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ORIGINAL CONTRIBUTION

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The effect of the exchangeable metallic cation on the colloid properties of laponite treated with acridine orange-a spectrophotometric study

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Abstract The adsorption of the cationic dye acridine orange (AO) by different monoionic laponites leads to changes in the colloid properties of this synthetic mineral in aqueous solutions. The organic cation is adsorbed by the mechanism of cation exchange. Small amounts of adsorbed dye keep the clay in a peptized state with all metallic cations. Greater amounts of AO result in the neutralization of the electric charge of the clay, and its flocculation. In excess AO the charge of the clay platelets becomes positive and the clay is peptized. The colloid properties are studied by absorbance curves in which the absorbance is described as a function of the degree of saturation with constant clay concentrations or with constant dye concentrations. In the absorbance curves three regions can be identified. The transition between the first and second or the second and third regions depend on the exchangeable metallic cation initially present in the clay. The spectrophotometric method is useful in identifying the presence of tactoids and flocculation mechanism, whether it results in card-house or in book-house flocs.

Key words Acridine orange – cation exchange – clay minerals – dye adsorption – flocculation – laponite – peptization

Introduction

The adsorption of cationic dyes by smectites occurs by the mechanism of cation exchange, the positive organic entity is attracted to the negative clay particle by electrostatic forces. However, as many investigators have shown, a complete exchange of inorganic cations by cationic dyes seems generally not to take place [1]. In addition to the long range electrostatic attractions, different types of short range interactions may occur between the dye cation and active sites on the surface of the minerals. These short-range interactions depend on the type of clay mineral [2] and the exchangeable metallic cation [3–5]. Consequently, different types of clay-dye associations with different fine structures are obtained with the different smectites [6].

The adsorption of the metachromic dye, acridine orange [AO, I, 3,6-Bis (dimethylamine) acridine hydrochloride], by the dioctahedral clay mineral montmorillonite, and the effect of the exchangeable metallic cation on this reaction, had been previously studied by visible spectroscopy and by x-ray diffraction [7]. In the presence of montomorillonite AO undergoes metachromasy. This was attributed to the interaction of the lone-pair electrons of the surface oxygens with the antibonding π orbitals of the dye. This kind of π interactions occurs with clays having tetrahedral substitutions of Si by Al. The trioctahedral clay mineral laponite, which is a synthetic hectorite, has no tetrahedral substitution. It is therefore expected that the short-range interactions of AO with this mineral differ from those occurring with montmorillonite. This has been proved by simultaneous DTA-EGA-MS [8]. In the present paper, we describe the adsorption of AO by several monoionic laponites and the effect of the organic cation on the colloid properties of the clay. The adsorption of AO by the other two smectite minerals, saponite and beidellite, will be described in future work.

The electronic spectra of aqueous solutions of cationic dyes are changed in the presence of laponite. These changes are dependent on the type of association between the clay mineral and the cationic dye [9, 10]. In a study of the electronic spectrum of crystal violet in the presence of Na-laponite it was demonstrated that different fine structures of the laponite–crystal violet associations were obtained in dye solutions to which different amounts of Na–laponite had been added [11]. The presence of several fine structures was confirmed by simultaneous DTA-EGA-MS [12]. From the location of the principal $\pi \rightarrow \pi^*$ absorption band, four different types of clay-dye association (labelled types A-D) were inferred. Types A and B were inferred from the location of band α. If this band appears at the same wavelength as that found in the spectrum of a dilute aqueous dye solution in the absence of clay, it characterizes adsorbed hydrated monomeric dye cations, located at the solid-liquid interface (association type A). If this adsorption band appears at a wavelength longer than that of a dilute aqueous solution, it characterizes monomeric dye cations located inside the interlayer space of a laponite tactoid (association type B). Interlayer water has been reported to be much more acidic than bulk liquid water [13–14] and the bathochromic shift of band α is due to high acidity in the environment of the dye. Type C was inferred from the appearance of a methachromic band β at wavelengths shorter than that of band α. Metachromasy, which represents dimers of the cationic dye, appeared together with the flocculation of the clay but disappeared when the clay was repeptized, and consequently, it was attributed to the dimerization of the cationic dye in the interparticle space of a floc. Type D was inferred from the appearance of band γ in the comparative spectrum at still a shorter wavelength than band β. This absorption band characterizes polymeric cationic species (quasi-micelles) which may be located in the interparticle space of a floc.

To the best of our knowledge, there is very little information on the effect of the exchangeable metallic cation initially saturating the clay, on the adsorption of cationic dyes by laponite and on the colloid properties of the clay. In this paper, we report the results of spectrophotometric measurements that have been designed to test the different types of association between AO and laponite and the effect of the exchangeable metallic cation on this association, the nature of the flocs which are formed from these associations and supplement the models that have been derived from results of spectroscopic investigation of the system Na-laponite/crystal violet. The purpose of the present paper was to examine whether these spectrophotometric measurements may supply reliable information on the colloidal properties of the system. We chose laponite as the adsorbing substrate because this mineral does not form π bonds with AO, and different visible spectra which are obtained under different conditions are associated with the colloidal properties of the system.

