

CHAPTER 5

INTERACTION OF DYES WITH MONTMORILLONITE AND ZEOLITE (ZSM-5) : SORPTION AND METACHROMASY

5.1 INTRODUCTION AND REVIEW OF THE PREVIOUS WORKS :

Interaction between organic matter and the clay minerals are important in many areas of geochemistry, agriculture and industry. Interests in the interaction of the dyes with clay minerals and zeolite are also stimulated in the present context due to the important role of such interactions in clay and zeolite modified electrodes as described in chapter 4. While sorption / ion exchange characteristics of these inorganic materials have direct implications on the physico-chemical nature of the electrodes, spectral changes observed in the above phenomena viz., metachromasy, gives some insight to the nature of bonding of dyes with the exchangers.

On the basis of crystal chemical approach, the correlation between the structures and the exchange properties of the clay minerals has been established from the important researches of Pauling (145), Bragg (146), Grauner (147), Brinddley (148), Hofmann (149), Marshal (150), Hendrics (151) and others (152-158). From these studies, clay minerals are recognised to consist essentially of two structural units. One is composed of two sheets of closely packed oxygens or hydroxyls in which aluminium or magnesium atoms are arranged in octahedral co-ordination so that they are equidistant from six oxygens or

hydroxyls, with aluminium in the octahedral position, only two-third of the possible positions are filled to balance the structure. The second unit is the tetrahedrally co-ordinated silica. A silicon atom being placed at the centre of a regular tetrahedron is equidistant from four oxygens or hydroxyls. The silica tetrahedra are joined together through oxygen to form a hexagonal network which is repeated indefinitely for forming a sheet composition $\text{Si}_4\text{O}_6(\text{OH})_4$. The tips of all the tetrahedra are in the same direction and toward the centre of the unit. The structure of montmorillonite which is a member of the smectite class of minerals is shown in fig. 93. Montmorillonite is a 2:1 type or trimorphic layered phyllosilicate in which the central octahedral aluminium sheet is surrounded by two tetrahedral silica sheets. Substitution by Fe^{+2} , Fe^{+3} or Mg^{+2} normally occurs in the octahedral position of aluminium (159).

The ion-exchange sorption of inorganic as well as organic ions are known to occur in clay minerals (160-164). The origin of the charge of the clay lattice are believed to be due to lattice imperfections, broken bonds at the edges of the particles and exposed structural hydroxyls in addition to the isomorphous substitution. The negative charge on the clay minerals is compensated by adsorption of cations. The counter-ions are held on the external surfaces of the aggregates and between the unit layers in clays which swell in aqueous suspension, whereas the sorption of counter-ions takes place onto the external surfaces

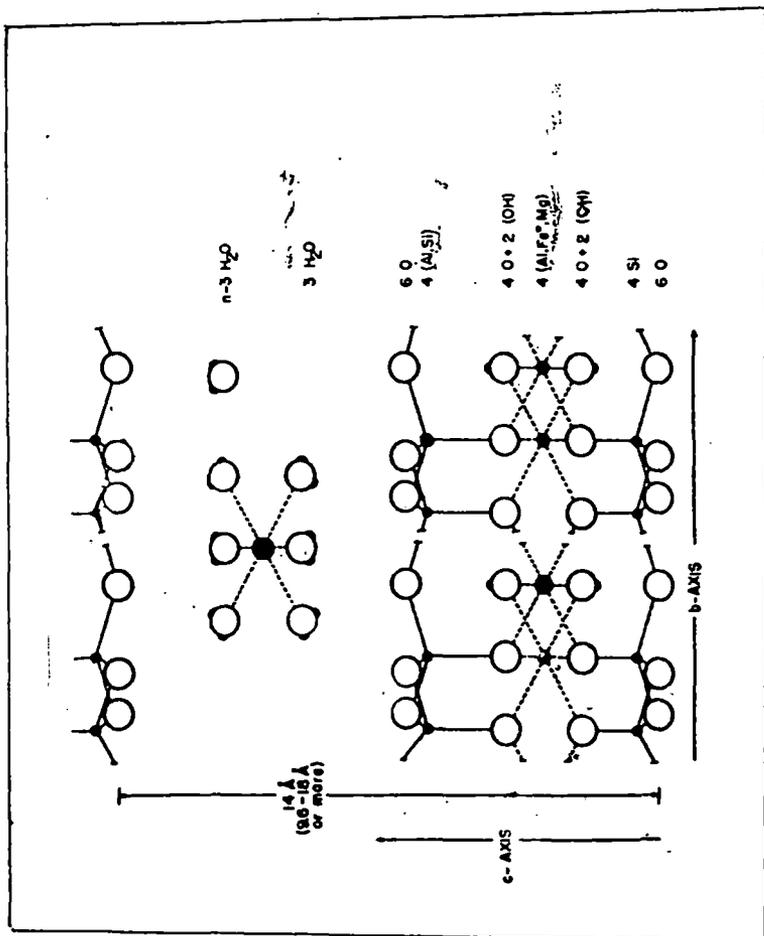


Fig. 93 : Structure of Montmorillonite

in non-swelling clays. In aqueous suspensions, some of these cations remain in a closet held stern layers, other diffuse away from the surface and thus form a diffused double layer. Provided that they are not fixed by engaging in strong, specific bonding with the clay or by being trapped between unit layers that have collapsed together irreversibly (lattice collapse) the counter-ion can undergo ion exchange with other cations present in the system. The magnitude of the CEC of a clay depends largely on the type of the clay and to a lesser extent on the source of a particular sample. Systematic studies of cation exchange in pure clay minerals were carried out by Page and Bayer (165), Bar and Tenderloo (166), Hendricks and Alexander (167), Schachtschabel (168), Mukherjee (169) and others. Most of the investigations were based on exchange reaction involving clay minerals with organic compounds have also been established by different scientists.

Adsorption studies of the dyes and large organic ions on different adsorbents, particularly on clays, have been made by many workers. Most of the studies were intended to measure the surface areas and CEC of the sorbents. As early as 1910 Mare (170) observed that dyes could be adsorbed by crystals up to a saturation value. Ramachandran and coworkers (171) measured the surface area by low temperature nitrogen adsorption of methylene blue, methyl violet and malacite green on the clay fraction of montmorillonite, kaolinite and illite. From the difference, the

actual extent of the area of contact was evaluated. This was found to be relatively small showing that while the surface is available for nitrogen adsorption, it is not accessible to dye molecules. The cation exchange capacity, found from methylene blue and methyl violet sorption on kaolinite and montmorillonite, was in close agreement with those found by standard methods. Brooks (172) adsorbed methylene blue on Na^+ forms (Na^{22} and Na^{23}) of montmorillonite, kaolinite and silica sand flour and found the amount of dye adsorbed to be equivalent to the sodium displaced. The author believed that the dyes were adsorbed on the clay mineral surface through ion-exchange process. Plesch and Robertson (173) also proposed two distinct mechanisms to operate in sorption of dyes on surfaces of clay minerals; namely, the partly irreversible ion exchange and the fully reversible physical adsorption. Bergmann and O'Konski (42) reported that the adsorption of methylene blue on montmorillonite took place first through irreversible ion exchange mechanism and then by physical adsorption and verified the equation of Plesch and Robertson with their experimental results.

Ewing and Liu (174) estimated the cross-sectional areas of crystal violet and orange II assuming that the dye molecules were adsorbed flat on the surface of the clay minerals and they estimated the cross sectional area of crystal violet to be 160 \AA^2 and 171 \AA^2 depending on whether the dye is adsorbed in the dehydrated or hydrated condition.

The surface area measured through dye adsorption, however, did not agree with those obtained by nitrogen adsorption in all cases. Kipling and Wilson (175) found discrepancies in specific surface areas of porous and non-porous active charcoal measured by methylene blue and nitrogen adsorption. Hofmann (176), on the basis of methylene blue and orange II adsorption on a wide variety of clays, showed that the surface area calculated was only 70% of the total surface area. Orr (177,178) found that the surface areas of two halloysite samples calculated by sorption of four dyes viz. malacite green oxalate, malacite green hydrochloride, amaranth and tetrazine, were apparently equal to 1/4 of the total surface. Similar discrepancies were also reported by Daran (179), Vander Grinter (180) and Bancelin (181) in their respective adsorption studies. Bancroft et al. (182) from adsorption of methylene blue on lead sulphate, Subramaya et al. (183) from crystal violet adsorption on glass and Doss and Singh (184) from thymol blue adsorption on active carbon, arrived at the similar unsatisfactory results.

Giles and coworkers (185) observed that the adsorption of basic dyes by silica from aqueous solution exceeded its monolayer coverage requirement. Association of the dye molecules in the adsorbed state has also been detected by electron micrography (186) that most of the dye molecules are associated in solution as micelles from 10 to 100 molecules units was reported by Lenhar and Smith (187,188), Vickerstaff and Lemin (189), Bergmann and

O'Konski (42), Mukherjee and Ghosh (35,190,191), Hertz et al. (192) and Hertz (193) also observed that dye molecules, of which the monovalent organocation are a sub-group, tend to aggregate into dimeric and polymeric species in aqueous solution. Kongonoviski (194) also observed the adsorption of dyes to take place through monolayer sorption of associated micelles. Brooks (172) advocated that the surface area and cation exchange capacity of the substrates, with methylene blue adsorption, could still be measured. To calculate CEC and surface areas he suggested addition of dye solution to a mineral suspension in small increments till the equilibrium concentration was 1×10^{-6} M indicated by a slight blue colour of the supernatant.

Thi and Brindley (195) asserted that methylene blue can be used for the measurement of both surface areas and CEC of clay minerals such as montmorillonite. They attributed the cause of failure in measuring surface areas and exchange capacities by Faruki et al. (196) and Bodenheimer and Heller (197) to the insufficient replacement of Ca^{+2} ions by methylene blue from Ca-montmorillonite used in their studies. Using Na-clay instead of the Ca-clay these authors calculated the surface areas from the amount of methylene blue adsorbed when optimum flocculation occurred. Fully exchanged values of methylene blue was used to calculate the CEC of montmorillonite. Methylene blue molecule was considered to possess approximately a rectangular volume of dimensions $17.0 \times 7.6 \times 3.25 \text{ \AA}^3$. They believed that coating of clay

particles occurred first and visualised a flat face-on orientation of methylene blue molecules (i.e. lying on the $17.0 \times 7.6 \text{ \AA}^2$ face) for effective coverage of surfaces. Flat face-on orientation of the dye (i.e. $17.0 \times 3.25 \text{ \AA}^2$) was assumed when full exchange takes place.

West, Carrol and Whitcomb (198) investigated systematically the adsorption characteristics of more than thirty dyes on photographic bromo-iodides and chloro-bromides suspensions in 70% aqueous gelatine solution in an attempt to correlate the sorption and optical sensitization. It was noticed in some cases that the dye adsorbed was very little at first but the rate of dye adsorption increased as more dye was adsorbed. They termed this as "co-operative adsorption". The intermolecular forces between the large dye molecules are so high that they polymerised when molecules came closer in the adsorbed state, giving rise to increased adsorption.

De and coworkers (199-205) made a series of studies on sorption of dyes onto clay minerals and their desorption from the clay-dye complexes by various inorganic and organic ions. They found Langmuir type of adsorption isotherms to operate in all cases. Surface area measurement, evaluation of CEC, determination of distribution coefficients and selectivity coefficient are the major part of their work. Narine and Guy (206) interacted thionine, methylene blue, new methylene blue, paraquat, diquat with bentonite in dilute aqueous systems. They noted that the dye

cations form aggregates on the clay surface and aggregation increases with ionic strength, raising the adsorption capacity by 25%. They also observed that changes in adsorption due to changes in temperature were small and the dyes were irreversibly bound by the clay matrix.

