlayer space. The formation of a charcoal layer inside the interlayer space may occur only if the precursor AO cations were located inside the interlayer (Yariv, 1991).

Three types of metachromasy should be considered in the adsorption of AO by smectites. These are $\pi$ interactions between the O plane and the aromatic ring, dimerization of AO in the interparticle space and adsorption of dimeric and polymeric cations on the surfaces of the tactoids. The surface basicity of dioctahedral smectites is greater than that of trioxahedral ones. Moreover, the surface basicity of clays with tetrahedral substitutions is greater than that of clays with octahedral substitution. Consequently, beidellite has the highest surface basicity of all common smectites (Yariv, 1992). In previous publications (Yariv, 1988, 1992), it was shown that when small
amounts of metachromic dyes are adsorbed by smectites with tetrahedral substitutions, metachromasy occurs. Metachromasy is an indication of \( \pi \) interactions in which the aromatic ring is involved (Robinson, 1994). It was suggested that in these \( \pi \) interactions the lone-pair electrons of the oxygens belonging to the O plane overlap the anti-bonding \( \pi \) orbitals of the aromatic rings. Consequently, band \( \alpha \), which is due to \( \pi \rightarrow \pi^* \) transition, is perturbed and is replaced by band \( \beta \). Metachromasy was shown to occur during the adsorption of small amounts of AO by montmorillonite which is a dioctahedral smectite and gains its charge mainly from octahedral substitutions, but to a small extent, also from tetrahedral substitutions (Cohen & Yariv, 1984). It was also shown to occur during the adsorption of AO by the trioctahedral clay saponite which gains its charge mainly from tetrahedral substitution (Garfinkel-Shweky & Yariv, 1997b). Now we show that this type of metachromasy also occurs during the adsorption of small amounts of AO by beidellite.

With saturations up to 15 mmol AO/100 g beidellite (first region in the absorbance curve), the clay was peptized and absorbance obeyed Beer’s law. A basal spacing of 1.27 nm indicated that monomeric AO cations were located in the interlayer space of small tactoids, parallel or almost so to the O planes, absorbing at 451–454 nm (band \( \beta \)). Thus it has been concluded that at this stage metachromasy was mainly due to \( \pi \) interactions between the inner-surface O plane of the clay and the aromatic dye. This type of clay-dye association was labelled B3. At this stage band \( \beta \) appears at higher wavelengths in the spectra of AO-montmorillonite (467 nm) and saponite (473 nm) and does not appear in the spectrum of Laponite which is trioctahedral and has no tetrahedral substitution. It should be noted that band \( \alpha \) which appeared as a shoulder, a weak band and the principal band in the normal spectra of AO adsorbed by montmorillonite, saponite and Laponite, respectively, is not detected in the spectrum of AO adsorbed by beidellite in the first region.

When the saturation was between 15 and 46 mmol AO/100 g beidellite, the clay flocculated and the absorbance decreased with increasing flocculation (second region in the absorbance curve). With a degree of saturation of 46 mmol dye per 100 g clay, maximum flocculation was obtained and light absorbance decreased to a minimum. At this stage band \( \beta \) was located at 452 nm.

Laponite flocculated when >15 mmol AO/100 g clay was adsorbed. This colloidal process was accompanied by the appearance of band \( \beta \). Since this mineral has no tetrahedral substitution, it was suggested that AO dimers were adsorbed into the interparticle space of the flocs (Garfinkel-Shweky & Yariv, 1995). At 25 mmol AO/g clay band \( \beta \) was located at 470 nm but it gradually shifted to lower wavelengths with increasing loadings. At 85 mmol AO/100 g Laponite it was located at 453 nm. With further loadings the clay was re-peptized and band...
\( \beta \) shifted to higher wavelengths. Saponite and montmorillonite behaved similarly and the shift of band \( \beta \) to lower wavelengths was attributed to the adsorption of AO dimers into the interparticle space of flocs. In the spectrum of AO-beidellite the shift of band \( \beta \) to lower wavelengths was not apparent in the first region because the location of this band was already at 451–454 nm.

In our previous studies on Laponite, saponite and montmorillonite the simultaneous appearance of both bands \( \alpha \) and \( \beta \) at this stage, led us to conclude that the flocculated clay formed a book-house structure with dimers located in the interparticle space (association type C2 and/or C3). In the transition between the second and third regions there was a reorganization of the structure of the flocculated clay and book-house flocs were transformed to card-house flocs (association type C1). This was inferred from the fact that the red-shifted band \( \alpha \) disappeared. It was impossible to identify the reorganization of the floc structure from the AO/beidellite spectra, because band \( \alpha \) was not observed in the normal spectroscopy study. It is assumed that the colloidal behaviour of beidellite is similar to that of the other smectites.

In the third region, the clay gradually peptized and the absorbance increased logarithmically with increasing degrees of saturation. At this stage, dimeric cations were located in the interparticle space of the small flocs, absorbing at 460–464 nm (associations type C). In the presence of a great excess of dye, deflocculation was completed and polymeric species were located on the tactoid surfaces, at the solid-liquid interface, absorbing at 440–448 nm (association type A\(_2\)). In addition to dimers absorbing at 476 nm (association Type A\(_2\)). A band at 505 nm in the comparative spectrum was attributed to interlayer AO cations, indicating that with excess dye beidellite formed tactoids. In conclusion, during the adsorption of AO, beidellite behaves similarly to montmorillonite and saponite but its tendency to cause metachromasy is higher because of its higher surface basicity.

ACKNOWLEDGMENTS

The authors wish to thank Mr Christian Drohmann from the University of Ulm and Mr Stefan Berger from the University of Heidelberg for performing some of the spectroscopic measurements. Financial support from the Alexander Silberman-Hebrew University Foundation for Applied Science is acknowledged.

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