Experimental

Materials

Laponite XLG (C.E.C. of 0.89 meq/g [15]) was kindly donated by Laporte Industries Ltd. (U.K.). A 1% colloidal solution was used as a stock solution. The clay was saturated with various cations by adding 20 ml of the appropriate chloride salt solution (0.1 molar) to 100 ml of the laponite stock solution. After 48 h the excess salt was washed out four to six times with distilled water by centrifugation. Acridine Orange was supplied by B.D.H.

Methods

Visible spectra of clay-dye aqueous suspensions were recorded in the 350–600 nm range using a Perkin Elmer Spectrophotometer model Lambda 5. The optical path was 10 mm. Aliquots of the various suspensions were separated by centrifugation and by sedimentation over a period of 7 days at 2°C, and the spectra of the supernatants were recorded. Spectra were recorded against water in the reference beam (normal spectroscopy) or against aqueous dye solution in the reference beam (comparative spectroscopy).

One series of laponite-dye suspensions was prepared in which the clay concentration was kept constant (0.016 or 0.0016 wt.%), but the dye concentration varied between 1×10^{-6} and 2×10^{-5} molar. For samples with a degree of saturation above 160 mmol AO per 100 g clay, the clay concentration was only 0.0016 wt.%. Another series of laponite-dye suspensions was prepared in which the dye concentration was kept constant (4×10^{-5} molar) but the clay concentration varied between 0.01 and 0.04 wt.%.

Results and discussion

Absorption spectrum of acridine orange in aqueous solutions

AO is a metachromic dye [16] and a dilute solution gives an absorption band with one maximum at 490 nm (band α). With more concentrated dye solutions two bands are observed (α and β) at 490 and 470 nm, respectively. A further increase in the dye concentration results in a change in the relative absorbance of the two bands and band β becomes more prominent and is displaced to wavelengths below 470 nm. Bands α and β characterize monomeric and dimeric AO species, respectively [7].

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

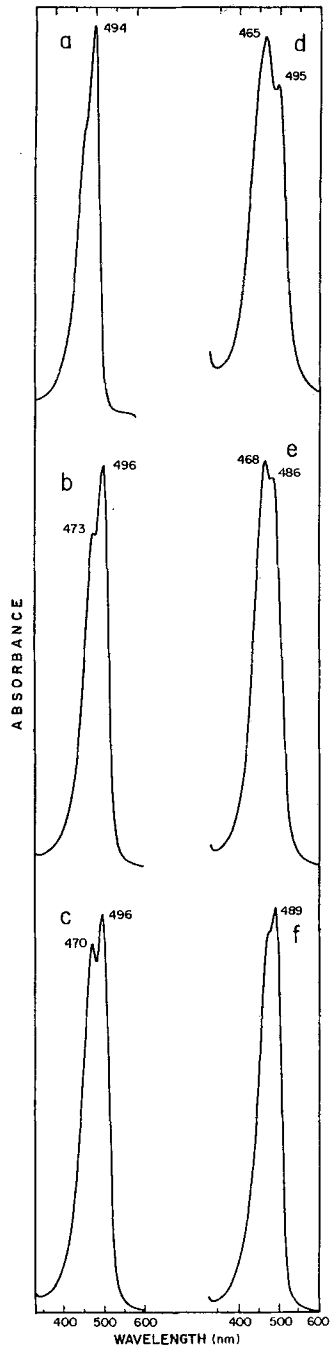
We shall first describe in more detail the spectra of Na-laponite/AO complexes. The spectra of the other monoionic laponites will be described in brief and will be related to that of Na-laponite.

Normal absorption spectra

Representative spectra of AO solutions to which different amounts of Na-laponite have been added (clay-dye suspensions) are shown in Fig. 1. In agreement with previous studies on the effect of laponite on the metachromasy of several cationic dyes, metachromasy was not observed as long as the degree of saturation was low. It was clearly observed only when the degree of saturation was above 36 mmol AO per 100 g clay. As the degree of saturation was above 64 mmol AO per 100 g clay band α disappeared and only a weak shoulder was observed. With a dye concentration of 4×10^{-5} molar band α reappeared when the degree of saturation was above 300 mmol AO per 100 g clay. Above 450 mmol AO per 100 g clay it became the principal absorption band. On the other hand, with higher dye concentrations band α was observed only as a weak shoulder and band β was the principal absorption band.

It has been previously shown that the colloidal state of montmorillonite or laponite, treated with cationic dyes, affected the absorbance of bands α and β [2, 17, 18]. Flocculation resulted in a decrease of absorbance, whereas with peptization the reverse phenomenon was observed. The absorbance of the of the maxima (band α or β), as a function of the degree of saturation for a constant clay concentration, is shown in Fig. 2. This absorbance curve can be divided into three distinct regions. In the *first region* (below 20 mmol AO per 100 g clay) there was a linear increase in absorbance, namely at low degrees of saturation the system obeys Beer's Law. In the *second region* (in the range 20–70 mmol AO per 100 g clay) there was almost no change in absorbance with increasing degrees of saturation. In the *third region* absorbance increased with increasing degrees of saturation in approximately a log shape. As one could observe with the naked eye, flocculation occurred in the second region, whereas in the first and third regions suspensions were peptized.