Yamagashi (207) recently studied the effect of alkyl chain length ($-\text{CH}_3$ to $\text{C}_{12}\text{H}_{29}$) for the adsorption of N-alkylated acridine orange cation on Na-montmorillonite. He observed that the length of the aliphatic tail had no appreciable effect on the binding constant and the rate of adsorption.

Zeolites are crystalline aluminosilicates with a great capacity of water and the ability to be completely hydrated and dehydrated without damage to the crystalline lattice. The intracrystalline architected diversity of the natural zeolite minerals and their synthetic analogues and extensions results from the three dimensional network formed from conjoining SiO_4 and AlO_4 tetrahedral building blocks; the ensuing structure is an inorganic cross-linked and crystalline macromolecules. Fig. 94 illustrates the oxygen sharing, Al-O-Si Linkages in a two dimensional representation of the aluminosilicate zeolite structure (117).

The tetrahedral coordination of Si-O and Al-O (generally referred to as T-O) permits a variety of ringed structures to form, like the six T atom rings shown in fig. 94. These rings link to form the cage and the channel structures that give rise

to the molecular discriminatory nature of zeolite. In addition to showing the preliminary stages of the zeolite framework also displays two chemical features of the aluminosilicate zeolites that provide much of the chemical diversity of the system. For every Al atom in the lattice, with its $\text{AlO}_2/\text{SiO}_2$ stoichiometry, a fixed negative charge results. These anionic sites are counterbalanced by mobile cations typically alkali metal or alkaline earth metal cations, that easily ion exchange for other metal cations or organic cations of appropriately small dimensions.

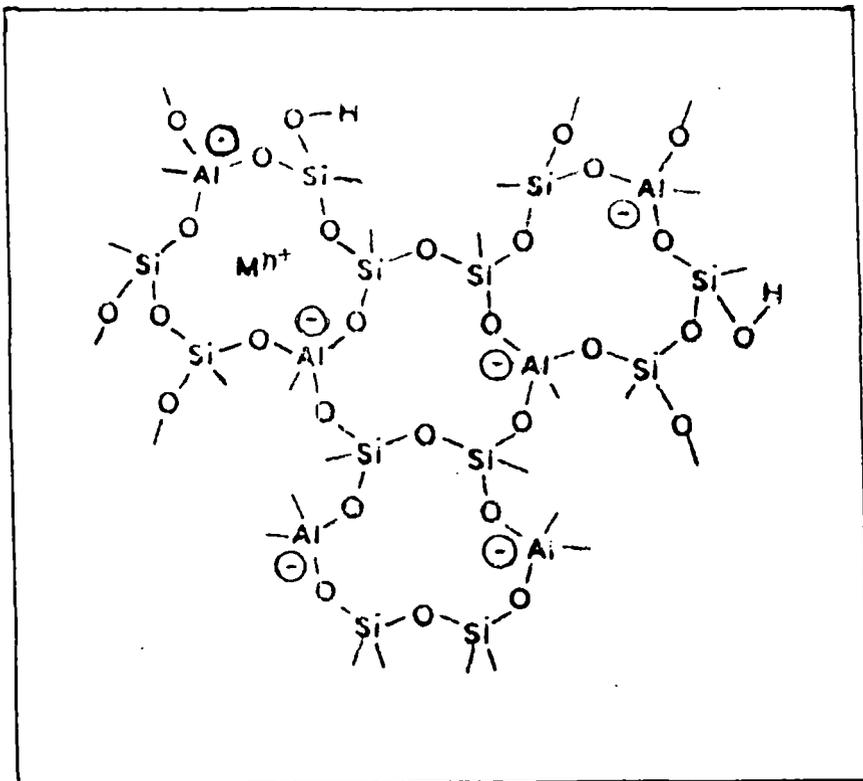


Fig. 94 : Structure of Zeolite

The second feature is the termination of bonding at the crystal faces with hydroxyl groups. Hydroxyls are the form in which protons are held in the zeolites and they are responsible for the strong acid nature of the aluminosilicate zeolite and their extensive use in acid catalysed reactions, not the least of which the cracking of petroleum. The incorporation of aluminium into the framework structure of the ZSM-5 type zeolite, which results in the occurrence of acid sites, provide a good example of the progressive change from a zeolite silica polymorph, silicate 1 to a high silica zeolite, ZSM-5. The intracrystalline catalytic activity of zeolite Al-ZSM-5 is dominated by shape selective reactions which occur within its channel structure through the external surface, which is affected by the adsorption of bases. It is argued that the adsorption of cationic dyes such as methylene blue by solid materials from aqueous solution is associated with the presence of acid sites and should provide a measure of their formation as a result of substitution on aluminium into the framework of silica polymorph (208,209,211).

METACHROMASY :

Adsorption of dyes by clay minerals often results in significant spectral changes specially in the electronic spectrum. The visible absorption spectrum is attributed to a

single electronic transition for each dye in the present investigation (chapter 3). The transition may be described in terms of a single vibronic progression (chapter 3). Moreover it has been shown that the excitonic interaction results in splitting of dimer spectra into two band systems one at lower and the other at higher wavelengths of the corresponding monomer spectrum. However, the gradual replacement of the principal band (the so called α band) by a band with a shorter wavelength (the β band) as a result of interaction between dye molecules (dimer formation) or with due to the interaction of dye with inorganic exchangers (metachromasy) has been described in the literature in a qualitative manner in search of an insight knowledge regarding the type of interaction and bonding. In the present chapter a similar qualitative description of the metachromasy of the five thiazine dyes with montmorillonite are presented briefly.

Vadeneva observed metachromasy i.e. the appearance of a hypsochromatically shifted band in clay minerals (210) by studying adsorption of malacite green and brilliant green by montmorillonite and kaolinite. She concluded that formation of ionic bonds between clays and dye caused a bathochromic shift, while the intensification of the dipole bond was hypsochromic. A qualitative theory of metachromasy in solution was proposed by Schubert and Levine (37). They postulated that the metachromasy is produced as a result of selective and reversible binding within an anionic cluster of a polymeric dye cation of highest

charge available.

Bergmann and O Kanski (42) described a spectroscopic study of methylene blue sorbed on montmorillonite. Spectral changes were found to follow changes in the amount of methylene blue sorbed on the clay surface. Due to the fact that these changes are similar to the spectral shifts accompanying dimerization and polymerization of methylene blue in aqueous solution these shifts were also attributed to dye-dye interaction on the surface of montmorillonite. According to these authors the dimer is held together by london dispersion forces and hydrophobic bonding.

Most researches on adsorption of organics by clays have focussed on smectite (212-215). Smectite clays have high adsorption capacities and generally form stable colloidal suspensions that can be investigated conveniently by various techniques suitable for suspensions. The high adsorption capacity make these clay-organics suitable for various thermal analysis investigations also.

The sorption of methylene blue by clay minerals was extensively applied by clay scientists in the determination of ion exchange capacity, surface area and for differentiation between various clay minerals. Since the publication of the paper by Bergmann and O Kanski (42) new knowledge has been gained, mainly from IR spectroscopy, on the mechanism of sorption of organic molecules by montmorillonite and on the nature of bonding occurring in the interlayer space (216).

The influence of solvent and concentration of aqueous solution on the spectrum of methylene blue was studied by Michaelis and coworkers. They found that Beer's law is obeyed in alcoholic solution but molar absorption depends on the concentration of the dye in aqueous solution. In alcoholic solution methylene blue shows a sharp and high peak with a maximum at 650 nm, due to $\pi-\pi^*$ transition (α band) (216). A shoulder at 590 nm is referred to as the β band. In very dilute aqueous solution the α band is displaced to 660 nm. As the concentration of methylene blue increases the α band intensity decreases and that of the β band increases considerably. Michealis states that the α band is the characteristics of monomeric cation and correspond to an electric oscillation along the X-axis of the molecule. The β band is the characteristics of the dimer and corresponds to an oscillator in the Y direction. Bergmann and O'Konski believe that β band is a transition moment which lies also along the long axis of the molecule but is perturbed due to an interaction between transition moments of the monomer units.

Schubert and Levine (211) differentiated between three bands α , β and γ at 665, 610 and 570 nm respectively. The γ band sometimes referred to as the "metachromatic band" is characteristics of polymeric cation. It is sometimes diffused and variable indicating that the observed peak is an envelope of overlapping bands (217). According to Schubert and Levine (211)

dimerization and polymerization lead to metachromasy due to interaction of some of the π electrons in level $N/2$, the most loosely bound electrons being responsible for the α band, and during polymerization a constraint is imposed.

Yariv and Lurie (216) studied the metachromasy of methylene blue in montmorillonite in terms of the knowledge about colloidal properties of clay suspensions and the mechanism of the peptization, aggregation and flocculation. They concluded that the metachromasy of methylene blue in montmorillonite is not connected with aggregation of the organic dye, but with the interactions of the oxygen sheet of silicate layer with the organic dye molecule (216). The intensity of the absorption bands of the sorbed methylene blue depends on the colloidal properties of the suspension. The effects are more the clay is peptized and less after coagulation. Three different modes of sorption of methylene blue were identified (a) hydrated form at the edges (b) metachromatic form almost to the oxygen sheet of the silicates and (c) possibly protonated form. Forms (a) and (c) are the first stages to occur during the sorption. The sorption takes place by a cation exchange mechanism.

Yamagishi and Soma (218) studied the adsorption of N-alkylated Acridine Orange (AO) by Na-montmorillonite. They showed that adsorption of the cationic dyes which belong to the AO family also results in metachromasy. They considered the clay minerals as a poly electrolyte and believed that the interaction

between the negatively charged mineral and the dye cation is a pure electrostatic attraction and that metachromasy resulted from the electronic interaction between neighbouring adsorbed cations.

The idea of π interactions between the aluminosilicate layer and the aromatic entity was later supported comparing the adsorption of dibenzotropone and dibenzosuberone by montmorillonite (219). Only in the first molecule is aromaticity induced, and its adsorption by montmorillonite results in π interactions between the organic molecule and the clay mineral. In rhodamine 6G the phenyl ring is sterically constrained to be roughly perpendicular to the planar xanthene group (220). Owing to this steric effect, π interactions between the organic dye cation and the aluminosilicate layer can not occur. Thus no metachromasy is observed when rhodamine 6G penetrates into interlayer space of montmorillonite. It may therefore be concluded that metachromasy of cationic dyes in montmorillonite suspensions is expected only if there is no steric hindrance and when π interactions may occur between the aromatic ring and the oxygen plane of the aluminosilicate layer.

Grauer coworkers studied the adsorption of pyronine Y (PY) on montmorillonite to show that in the absence of the steric hindrance, π interactions between the dye cation and the aluminosilicate layer do occur (221). They showed that the adsorption of PY by montmorillonite results in metachromasy, namely a pronounced β band appears. In the presence of small

amount of clay (or a high degree of formal saturation) soluble PY contributes to the adsorption spectrum and the spectrum shows a high intensity of band α at 545 nm. with increasing clay concentrations (or decreasing formal degree of saturation) no PY remains in the aqueous phase and the β band increases. Adsorbed PY shows a bathochromic shift of α to 550 nm. The intensity of the shifted α band increases with the increase of clay concentration. They also showed the effect of clay concentrations in the suspension on the location of bands α and β in the absorption spectrum of the dye. From these spectroscopic studies they deduced the conclusions that (i) metachromasy in montmorillonite takes place even at very dilute solutions of the dye, which are not shown in the absence of the clay (ii) metachromasy in montmorillonite is observed at a very low formal degree of saturation, namely its occurrence does not depend on the surface concentration of the dye (221).