Fig. 1 Electronic spectra of aqueous suspensions of Na-laponite (0.0166%) treated with different amounts of AO. a) 4.8; b) 12; c) 30; d) 60; e) 320; f) 2400 mmol AO per 100 g clay



The absorbance of the maxima (bands α and β), as a function of the degree of saturation for a constant dye concentration, is shown in Fig. 3. Since a constant dye concentration was applied for this series, the change in absorbance resulted from the flocculation of the clay. This curve can be divided into three distinct regions which are

Fig. 2 Absorbance curve of aqueous suspensions of Na-laponite (0.0166%) treated with different amounts of AO. The absorbance (in absorbance units) of bands α and β is given versus the degree of saturation (in mmol AO per 100 g clay) for a constant clay concentration

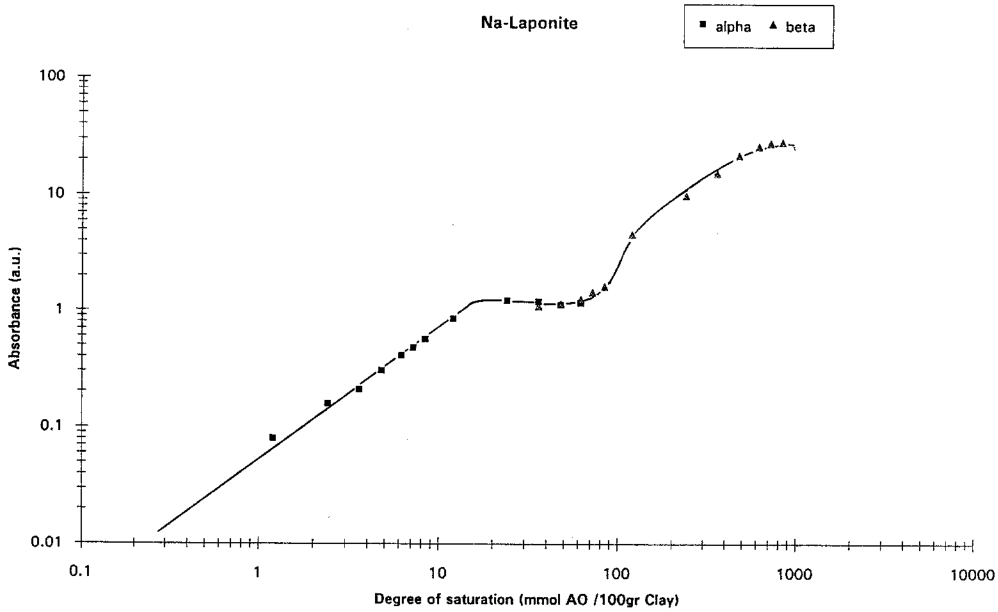
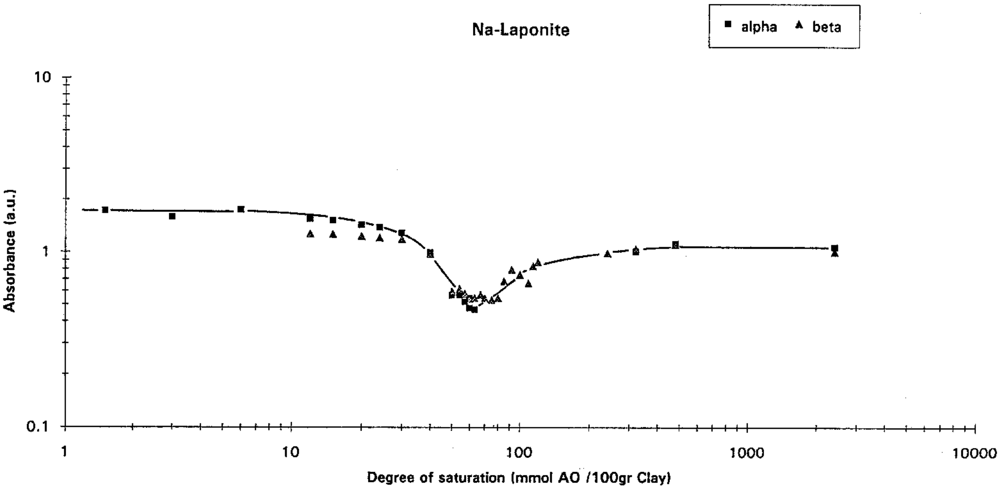


Fig. 3 Absorbance curve of aqueous suspensions of Na-laponite (different concentrations) treated with AO (5.33×10^{-5} molar). The absorbance (in absorbance units) of bands α and β is given versus degree of saturation for a constant dye concentration



equivalent to the three regions of Fig. 2. In the first region, where the clay was well peptized, there was almost no change in the absorbance due to increasing degrees of saturation. In the second region, in which the clay was repeptized, absorbance decreased with increasing degrees of saturation. In the third region, in which the clay flocculated absorbance increased with increasing degrees of saturation. At the transition between the second and third regions a plateau was obtained. As will be explained later, the flocculation in the second and third regions gave flocs with book house and card house structures, respectively. In this transition stage, both kinds of flocs were obtained.

Adsorbed monomeric AO cations can be located at the water/solid interface, on the external oxygen planes of the well dispersed layers (clay-dye association type A), or inside an interlayer space between two parallel face to face clay layers (clay-dye association type B). The former is identified from the location of band α at ≤ 490 nm, whereas the latter, from the red shift of band α. The appearance of band α at 490 nm, as in the spectrum of a dilute aqueous solution, indicates that a monomeric AO cation was located in the clay-water interface. The bathochromic shift is characteristic of a high acidic environment and is therefore obtained for cationic dyes inside the interlayer space. In the first and second regions of the absorbance curve band α was located at 495 nm, indicating that monomeric AO cations were located in the interlayer space of laponite tactoids (type B). It was the dominant band in the first region and its relative intensity decreased towards the end of the second region. Band β, which represents dimers, was gradually developed in the second region with the flocculation of the clay. Towards the end of this region, where flocculation was maximal and the supernatant was free of any clay, band β became the principal absorption band. We therefore assume that metachromasy was due to dimerization of adsorbed AO cations in the interparticle spaces of flocs (clay-dye association type C). The presence of clay/dye associations of types B and C simultaneously indicate that the flocs had the book-house structure.

The transition range between the second and third regions is characterized by the disappearance of band α and the increase in the absorbance of band β. This may be due to a crucial reorganization of the flocs structure from book-house to card-house. This change was associated with the neutralization of the electric charge of the clay platelets.

In the third region of the absorbance curve the spectra depended on the total concentration of the dye. In those samples in which the dye concentration was above 4×10^{-5} molar, band β was observed along the third region, whereas band α appeared as a shoulder. In these dye concentration the dimerization of AO occurs to some extent in the aqueous solution in the absence of any clay. From the spectra of the supernatants it was obvious that dimers were adsorbed in amounts greater than the cation exchange capacity of laponite. The location of band β gradually shifted from 470 to 453 nm at 35 (second region) and 85 mmol AO per 100 g clay, respectively. With higher degrees of saturation it gradually returned to higher wavelengths.

In those samples in which the maximum dye concentration was $\leq 4 \times 10^{-5}$ molar, at the beginning of the third region, band β was the only absorption band as long as the degree of saturation was below 300 mmol AO per 100 g clay. With higher saturations band α reappeared and the relative intensity of band β to that of band α decreased with the increasing degrees of saturation. When band α reappeared, it was located at $\leq$ 490 nm, which is characteristic for type A. From the spectra of the supernatants it was obvious that the adsorption of AO was greater than the cation exchange capacity of laponite and one would expect that the platelets with the adsorbed organic cations would gain a positive charge and peptize.

The blue shift of band β in the second region indicated that the π interactions in the associated AO species became stronger in the second region with the flocculation of the clay (type C). This is due to the fact that with increasing saturation and floc size, the interparticle space becomes more hydrophobic and the interionic association, which is a hydrophobic reaction, becomes very strong. In the third region dimers of AO cations were located in the clay water interface and the π interactions between the associated cations were weaker than those found in type C, consequently, band β shifted to longer wavelengths.

Comparative clay-dye/dye absorption spectra

The spectra of the clay-dye suspensions were recorded against the spectrum of an aqueous dye solution. Equal dye concentrations were present in the sample and reference cells. Representative curves are shown in Fig. 4. This spectroscopic technique cannot be used for quantitative analysis, but is very useful for qualitative determinations of the different adsorbed species. In Fig. 5 the absorbance of the clay-dye suspension in the comparative spectrum at different wavelengths relative to the base-lines, is described as a function of the degree of saturation. Band α appeared above 500 nm proving that monomeric species were located in an acid environment which is the interlayer space (type B). This band, intense in the first region decreased in the second region because of the flocculation of the clay and the dimerization of the dye to form associations type C. It became very weak in the presence of excess of dye (third region) because association type A was obtained and only traces of AO formed association type B. A very weak band γ appeared below 450 nm, when the degree of saturation was above 10 mmol AO per 100 g clay. This band does not appear in the spectrum of the AO aqueous solutions in the concentrations used in the present study. The appearance of this band in the comparative spectrum proves that trace amounts of polymeric species were located in the interparticle space of the floc (type D). The intensity of the band increased with the degree of saturation in the first region. It became weak in the second region because of the high flocculation of the clay. In the third region when the clay was repeptized this band was observed, at first intense, but became weaker with increasing degrees of saturation, indicating that more of the clay was peptized.

At 490 nm, which is the location of band α in the spectrum of an aqueous AO solution, a negative peak α appeared (Fig. 5). With a small degree of saturation, when the clay was almost completely peptized, the absorbance of the clay dye suspension was higher than that of the pure aqueous dye solution and the absorbance at 490 nm was above zero. This indicates that dimeric cations which had been present in the aqueous AO solution dissociated to monomers when they were adsorbed by laponite. With higher degrees of saturation the absorbance at 490 nm was below zero, indicating that the apparent molar extinction