Metachromasy in montmorillonite is attributed to the interaction of the lone pair electrons of the surface oxygens with the π electrons of the dye. This kind of interaction may occur only with clays having a tetrahedral substitution of Si by Al (222). Grauer and coworkers (221) compared the behaviour of laponite to that of montmorillonite and showed that the process which gives rise to metachromasy in laponite systems differs from that occurring in montmorillonite systems. In montmorillonite suspensions metachromasy occurs even with very low degree of

saturation, whereas in laponite suspensions metachromasy occur only when the degree of saturation is about the same as the cation exchange capacity of this mineral. They concluded that in the laponite system metachromasy is associated with the dimerization of the dye cation on the surface of this mineral. Cenens (223,224) coworkers also agreed with the above explanation of metachromasy in laponite.

5.2 EXPERIMENTAL :

The electroanalytical behaviour of the montmorillonite and ZSM-5 in the modified electrode makes it imperative for studying their sorption characteristics as an adsorbent.

various characteristics of the dyes, their structure and method of purification are presented in chapter 3. The characteristics of montmorillonite and ZSM-5 used in the present study are given below :

Sample	Description	CEC	Source
Montmorillonite	Light grey powder	80*	Evans. medical Ltd. Liverpool England.
ZSM-5	White powder	47 (ref.208)	Dr. T. D. Smith Monas University Australia

* Determined by $\text{BaCl}_2\text{-Ba(OH)}_2$ method.

The clay fractions of montmorillonite clay minerals having size less than 2 μ were isolated by the usual method of dispersion and sedimentation. The fraction thus collected were treated several times with dilute HCl, and after removal of the acid, warmed with 6% H_2O_2 in water bath to remove trace of any organic matter present. Excess H_2O_2 was decomposed by heating the samples in water bath. The iron present in the clay minerals was then removed by treating the clay samples with sodium metabisulphite and dithionate in acetate buffer solution at 60°C followed by centrifugation, washing etc. as recommended by Bromfield (225). Finally the clay residues were washed to dispersion and dialysed. The clay suspension was then converted into the Na-form by stirring an approximately 2% suspension of the clay minerals with ion exchange resin (Dowex 50w x 80) in Na-form for about 4 hours. Na-clay ($pH=7$) thus formed was used for the study. ZSM-5 sample, as received from the source, was used for the preparation of suspension.

Preparation of the suspension for adsorption study :

A certain amount of montmorillonite (7.4 g/lit.) and ZSM-5 (0.248 g/lit.) suspension were taken with the varying amount of dye solutions ($5 \times 10^{-5} M$) and the final volume was made 20 ml by adding required amount of distilled water. ZSM-5 suspensions were found unstable above that concentration. The

suspensions (dye-mont. and dye-ZSM-5) were then shaken for 6 hours and kept at rest overnight for attaining the exchange equilibrium. The resulting exchanged residues were then centrifugated (10,000 rpm) for 10 minutes and the supernatant solutions were analysed spectrophotometrically. From the differences between the initial concentration and the equilibrium concentration, the amount adsorbed was determined. The entire experiment was carried out at room temperature ($25 \pm 1^\circ \text{C}$)

Metachromasy :

A series of clay-dye suspensions with varying clay concentration (0.3×10^{-3} to 1.5×10^{-3} wt%) were prepared, keeping the concentration of the dyes in each sample at a fixed value of 9×10^{-6} M. The spectra of the clay-dye suspensions (montmorillonite) were recorded within 2 hours of preparation at room temperature ($25 \pm 1^\circ \text{C}$) using Shimadzu UV-240 model, in the range of 800-400 nm. The optical path length of the cell used was 1.0 cm.

5.3. RESULTS AND DISCUSSION :

5.3.1 Studies on Sorption :

The adsorption isotherm and the corresponding reciprocal

Langmuir plots of the dyes on montmorillonite and ZSM-5 are shown in the figs. 95-100. The adsorption isotherms are of H-type i.e., of high affinity class of Giles and coworkers (226) and is indicative of species adsorbed flat on the surface. and H-type curve is a special case of the L-type, caused by a very strong solute/substrate interaction.

The adsorption data are seen to fit the linear form of the Langmuir adsorption equation. Accordingly the plot of C/x vs C , where C is the equilibrium concentration of the dye and x is the amount adsorbed in mmol per 100 g of montmorillonite or ZSM-5 yields a good straight line (figs. 95-100). From the slope of the line, the value of x_m (the amount required to form a complete monolayer) is calculated in both the cases. The values are given in the table 24.

Table-24

Dye	Montmorillonite		ZSM-5	
	x_m (mmol/100g)	$k \times 10^{-5}$	x_m (mmol/100g)	$k \times 10^{-5}$
Th	93	4.6	44	3.1
AzC	94	5.0	42	3.7
AzA	95	5.3	42	3.9
AzB	100	6.5	43	4.4
MB	96	5.9	40	4.1

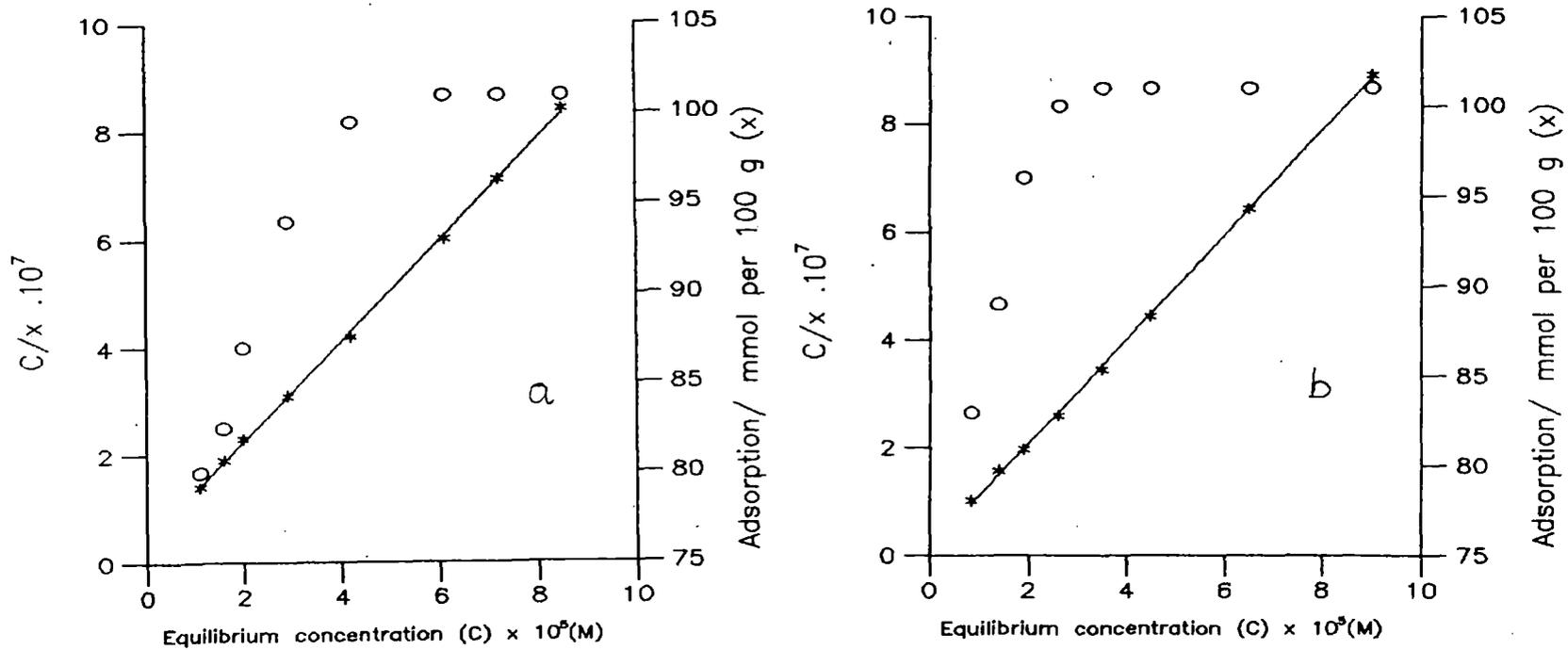


Fig. 95 : Adsorption isotherm and Langmuir plot of (a) Thionine and (b) Azure A in the presence of Montmorillonite.

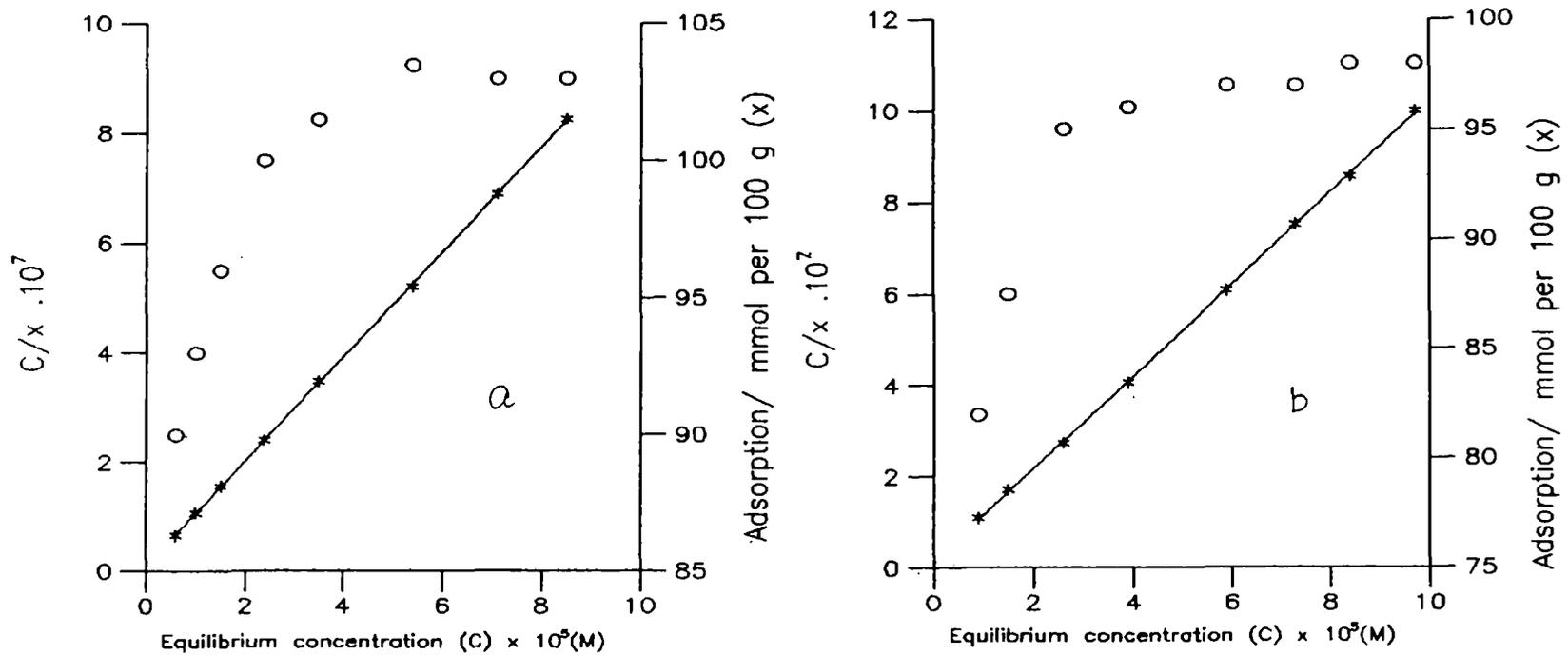


Fig. 96 : Adsorption isotherm and Langmuir plot of (a) Methylene Blue and (b) Azure C in the presence of Montmorillonite.

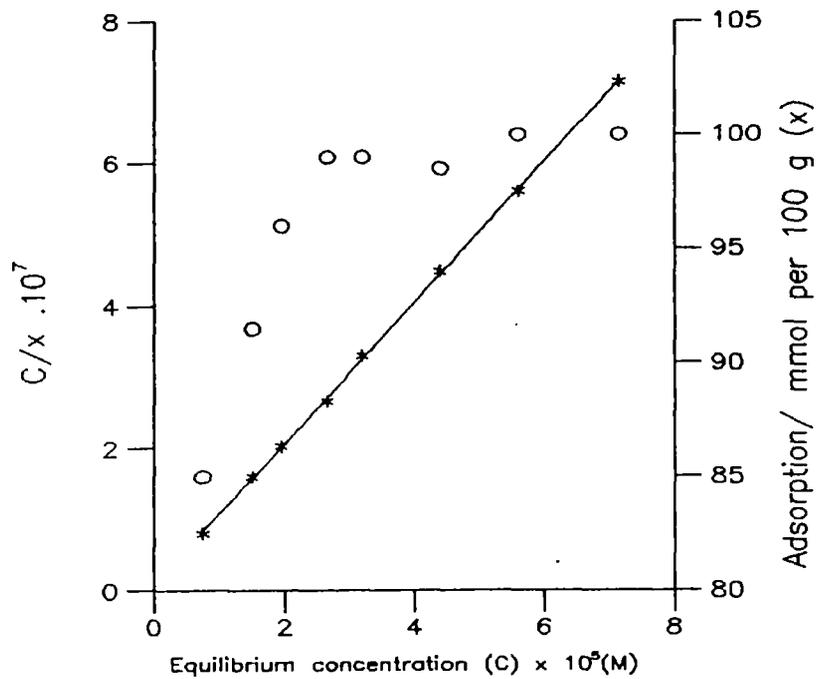


Fig. 97 : Adsorption isotherm and Langmuir plot of Azure B in the presence of Montmorillonite.

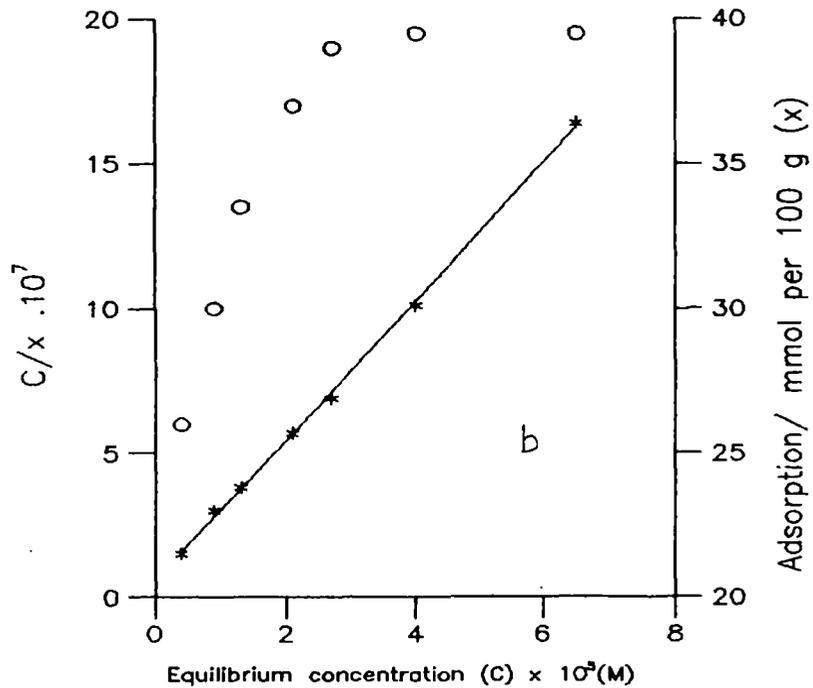
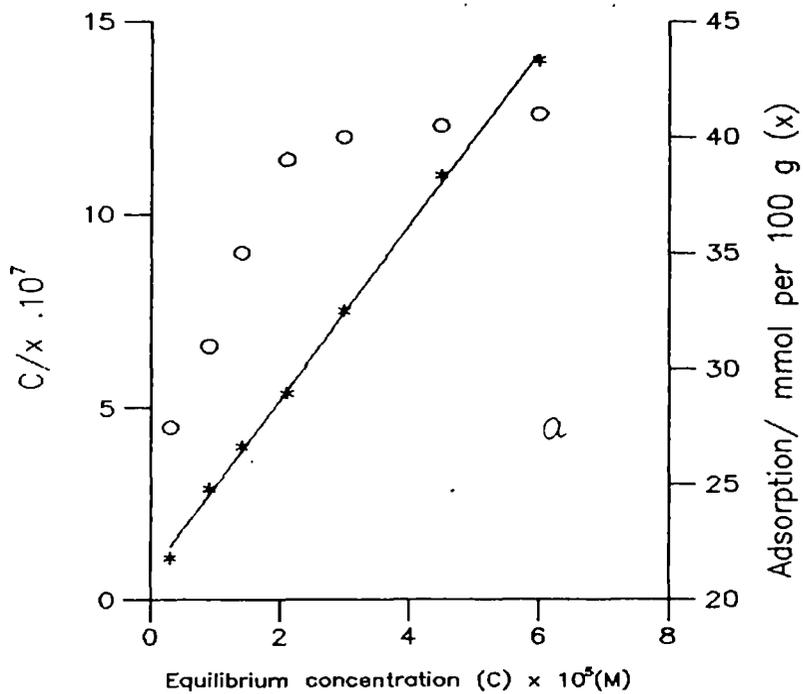


Fig. 98 : Adsorption isotherm and Langmuir plot of (a) Thionine and (b) Azure C in the presence of ZSM-5.

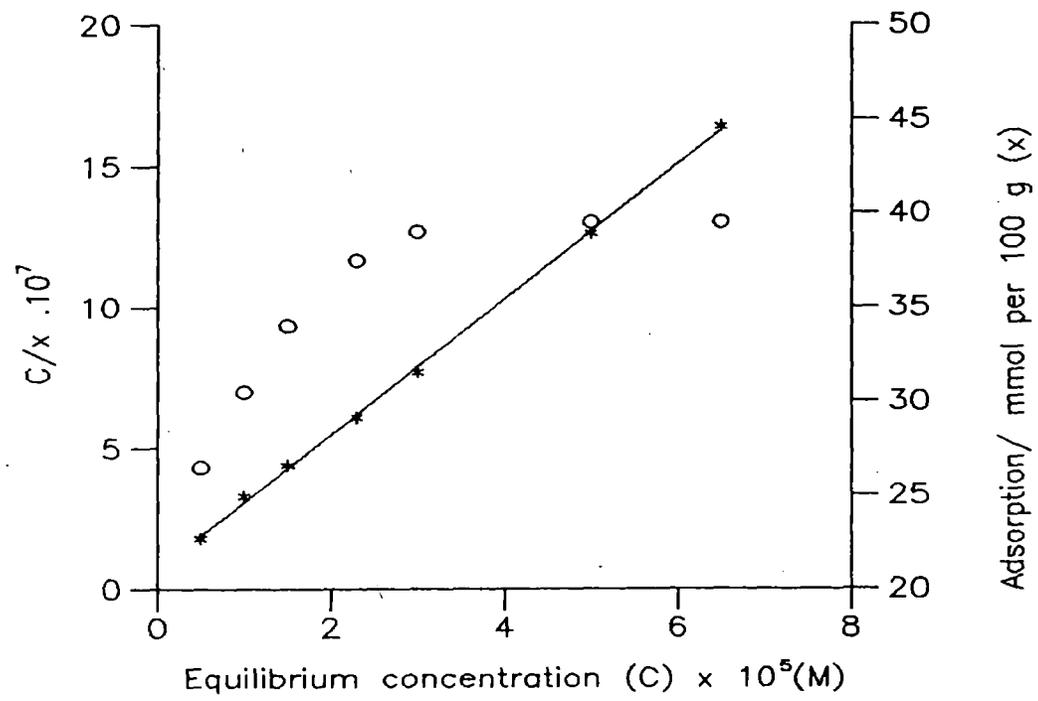


Fig. 99 : Adsorption isotherm and Langmuir plot of Azure A in the presence of ZSM - 5.

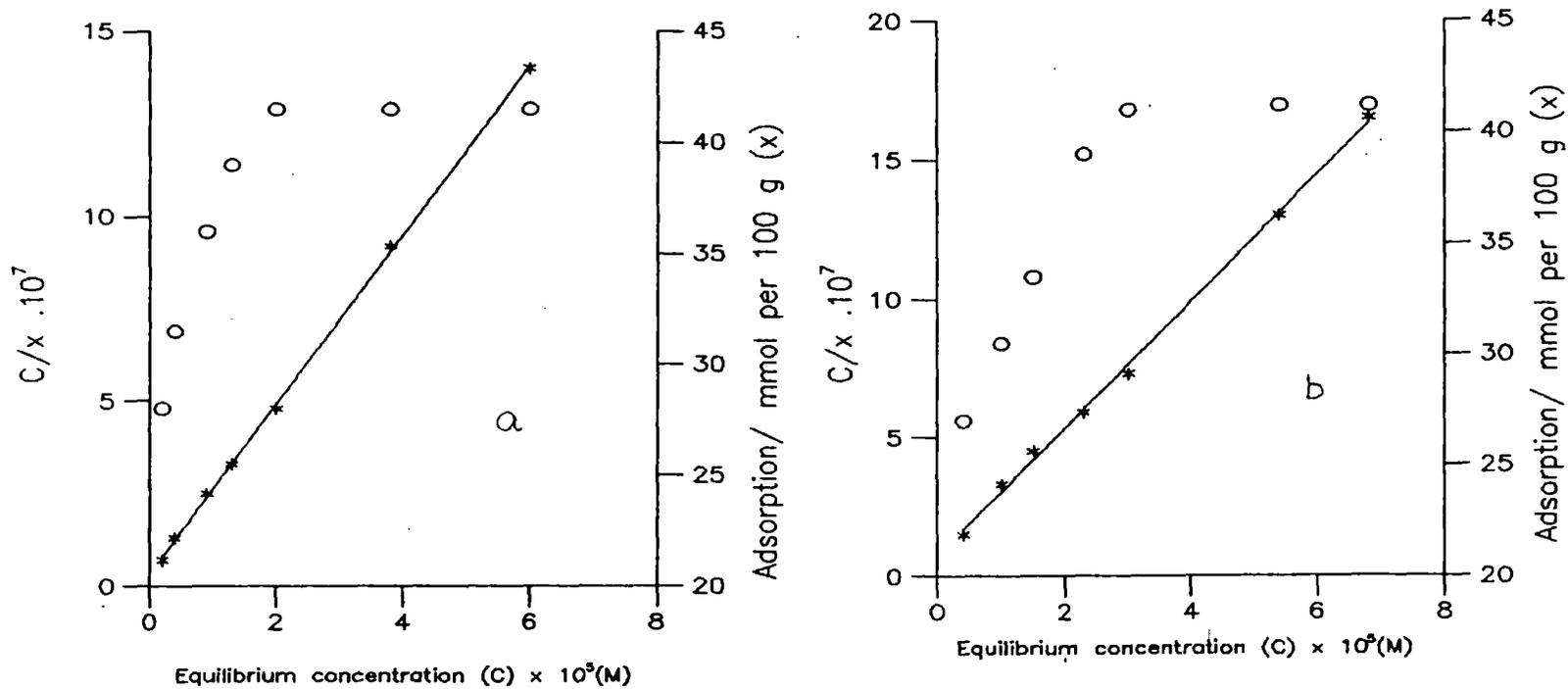


Fig.100 : Adsorption isotherm and Langmuir plot of (a) Azure B and (b) Methylene Blue in the presence of ZSM - 5.