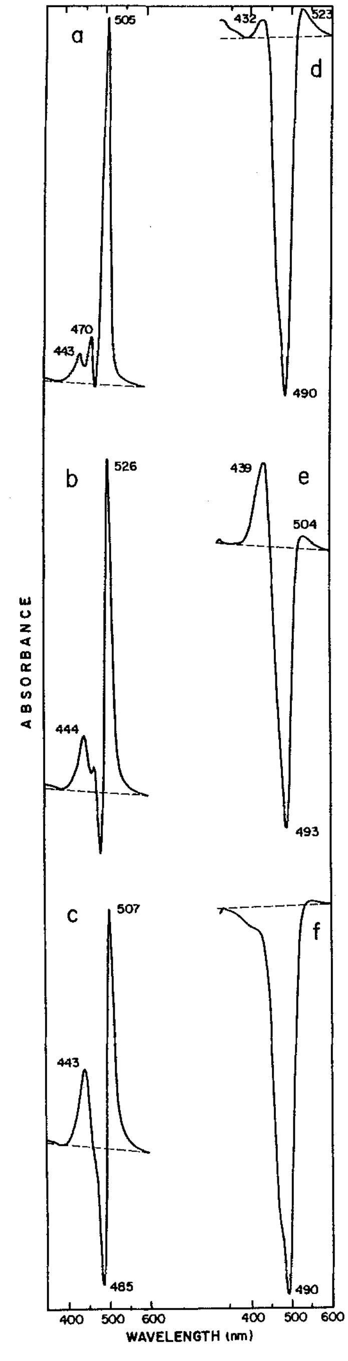


Fig. 4 Comparative clay-dye/dye absorption spectra of aqueous suspensions of Na-laponite (different amounts) treated with AO (5.33×10^{-5} molar). a) 12; b) 20; c) 30; d) 60; e) 320; f) 2400 mmol AO per 100 g clay

coefficient of AO in the clay suspension was smaller at this wavelength than that of the pure aqueous dye solution (without clay).

Figure 5 shows that the apparent molar extinction coefficient of AO in the clay suspension at this wavelength decreased with each increasing degree of saturation up to the end of the second region and then increased. The decrease in the extinction coefficient in the first region resulted from the penetration of AO cations into the interlayer space which led to a shift of the maximum of band α towards higher wavelengths and in the second region from: 1) the flocculation of the clay which led to a decrease in the absorbance and 2) the association of the dye monomers and the appearance of band β (metachromasy). The peptization of the clay was responsible for the shape of the comparative spectra of samples of the third region. Most of the clay was delaminated and only traces of AO cations were located in an interlayer space, showing a red shift.

Effect of the exchangeable metallic cation of laponite on the absorption spectrum of acridine orange

Visible spectra of the different clay-dye suspensions were recorded and curves describing absorbance as a function of the degree of saturation for constant dye or constant clay were prepared. Most features of the absorbance curves of the different monoionic laponites were very similar to those of Na-laponite and they could be divided into three regions. Transitions between the first and second regions and between the second and third regions are summarized in Table 1. The transitions between the second and third regions depended on the aging of the clay suspensions. In Table 1, transition points and absorbance values are given immediately after the preparation of the clay-dye suspensions and after 30 days. The table shows that after 30 days the transition points were shifted to higher degrees of saturation and the absorbance decreased. This is an indication that during this aging period, the size of the flocs increased, and that after the aging period and the increment of the flocs, greater amounts of AO were necessary in order to peptize the clay. Spectra of some suspensions were recorded after an aging period of 2 years. In all cases, transitions appeared with degrees of saturation slightly lower than those determined after 1 month of aging. Comparative clay-dye/dye absorption spectra of the different monoionic laponites treated with AO were also recorded and showed some dissimilarities to Na-laponite. The dissimilarities will be discussed in connection with the description of the spectra of the three regions.

Degrees of saturation of the transition points between the first and second regions were determined from the absorbance curves obtained for constant clay. Degrees of saturation which make transition points between the second and third regions, were determined from the absorbance curves obtained for constant dye. In reality, both absorbance curves gave similar transitions. However, because of practical reasons the former were determined from the break of the straight part of the absorbance curves obtained for constant clay, whereas the latter were