There is a marked difference in the maximum amount dye adsorbed by montmorillonite and ZSM-5. In case of montmorillonite the value is high than that of ZSM-5. It is expected as the CEC of montmorillonite (80 mmol/100 g) is much higher than ZSM-5 (47 mmol/100 g) (208). Moreover, some dye molecules may enter into the interlayer space of the montmorillonite when the dye concentration in the suspension is increased. The possibility of entering the dye molecules into the interlayer space is evident from the metachromasy of the dyes in the presence of montmorillonite (see section 5.3.2). But in the case of ZSM-5 the orientation of the dye molecules into the interlayer lattice is not possible as the dimension of the channels are not sufficient to accommodate the dye molecules having approximately a rectangular volume of $17.0 \times 7.6 \times 3.25 \text{ \AA}^3$. The maximum amount of dye molecules adsorbed onto the montmorillonite exceeds the CEC which may be explained by assuming multilayer formation of the adsorbed dye molecules due to dye-dye interaction and sorption of aggregated cations (42). Intercalation of dye molecules may also be taken into account for the sorption beyond CEC. A similar observation was also made by De and coworkers (227) in their work on methylene blue, crystal violet and malachite green. In the case of ZSM-5 the maximum amount of dye molecules adsorbed for the formation of complete monolayer is very close to its CEC (47 mmol/100 g). It indicates that multilayer formation and the sorption of aggregated dye cations is little in the case of

ZSM-5. Moreover, the strength of bonding of the dyes with ZSM-5 is probably weaker than that with montmorillonite. This is consistent with the observed electrochemical behaviour of the modified electrode where the cathodic current output was greater than that of montmorillonite modified electrode (table 21-22). In both the cases of montmorillonite and ZSM-5 the maximum amount of dye molecules adsorbed for the formation of monolayer onto the surfaces do not vary widely from dye to dye (table 24). The slight differences observed may be attributed to the structure, the mode of orientation and the hydrophobicity of the individual dye molecules. It is believed that the adsorption in the case of montmorillonite is mostly due to electrostatic and Vander waals forces up to the cation exchange capacity and due solely to Vander waals forces beyond it.

The values of the equilibrium constant (Langmuir bonding constants) of the dyes are calculated from the linear plots (Figs. 95-100) are given in table 24. It should be pointed out that when adsorption is in excess of CEC due to sorption of aggregated dye species, the original meaning of the calculated values of x_m and the equilibrium constants is somewhat altered. Nevertheless, the latter parameter still gives some idea about the relative bonding strengths of adsorbents sorbed onto a particular substrate. It is seen from the table 24 that the variation of the values of equilibrium constants maintain a similar order in both the cases i.e., the value increases from Th

to AzB and then decreases in MB and the values observed in montmorillonite and ZSM-5 for an individual dye are very close to each other. It is to be mentioned that the dimerization constants of Th, AzC, AzA, AzB and MB in aqueous medium are determined as 1.76×10^3 , 2.35×10^3 , 3.38×10^3 , 6.25×10^3 , and 3.68×10^3 lit mol⁻¹ respectively at 30°C (section 3.3.1). It is thus expected that when the sorption takes place from their solutions, AzB should be sorbed with larger fraction of the aggregates than that of other form of dyes. But the amount of maximum adsorption does not follow the order. It seems apparent that steric hindrance, hydrophobicity and the specific orientation of the dye molecules on the surfaces are operative simultaneously.

5.3.2. Studies on Metachromasy :

The spectrum of the dilute aqueous solutions (without clay) is shown in figs. 101-103. The prominent band at higher wavelength (α band) and the shoulder at lower wavelength (β band) of the dyes are recorded in table 25. In case of AzC and AzA no shoulder appears in the spectrum in this dilution.

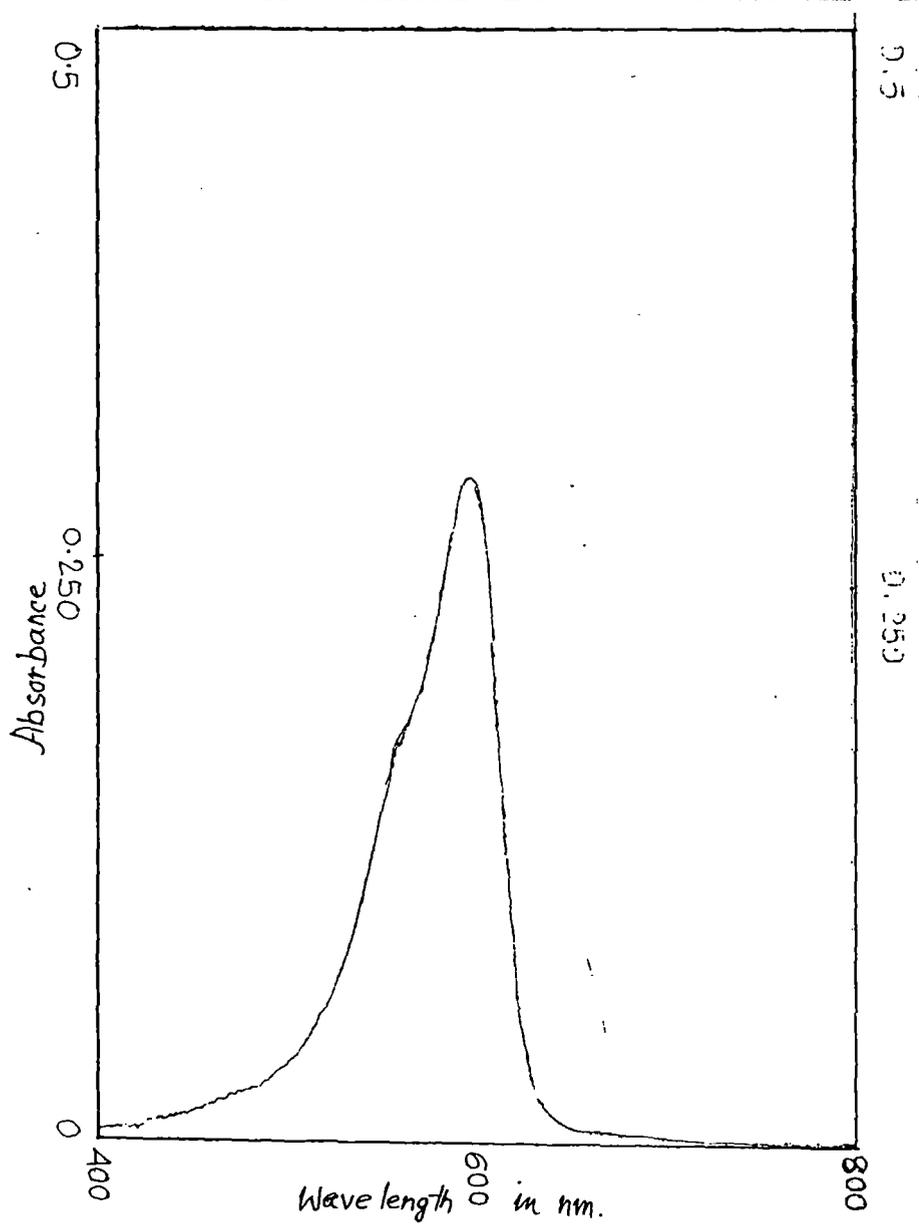


Fig. 101 : Visible absorption spectra of Thionine ($5 \times 10^{-6} \text{ M}$) in the absence of clay (montmorillonite)

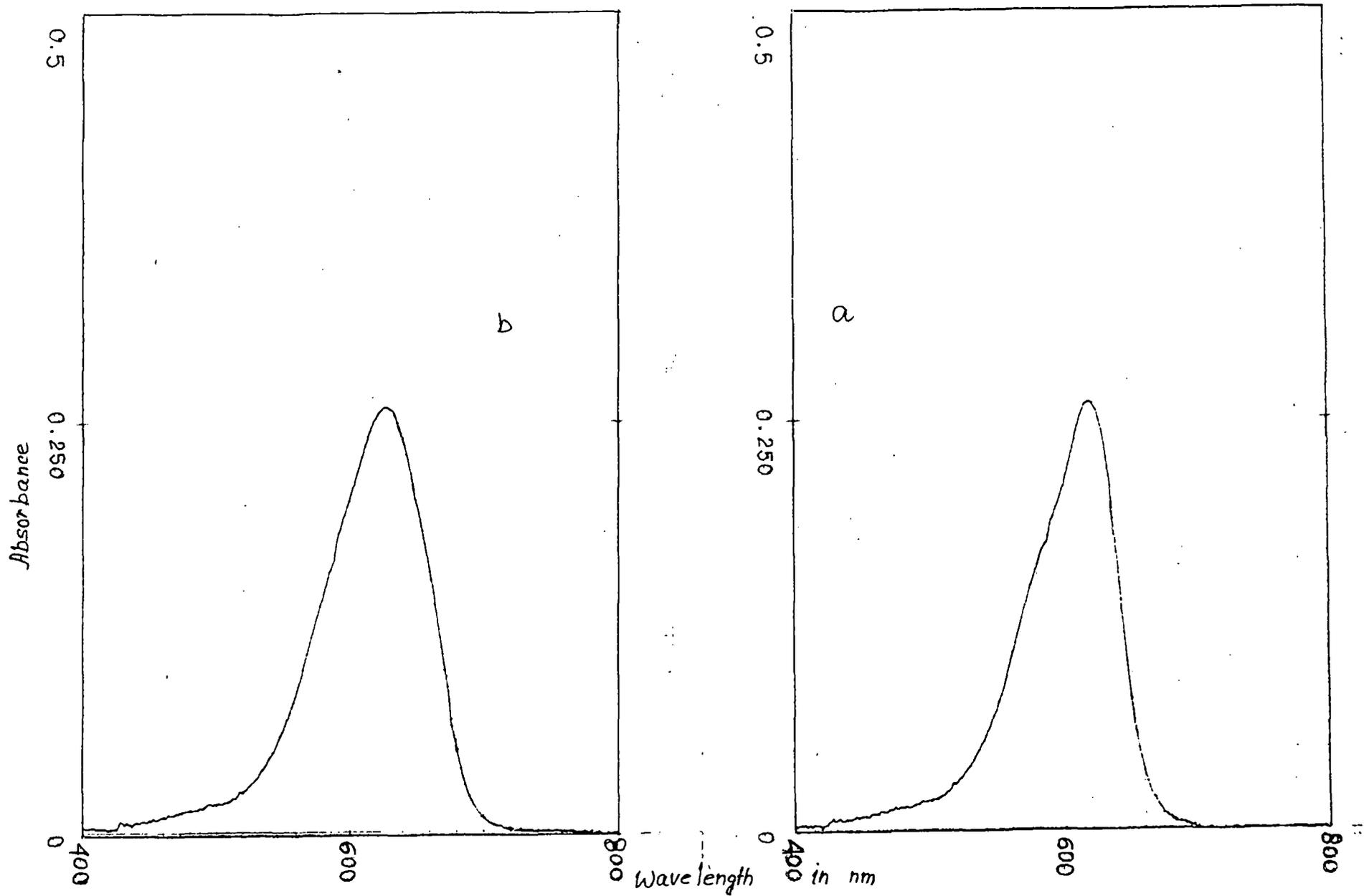


Fig. 102 : Visible adsorption spectra of (a) Azure C ($5 \times 10^{-6} \text{M}$) and (b) Azure A ($5 \times 10^{-6} \text{M}$) in the absence of clay (Montmorillonite).

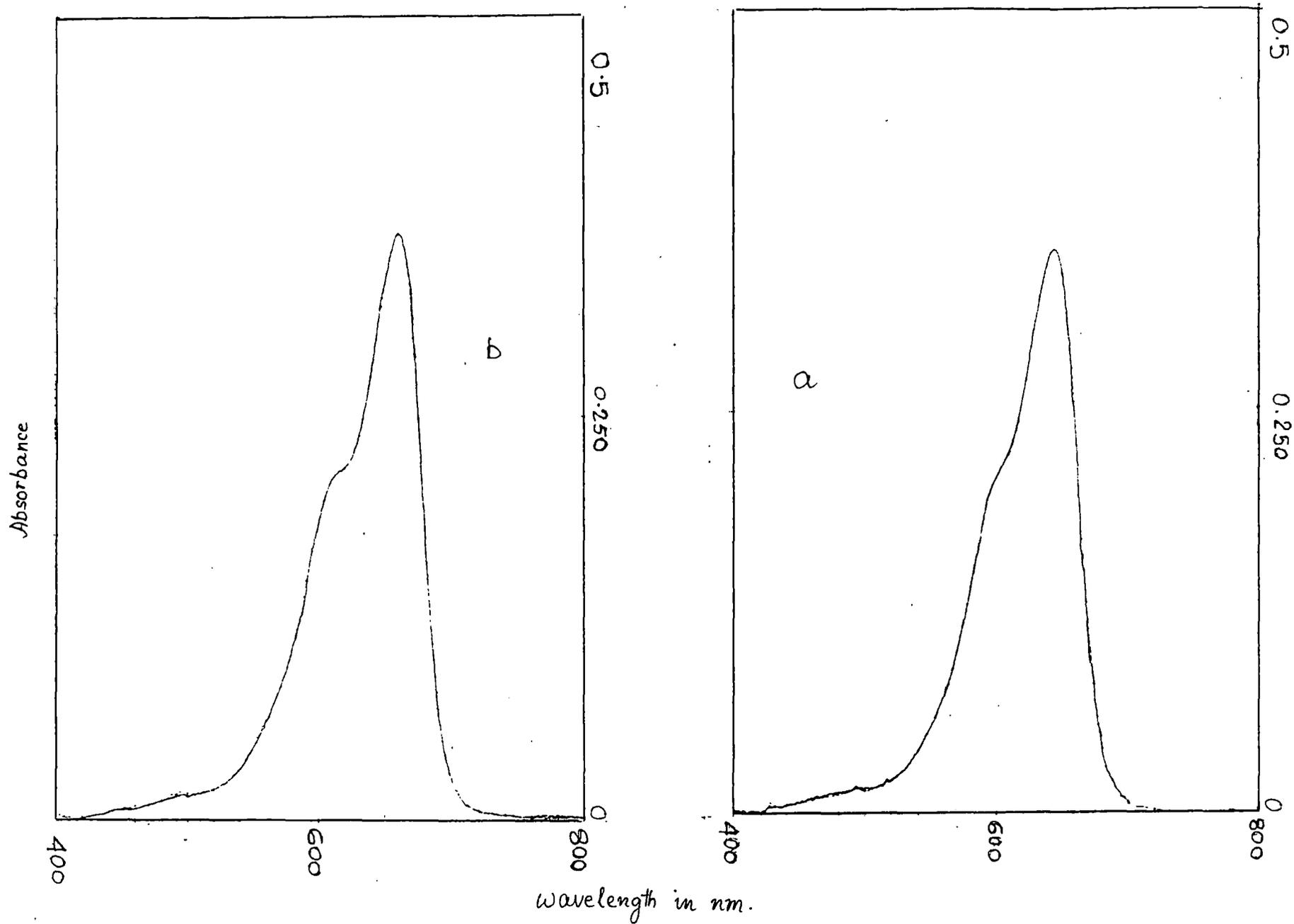


Fig. 103 : Visible Adsorption spectra of (a) Azure B ($5 \times 10^{-6} \text{M}$) and (b) Methylene Blue ($5 \times 10^{-6} \text{M}$) in the absence of clay (Montmorillonite).

Table-25

Dye	λ_{\max} in nm.	
	(α)	(β)
Th	596	564(s)
AzC	620	—
AzA	630	—
AzB	645	598(s)
MB	661	612(s)

(s) = Shoulder

The spectra of clay-dye suspensions show that the adsorption of the dye by montmorillonite results in metachromasy i.e., a gradual replacement of the principal α band by β band with a shorter wave length. In an aqueous dye solution the shift of the absorption peak in the visible region to shorter wave length occurs as the dye concentration increases and has been ascribed to the formation of dimers and higher aggregates. The α band is attributed to monomeric forms of the dye while the β band is attributed to dimeric forms. It is observed that when the concentration of the clay is very small (or a high formal degree of saturation) the spectrum is very similar to that of the corresponding aqueous solution of all the dyes. It is due to the fact that the adsorbed monomeric cations are in the environments in which the polarity is similar to that of the bulk solution. This environment is probably at the water clay interface, outside the interlayer space. This kind of adsorption or interaction

has been labelled as 'type A' (fig. 104, ref.230). As the concentration of the suspended clay increases (or decreasing formal degree of saturation) β band becomes more prominent. In the case of AzC at 12.0 mmol dye per 100 g clay, the α band becomes practically undetectable. With the larger concentration of clay the band α is shifted bathochromically (to longer wave length) followed by the hypsochromic shift (to shorter wave length) of the β bands. A bathochromic shift of α band due to adsorption by montmorillonite was observed previously by many workers (228,229). The shifting of the band maxima of the five dyes as a function of formal degree of saturation are shown in figs. 105-109. The shiftings from the lowest to the highest clay content of the suspensions are summerized in table 26.

Table-26

Dye	Bathochromic (λ in nm.)	Hypsochromic (λ in nm.)
Th	596-630	564-530
AzC	620- *	572-540
AzA	630-678	576-550
AzB	645-664	598-560
MB	661-675	612-568

* α band not detectable.

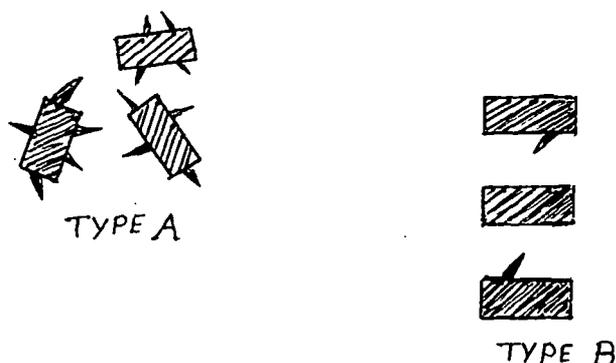


Fig. 104 : Schematic presentation of Adsorption.

The bathochromic shift is often due to an increase in environmental acidity. The interlayer water is also reported to be much more acidic than bulk water (231), and thus 'type B' (fig. 104, ref. 230) adsorption can be attributed 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 (229-232) being the principal binding force. An interlayer space is found between parallel layers which form a tactoid. The formation of tactoid increases with increase in clay concentration in the suspension and the type B adsorption also increases

It is assumed that metachromasy in montmorillonite is the consequence of π interaction between the oxygen plane of the aluminosilicate layers and the aromatic dye, then the hypsochromic shift is an indication of stronger π interactions. Such strengthening trend is expected in the system owing to the increase in hydrophobic character of the interlayer space. This occurs because of the exchange of the inorganic hydrophilic cation with the organic cationic dye (213).

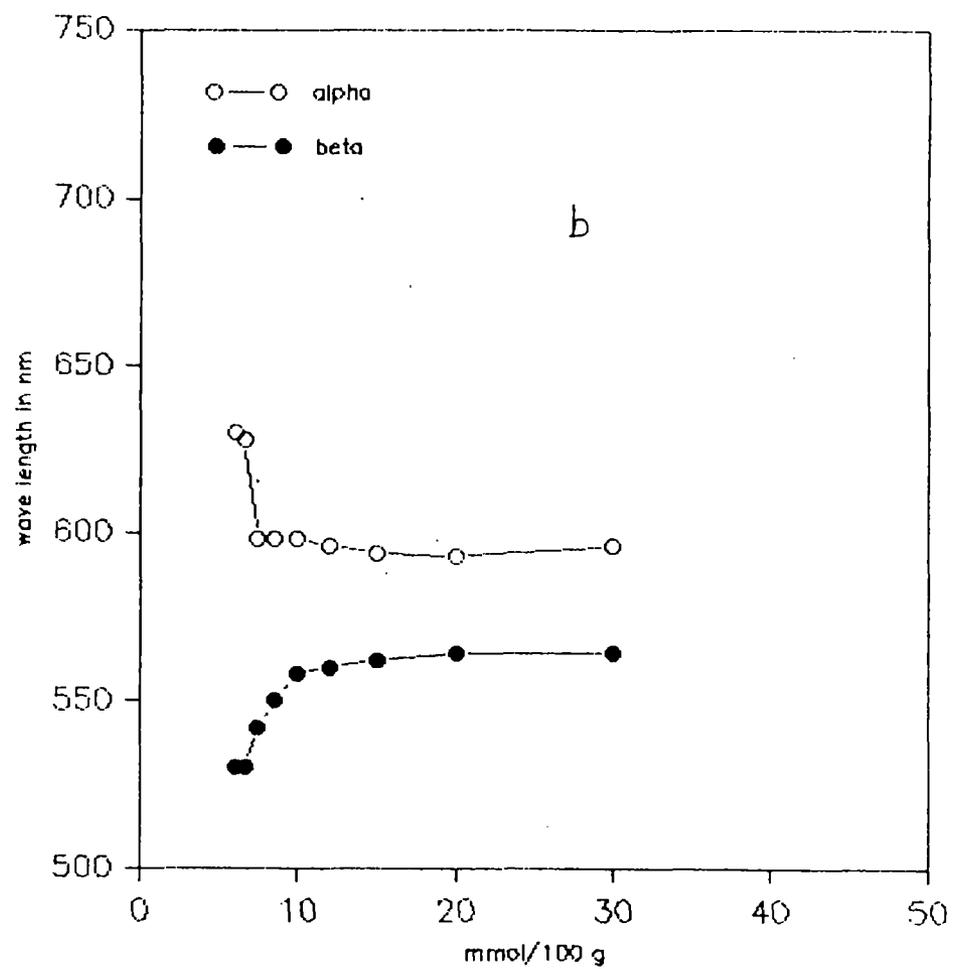
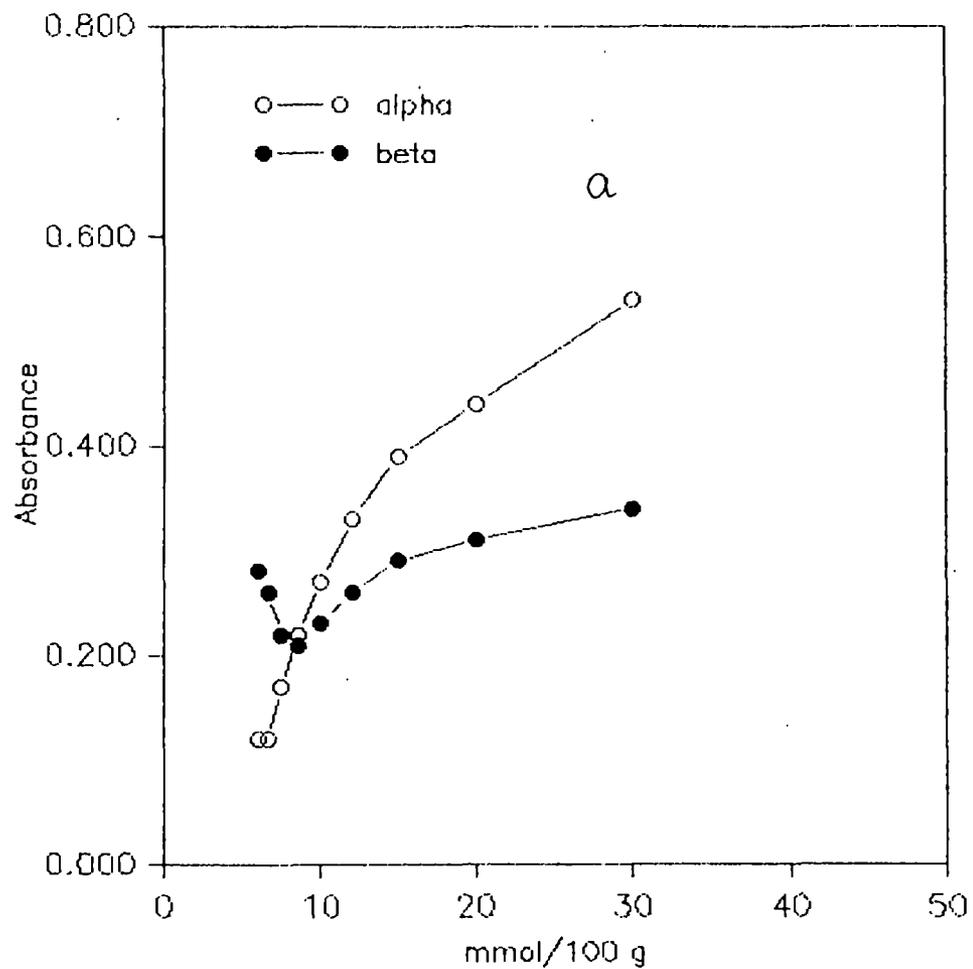


Fig. 105 : (a) Variation of absorbance and (b) shifting of band maxima as a function of Formal degree of saturation (mmol/100g) for Thionine in the presence of clay (Montmorillonite).