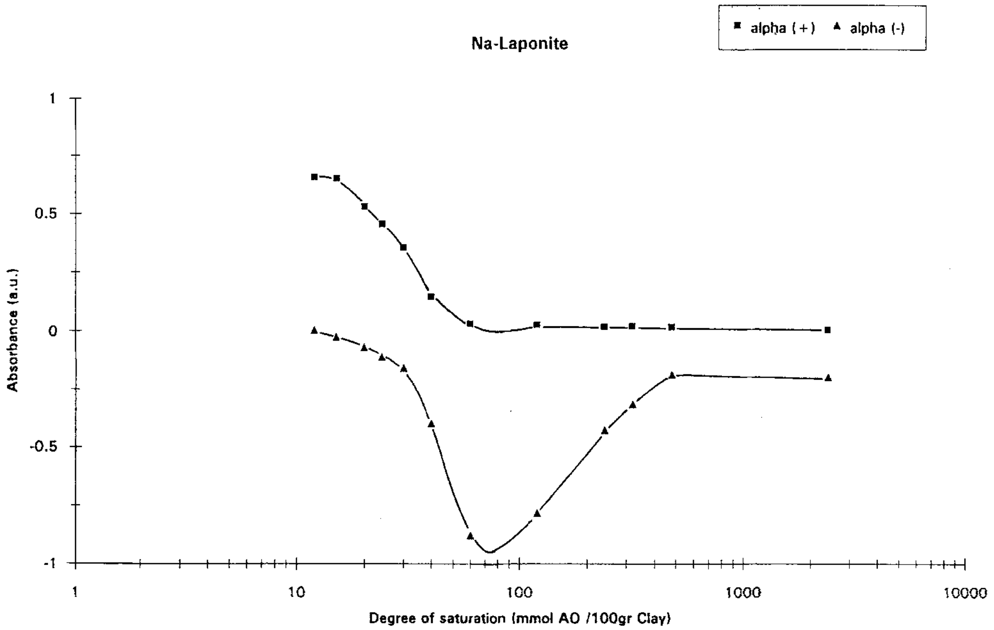


Fig. 5 Absorbance of positive and negative bands α in the comparative spectra of the clay suspensions treated with AO (5.33×10^{-5} molar) as a function of the degree of saturation

Table 1 Transition points (in mmol AO per 100 gr clay) in the absorbance curves of monoionic laponites and absorbance obtained for a constant dye concentration

Exchangeable Cation	Transition							
	1st-2nd regions		2nd-3rd regions					
			(1)		(2)		(3)	
	D.O.S.	Absorbance	D.O.S.	Absorbance	D.O.S.	Absorbance	D.O.S.	Absorbance
Li	15	1.25	85	0.432	114	0.248	85	0.365
Na	15	1.52	75	0.534	114	0.309	N.D.	N.D.
K	25	1.58	75	0.560	N.D.*	N.D.	N.D.	N.D.
Cs	25	1.40	60	0.468	114	0.367	104	0.423
Mg	15	1.03	46	0.516	85	0.305	N.D.	N.D.
Ca	12	0.74	30	0.477	70	0.232	N.D.	N.D.
Ba	12	0.81	63	0.409	67	0.418	N.D.	N.D.
Co	8	1.40	57	0.379	120	0.223	115	0.209
Cu	8	1.06	57	0.363	92	0.204	85	0.134
Al	12	0.34	67	0.144	70	0.047	N.D.	N.D.

(1)-in fresh samples; (2)-after 30 days; (3)-after 2 years.
*N.D – not determined

determined from the minimum in the absorbance curves obtained for constant dye and was ascertained by the comparative spectra which also required constant dye solutions.

First region

With monovalent cations band α was the principal detected band, whereas band β appeared only as a very weak shoulder. With polyvalent cations the appearance of band β depended on whether or not the clay had been dried before it was treated with the dye. If the monoionic laponite, which had been prepared from Na-laponite, was kept in aqueous suspension before the treatment with the dye, band α was the principal band. Band β, although appeared, was relatively weak. Its relative intensity increased in the order $Co^{2+} = Cu^{2+} < Ba^{2+} < Mg^{2+} < Ca^{2+} < Al^{3+}$. If the laponite was dried after it had been prepared from the Na laponite and later resuspended, the intensity of band β increased, but was slightly weaker than band α. Its relative intensity increased in the order $Co^{2+} < Ba^{2+} < Mg^{2+} < Ca^{2+} < Cu^{2+} < Al^{3+}$. The presence of band β which is characteristic of dimers present in the interparticle space of a floc, indicates that polyvalent laponites suspensions contained some flocs. As a result of the drying stage, the number of flocs increased.

The location of band α was at wavelengths longer than the wavelength of this band in the spectrum of an aqueous solution of AO (Table 2). The red shift is an indication that monomeric dye species are located in an acidic environment, i.e., in the interlayer space. The acidity of the interlayer space depends on the nature of the exchangeable metallic cation, and consequently, except for Cs, the acidity increased with the cationic charge. Due to its large size, Cs^+ is water structure beaker [13]. Monomeric water molecules in the interlayer space of Cs-laponite react like a strong acid leading to the high red shift. Red shifts were confirmed by the comparative clay-dye/dye absorption spectra. In the comparative spectra of the monovalent and Ba laponites band α was located at 505–508 nm. It was shifted to 510–517 nm in the spectra of the divalent laponites and to 535 nm in the spectrum of Al-laponite. The presence of an acidic interlayer space in these suspensions requires that all the monoionic laponites form small tactoids in which the layers are face-to-face associated.

Since the first region shows a linear relationship between absorbance and the degree of saturation, it is supposed that there was almost no change in the size and shape of the clay tactoids during the adsorption of AO and that the extinction of the dye in the first region might give information on the relative sizes of the laponite particles. Yet there is no quantitative treatment which relates between a particle size and the extinction coefficient in the absorption spectrum of the adsorbed dyes. However, we suppose that comparing between slopes of the absorbance curves of AO adsorbed on different monoionic laponites will supply information on the relative tactoid size of the different laponites. Slopes in absorbance units per 1 mmol AO are shown in Table 2. The table shows that the slopes obtained for laponites saturated with monovalent cations were larger than that obtained for the aqueous solution of AO. Polyvalnet cations gave smaller slopes indicating that their particles were larger. Except for Li and Co, the size of the tactoid increases with the charge of the exchangeable cation.