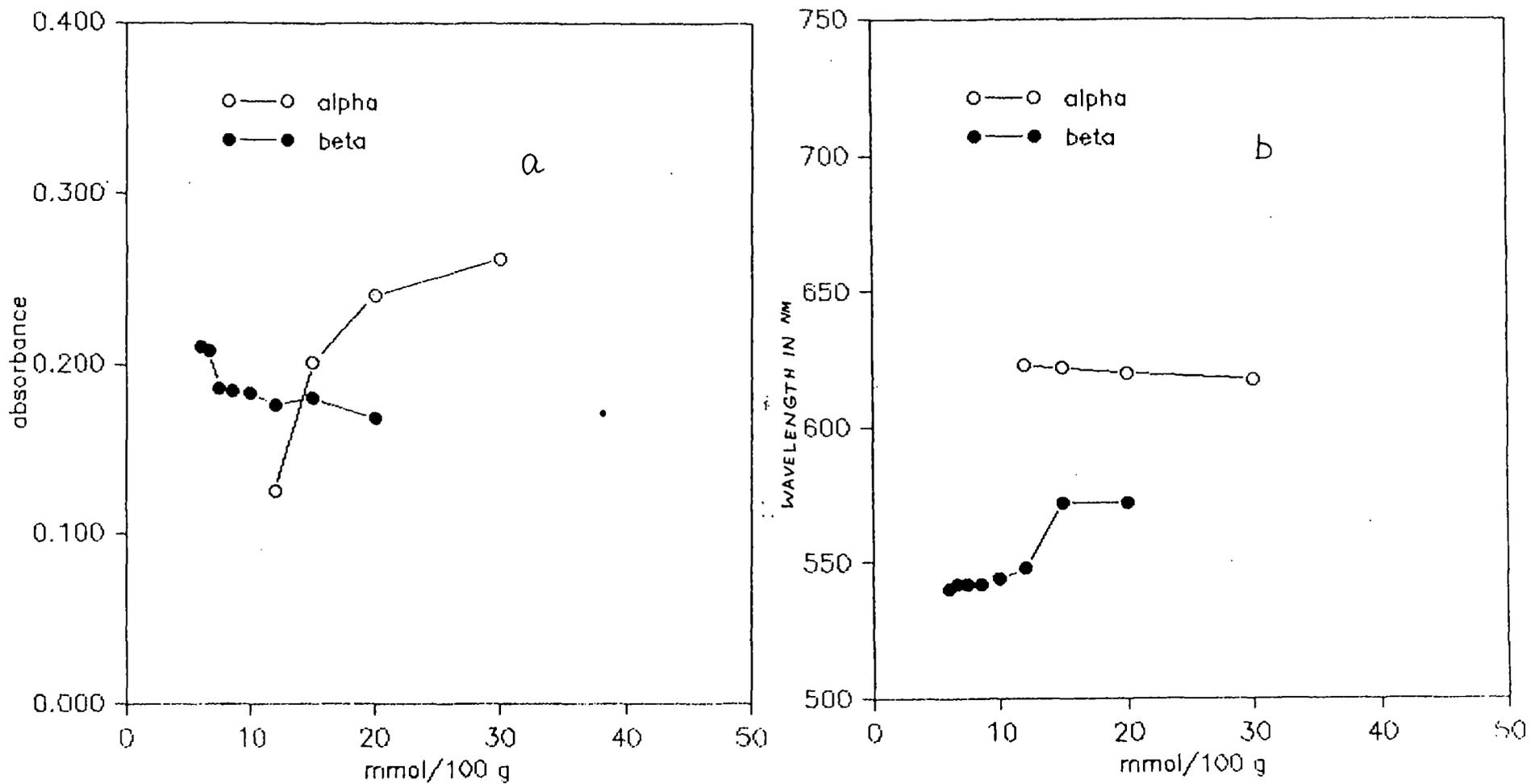


Fig. 106 : (a) Variation of absorbance and (b) shifting of band maxima as a function of Formal degree of saturation (mmol/100g) for Azure C in the presence of clay (Montmorillonite).

HA
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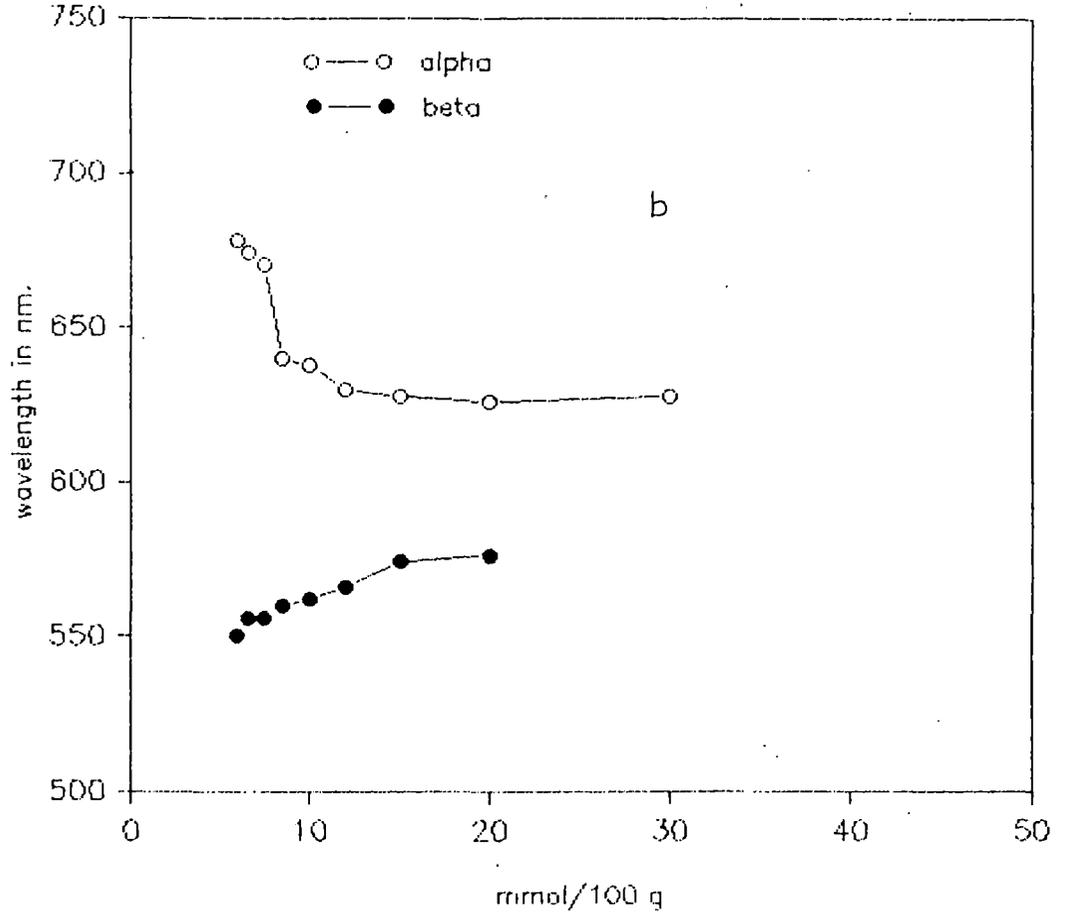
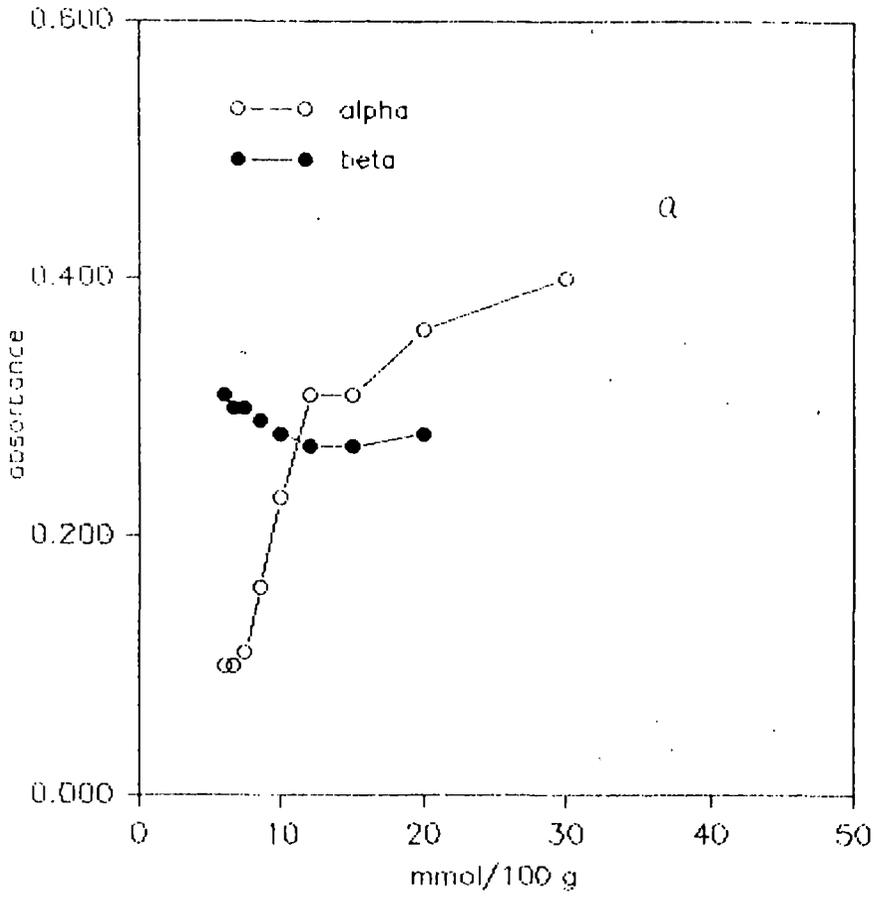


Fig. 107 : (a) Variation of absorbance and (b) shifting of band maxima as a function of Formal degree of saturation (mmol/100g) for Azure A in the presence of clay (Montmorillonite).

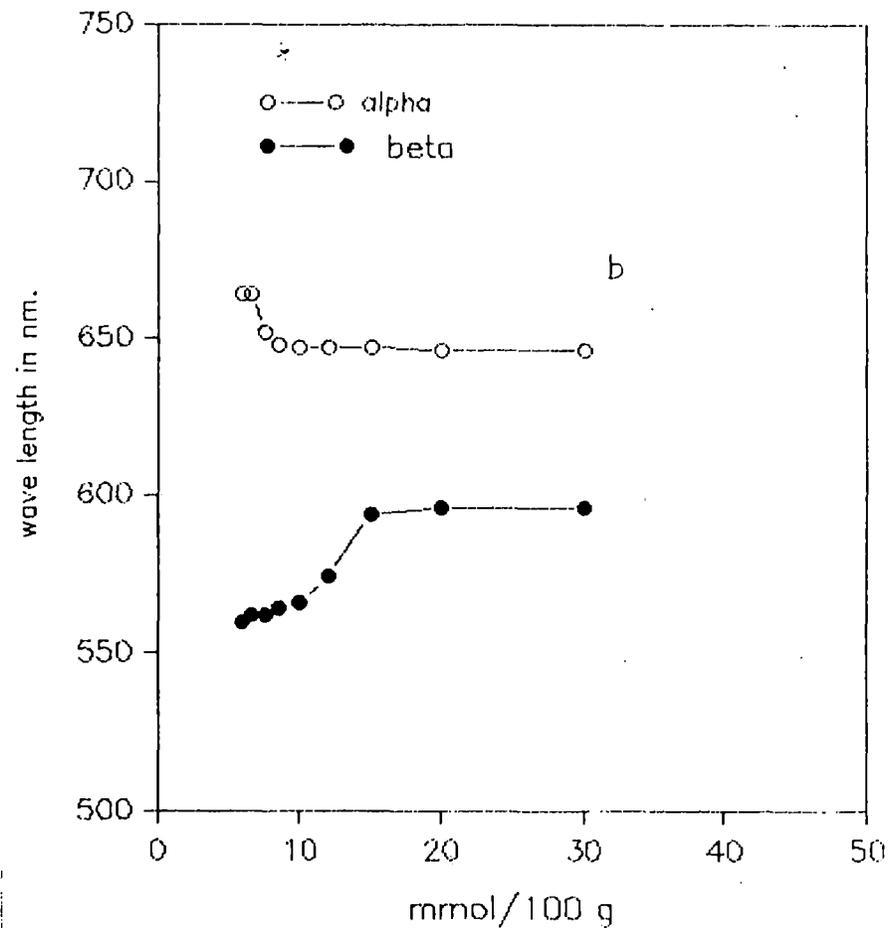
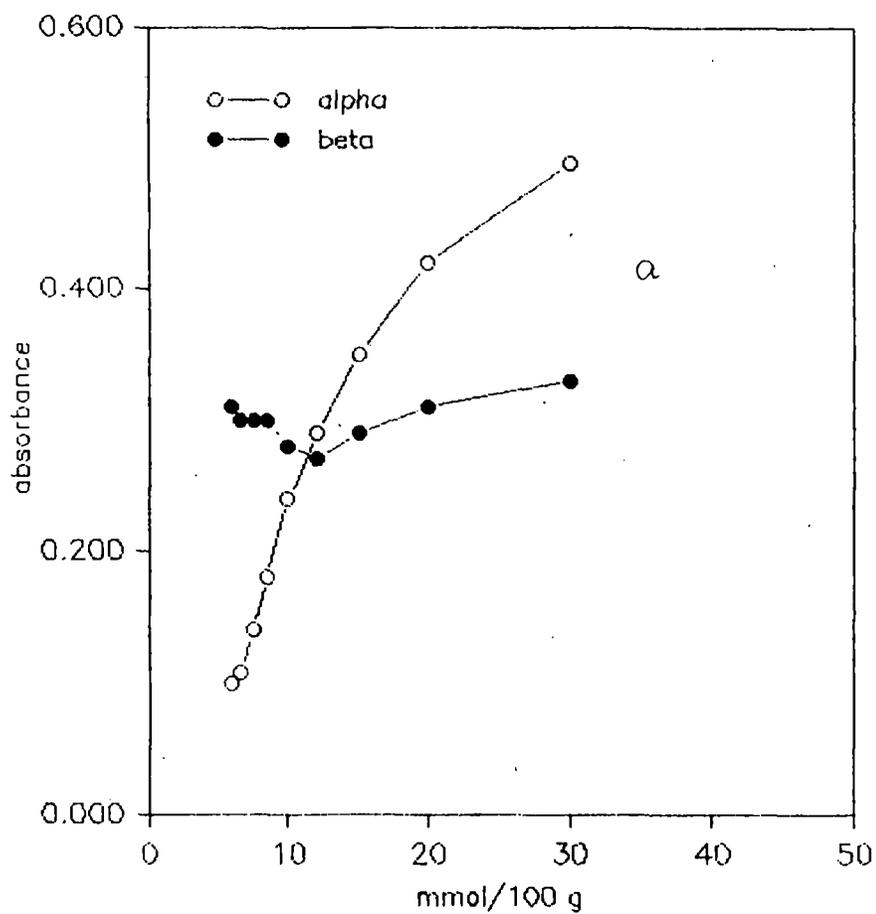


Fig. 108 : (a) Variation of absorbance and (b) shifting of band maxima as a function of Formal degree of saturation (mmol/100g) for Azure B in the presence of clay (Montmorillonite).

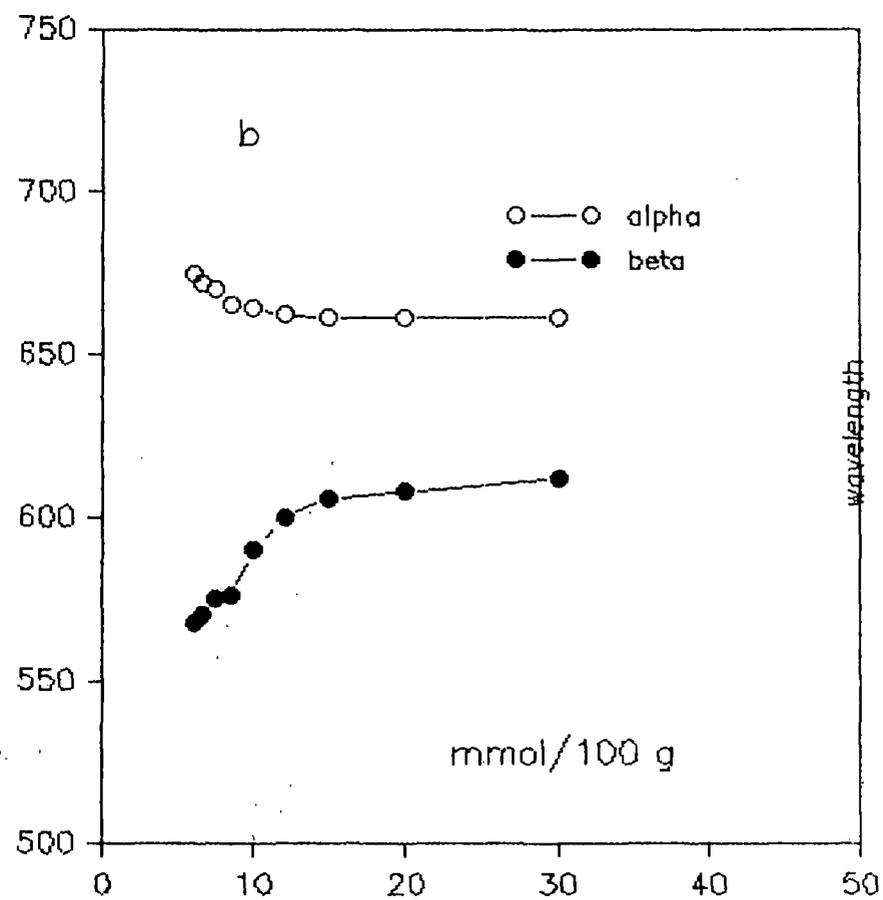
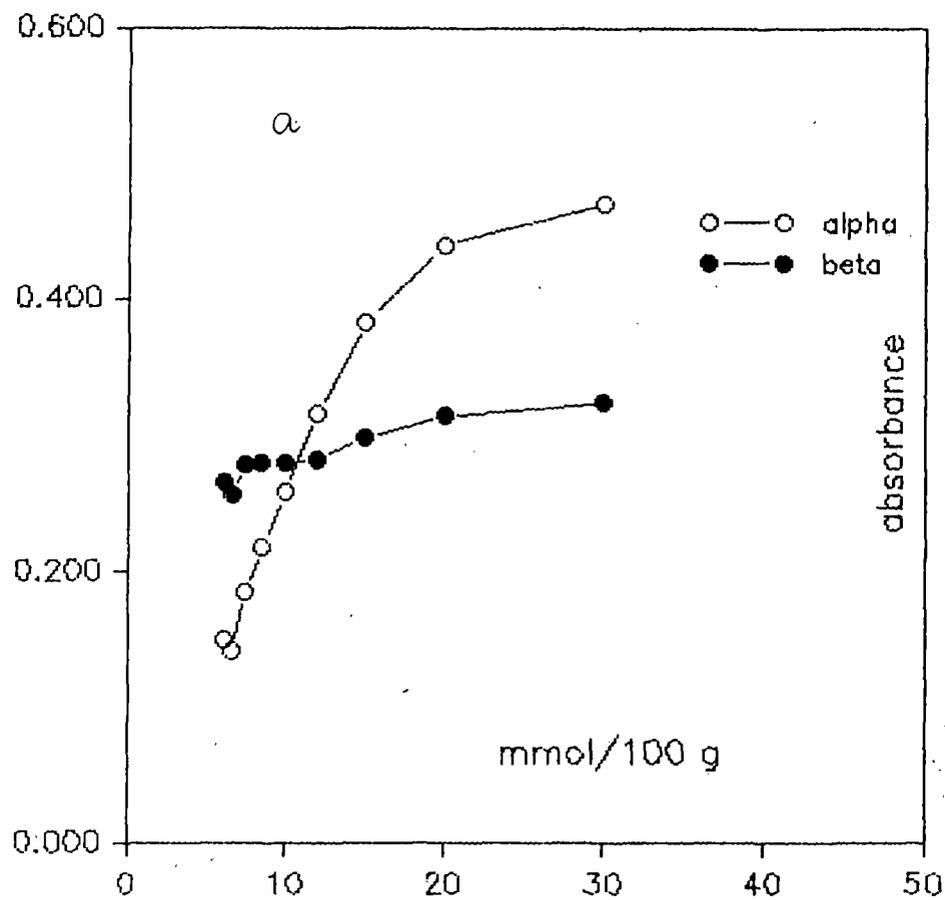


Fig. 109 : (a) Variation of absorbance and (b) shifting of band maxima as a function of Formal degree of saturation (mmol/100g) for Methylene Blue in the presence of clay (Montmorillonite).

Since the dye concentration was fixed in all the clay-dye suspensions in the present study, it was expected that the absorbance of band β would increase as α has decreased and *vice versa* (221). In the present study it is observed that the adsorption of the dye by montmorillonite resulted in considerable decrease in the intensities of α band in all the cases but the change in the intensity of the β band does not follow the order as expected. The changes in absorbance of the bands as a function of the formal degree of clay saturation are shown in Figs. 105-109. It is reported that the flocculation of montmorillonite affects the absorbance of bands α and β (230). Flocculation results in a decrease of absorbance, whereas with peptization the reverse process occurs. The absorbance intensity of the β band of MB follows the order of change as that of α band i.e., decreases with increase in clay concentration in the suspension. In the case of AzB, AzA, AzC and Th the absorbance intensity of β band becomes minimum around 10 mmol dye per 100 g clay and the intensity increases further as the formal degree of saturation decreases. From the observation it may be inferred that the differences in the structures and hydrophobicities of the dye molecules influence the processes of flocculation and peptization of montmorillonite.

The Metachromatic behaviour of the thiazine dyes in the presence of ZSM-5 could not be studied precisely because of the excessive scattering of light by the zeolite particles.