Table 2 Locations of the maxima of band α (in nm) and slopes of absorbance curves (in absorbance units per mmol AO) in the first region of spectra of monoionic laponites treated with AO, determined in the range 0–7.2 mmol AO per 100 g day

Exchangeable cation	location of band α (nm)	slope of absorbance curve (a.u. per mmol AO)
Li	495	0.051
Na	495	0.060
K	495	0.070
Cs	500	0.067
Mg	497	0.058
Ca	497	0.054
Ba	495	0.048
Co	496	0.064
Cu	496	0.051
Al	500	0.024

Second region

The second region of the absorbance curves is associated with the flocculation of the clay-dye complex, and the transition points between the first and second regions indicate the beginning of the flocculation process. Table 1 shows that monovalent cations required higher amounts of AO to start with the flocculation, whereas polyvalent cations required smaller amounts for the flocculation. At the beginning of this region the red shifted band α was the principal absorption band, indicating that at this stage most of the absorbed dye was located inside the interlayer space (association type B). With increasing degrees of saturation, flocculation was observed by the naked eye. In the absorbance curve of the series of constant clay, the absorbance in this region remained constant or slightly fluctuated, although the concentration of the dye increased with increasing degrees of saturation. This means that the extinction coefficient of the dye decreased with increasing degrees of saturation due to an increase in the size of flocs. The absorbance values depended on the exchangeable cation indicating that the shapes and sizes of the primary particles and of the flocs were controlled by the exchangeable metallic cations. In addition to band α, band β, at about 470 nm, also appeared during this stage (association type C). The degree of saturation of the first appearance of this band depended on the exchangeable metallic cation (Table 3). The intensity of band β was first weaker than that of band α, but with increasing degrees of saturation band β became more intense and band α became a shoulder. The highest degree of saturation in which this band appeared in the spectra of the different series of monoionic laponites in fresh suspensions and after 30 days are shown in Table 4. Monovalent cations showed no difference with time in the degree of saturation in which band α disappeared. Polyvalent cations, on the other hand, showed that after aging band α was detected with higher degrees of saturation. Suspensions which show only band β are composed of flocs hosting AO dimers (association type C). When the suspensions were fresh the flocs had the card-house structure. If band α appeared upon aging, the

Table 3 Characteristic features of band β in the second region of the spectra of monoionic laponites treated with AO. (D.O.S. = degree of saturation

Exchangeable cation	First appearance of band β D.O.S. mmol per 100 g clay	shortest wavelength of band β			
		wave length nm	D.O.S. mmol per 100 g clay	Absorbance a.u.	Absorbance after 30 days a.u.
Li	30	452	100	0.574	0.330
Na	12	453	92	0.798	0.393
K	60	454	110	0.850	0.510
Cs	40	453	67–104	0.805–0.827	0.450–0.407
Mg	> 1.5	456	60	0.660	0.345
Ca	> 1.5	458	40	0.544	0.468
Ba	24	459	54	0.476	0.257
Co	24	455	70	0.515	0.325
Cu	12	458	46	0.395	0.287
Al	> 1.5	469	50	0.180	0.070

Table 4 The degree pf saturation (D.O.S.) of the last appearance of band $\alpha > 490$ nm and first apperance in the third region of band $\alpha \leq 490$ nm

Exchangeable cation	Last appearance of band $\alpha > 490$ nm D.O.S. mmol AO per 100 g clay*)		First appearance in the third region of band $\alpha \leq 490$ D.O.S. mmol AO per 100 g clay
	initially	after 30 days	
Li	83	83	200
Na	64	67	300
K	80	80	480
Cs	64	64	240
Mg	46	67	200
Ca	35	67	100
Ba	54	85	200
Co	60	70	200
Cu	46	67	40
Al	47	60	70

*) dye concentration 5.10^{-5}M

flocs changed from card-house to book-house. In addition to type C, associations of type B were also obtained.

At the end of this region flocculation was maximal and the supernatent was free of any clay or dye. From the minima in the absorbance curves of the different monoionic laponites obtained at constant dye concentration (4×10^{-5} molar) (Table 1), the order of increasing flocculation at the transition point between the Second and Third Region can be obtained. The table shows that the degree of flocculation increases with the charge of the exchangeable cation.

The comparative clay-dye/dye absorption spectra of monovalent laponites and of Ba and Co clays showed the presence of band γ. This band, which appeared when the degree of saturation was above 10 mmol per 100 g clay (the last stages of the First Region) was extremely weak but became more intense with the flocculation of the clay. It indicates that trace amounts of polymeric species are present in the interparticle space of the flocs (type D). Band γ was not detected in the spectra of Mg–, Ca–, Cu– and Al– laponites.

Third region

This region in the absorbance curves is associated with the peptization of the clay-dye complex. The absorbance of the suspensions in the series of constant clay or constant dye increased with increasing degrees of saturation. At the beginning of this region only band β was observed in the spectra of fresh suspensions. With increasing degrees of saturation the location of this band shifted first to lower

Table 5 Absorbance of negative peak α (in a.u.) in the comparative spectra of different monoionic laponites saturated with AO.

Exchangeable cation	D.O.S. mmol AO*) per 100 g clay					
	12	24	40	60	120	240
Li	0.045	− 0.205	− 0.483	− 0.718	− 0.685	− 0.325
Na	0.004	− 0.111	− 0.400	− 0.877	− 0.781	− 0.428
K	0.042	− 0.217	− 0.092	− 0.487	− 0.817	− 0.688
Cs	0.107	− 0.066	− 0.479	− 0.900	− 0.677	− 0.496
Mg	− 0.280	− 0.486	− 0.843	− 0.900	− 0.715	− 0.395
Ca	− 0.504	− 0.773	− 1.008	− 0.966	− 0.757	− 0.429
Ba	− 0.063	− 0.371	− 1.027	− 0.553	− 0.509	− 0.206
Co	− 0.189	− 0.416	− 0.697	− 0.817	− 0.727	− 0.458
Cu	− 0.557	− 0.838	− 1.009	− 1.034	− 0.784	− 0.412
Al	− 0.840	− 0.951	− 1.249	− 1.064	− 0.879	− 0.457

*) concentration of AO 5.10^{-5}M

values; later on to higher values. The minimum wavelength and the degree of saturation which was responsible for this minimum are given in Table 3. In the case of Ba, this minimum occurred in the second region. The spectra were changed with time, and especially those of suspensions containing less than 200 mmol dye per 100 g clay. In these samples the size of the flocs increased with time and the absorbance of band β decreased.

After 30 days of aging supernatants of monovalent and divalent laponites containing up to 150 and 100 mmol AO per 100 g clay, respectively, showed that the dye was completely adsorbed by the clays. With higher saturations additional amounts of AO were adsorbed by the different laponites and only traces were found in the supernatants. Also, band α reappeared; however, it was located at $\leq$ 490 nm (association type A) and its intensity relative to that of band β increased with increasing degrees of saturation. The degrees of saturation in which band α reappeared in the spectra of the different monoionic laponites are presented in Table 4.

Band γ, which was observed in the comparative clay-dye/dye absorption spectra of monovalent laponites and of Ba and Co clays, in the second region, was very intense at the beginning of the third region but disappeared with the peptization of the clay.

Negative peak α as a measure of the degree of flocculation

The comparative clay-dye/dye absorption spectra of the different samples show a negative peak α at 483–490 nm. All curves describing the absorbance of monoionic laponites–dye suspensions at this negative peak, relative to the baseline as a function of the degree of saturation were similar to that of Na–laponite. This absorbance decreased with the degree of saturation up to the end of the second region, as a result of the progressive flocculation of the clay. In the third region, when the clay was repeptized, the absorbance at 490 nm was increased with increasing degrees of saturation.

Selected absorbance values of the negative peak α, relative to the baselines, are shown in Table 5. With a certain degree of saturation, the different monoionic laponites give different absorbance values, due to different degrees of flocculation. The more negative the absorbance is, the higher is the degree of flocculation.

With a degree of saturation of 12 mmol AO per 100 g clay, comparative spectra of samples saturated with monovalent ions that belong to the first region (peptization region), show a positive absorbance at 490 nm, whereas comparative spectra of polyvalent laponites, which either belong to the second region (flocculation region) or are at the transition point between the first and second regions, have a negative absorbance at this wavelength.

With 24 mmol AO per 100 g clay, all the samples belong to the second region of the absorbance curve and the comparative spectra show that the flocculation is higher with polyvalent cations as compared with monovalent cations. With 60 mmol AO per 100 g clay, polyvalent and Cs-laponite are in the transition point between the second and third regions and show maximum flocculation. With 120 mmol AO per 100 g clay and higher dye saturations the samples belong to the third region (peptization region) and the absolute values of the negative peaks decrease, as one would expect.

Conclusions

The visible spectrum of aqueous AO solution is changed as a result of the interactions between this dye and laponite. The spectroscopic characterization obtained by normal and comparative measurements were applied to study the colloid properties of the clay-dye system as a function of the degree of saturation of the clay by AO. Absorbance curves which describe the absorbance of AO versus the degree of saturation can be divided into three regions which are associated with the colloid state of the system. With small degrees of AO saturation, the clay is peptized. At this stage, very small tactoids are formed with face-to-face association. Peptized systems obey Beer's law. The slopes of straight lines describing absorbance as a function of the degree of AO saturation, obtained with constant clay, can give information on the relative sizes of the tactoids of the different monoionic laponites–AO complexes. Thus, the spectroscopic phenomena must be associated with changes in the colloidal properties of the system.

With higher degrees of saturation the clay flocculates. As a result of flocculation, the extinction coefficient of adsorbed AO decreases. Changes in absorbance, obtained with constant dye, may give information on the degree of flocculation and on the relative size of flocs of the different monoionic laponites–AO complexes. From the spectrum it is possible to differentiate between flocs with book-house structure and flocs with card-house structure. The former are obtained first, whereas the latter are obtained in the presence of excess dye. With a great excess of AO most of the clay is peptized by the adsorption of the dye in excess to cation exchange capacity of the clay. The visible spectra of the different samples show that at this stage the peptized particles are composed of monomeric lamellae whereas the peptized particles which are obtained with a small degree of AO saturation, are composed of small tactoids. A very small amount of tactoids were detected by the comparative spectra in the suspensions containing excess dye.

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