CHAPTER - VIII

Metachromasy of the thiazine dyes in clay minerals.

Various conflicting views exist on the causes of metachromasy when cationic dyes are sorbed onto clay minerals. Schubert and Levine (1), Bergmann and O'Konski (2), Yamagashi and Soma (3) view metachromasy as a result of dye-dye interactions between benzene ring π electrons. Yariv and Lurie (4), and Cohen and Yariv (5) regard it as the result of π interactions between the oxygen of the aluminosilicate and the aromatic ring.

The present study has been carried out to throw further light in this field by investigating the spectral behaviour of TMPT, TMBT, DEMPT and DEMBT when sorbed by montmorillonite, vermiculite and Laponite.

Electronic spectra of TMPT, TMBT, DEMPT and DEMBT

Figs. 4, 5, 6 and 7 show the electronic spectra of the above dyes in the visible regions at various concentrations of the dyes in aqueous medium. In alcoholic solutions these dyes show peaks 640 nm for tirmethyl propyl thionine, 640 nm for trimethyl butyl thionine, 646 nm for Diethyl propyl thionine and 642 nm for Diethyl butyl thionine, which are shifted to 650 nm, 645 nm, 657 nm and 653 nm, respectively in dilute aqueous solution due to solvent effect (4). These maxima are due to π-π^* transition and is referred to as α band (6). Shoulders are observed for either of the dyes at the following wavelengths:

Trimethyl propyl thionine 609 nm, trimethyl butyl thionine 597 nm, diethyl methyl propyl thionine 595 nm, and diethyl methyl butyl thionine 590 nm. These are referred to as β -band. With the increase in the concentration of the dyes, the α-band intensity is seen to decrease with corresponding increase in the β -band intensity. According to Michaelis (6) the α-band is characteristic of the monomeric cation and corresponds to an electric oscillation along the X-axis of the molecule (the long axis). The β-band is characteristic of the dimer and corresponds to an oscillator in the y-direction (shorter axis in the plane of the molecule). Bergmann and O'Konski (2) believe that the β -band is a transition moment which lies also along the long axis of the molecule but is perturbed due to an interaction between the transition moments of the monomer units.

On further increasing the dye concentrations, the β -band gives place to a band towards still shorter wavelength. This band is rather diffuse and is referred to as γ -band and is characteristic of polymeric cation.

Metachromasy due to sorption of TMBT, TMPT, DEMPT and DEMBT by Montmorillonite

Sorption of TMPT on Na-montmorillonite: The visible spectra of the clay-dye suspensions prepared and determined by the method described (in page 46) are given in Fig. 107. The spectra were recorded at 3 meq, 6.5 meq, 13 meq, 26 meq, 39 meq of trimethyl propyl thionine adsorbed per 100 gm of Na-montmorillonite. The UV spectrum of trimethyl propyl thionine in aqueous medium with peaks at 286 nm and 245 nm does not show any appreciable change during this study. Very great changes were, however, noticed with the $\pi-\pi^*$ transition band of trimethyl propyl thionine in the visible spectrum when sorbed onto Na-montmorillonite samples, similar to those observed for methylene blue and acridine orange by earlier workers (2-5). The λ_{max} values for each curve are given in Table 26. The intensity of β band is seen to increase as more amount of trimethyl propyl thionine is sorbed by the clay and the large amount of dye sorbed to give β -band indicates that metachromasy may have its origin in the interlayer space of the clay structure (4).

X-ray diffraction measurements: d_{001} basal spacing of oriented powdered samples of Na-montmorillonite with a 25%, 35%, 50% and 100% of trimethyl propyl thionine adsorbed were determined with samples vacuum dried at 120°C for 24 hours shown in Table - 31.

With increasing amounts of trimethyl propyl thionine sorbed the C-spacings gradually increase suggesting interlayer penetration of the dye. With 50% of trimethyl propyl thionine adsorbed onto Na-montmorillonite, the effective molecular thickness is 13.8755-9.4 Å (the effective thickness of the silicate sheet) = 4.4755 Å, which agrees well with the small dimension of the dye molecule (7, 8) in flatly oriented monomeric form. According to Bergmann and O'Konski (2) in the case of methylene blue, the dimer is held together by London dispersion forces and hydrophobic bonding which overcome the electrostatic repulsion between two dye cations. The dispersion forces should be greatest when the monomer units are in a sandwich with principal molecular axes almost parallel. The coulombic repulsion will be minimised when the charged amino groups lie along opposite edges of the sandwich. The structure originally proposed by Förster (9) has a z-axis with unit lengths of at least 6^{O}A. For montmorillonite, it means that when a dimer of methylene blue is present in the interlayer space, a c-spacing of about 15.5A^{O} is expected. A similar conclusion has been arrived at by Hang and Brindley (8) who noted that a C-spacing of about 15.6^{O}A is required in the interlayer space of montmorillonite to accommodate a double layer of flat lying methylene blue molecules. However, these values would be somewhat higher for trimethyl propyl thionine and for diethyl methyl butyl thionine because they have three methyl groups and one bigger propyl or butyl group instead of four methyl groups of methylene blue structure. According to Yariv and Laurie (4) and Cohen & Yariv (5) in the cases of methylene blue, acridine orange sorption on montmorillonite, a monolayer of the dyes in the interlayer space with the aromatic rings parallel to the aluminosilicate layer (7) is expected upto a C-spacing values of 13.0A^{O} approximately. So it is clear from the above discussion and X-ray diffraction data that only a monomolecular layer is present in the interlayer space of the montmorillonite upto about 50% sorption of Trimethyl propyl thionine, the aromatic rings lying parallel to the aluminosilicate layer (7). Thus, metachromasy of TMPT upto 50% adsorption cannot be attributed to its dimerisation or polymerisation as suggested by Bergmann and O'Konski (2) and Yamagashi and Soma (3) but may have been caused by π interactions between the oxygen plane of the aluminosilicate and the aromatic dye as suggested earlier by Yariv and Lurie (4) and Cohen and Yariv (5). With the larger amount of TMPT sorption, however, the C-spacings of thermally vacuum dried samples are greater than 13.0A° indicating the presence of a bi layer or tilting of the cationic dye molecules relative to the alumino-silicate layer (7).

Sorption of Trimethyl propyl thionine on H-montmorillonite:

Fig. 111 depicts the spectra of different amounts of trimethyl propyl thionine adsorbed onto H-montmorillonite. Unlike in Na-montmorillonite system, the β -band is prominent with the α band almost completely suppressed even at as a low an adsorption as 3 meq/100 g of the H-clay. The pH of the H-clay is amount 3.5 to 4 and it is believed that the positively charged electrical double layer on the edges of the clay at such low pH remains in effective for exchange of the cationic dye ions due to repulsion between similar charges (10). The substrates, thus, must enter the interlayer of the mineral without prior covering of the edge exchange sites in H-montmorillonite. Since dye aggregation at such low value of adsorption (3 meq/100 g) is improbable, the metachromasy is perhaps initiated in the interlamellar space through π interaction between the dye molecule and the silicate layers.

In Na-montmorillonite (pH = 7), on the other hand, both the electrical double layers at the edges and in the interlamellar space are negatively charged and the former constitutes about 20% of the total c.e.c. of the mineral (11). When small amount of the dye is added to Na-clay, it is first adsorbed onto the edges of the clay platelets (4). At this stage the adsorption band is similar to that of the dilute aqueous solution (α-band), indicating that the hydration state of the sorbed organic molecule and of the dilute aqueous solution are similar. But as more and more dye is adsorbed by the Na-clay the β-band gradually attains prominence suggesting that the metachromatic band (β-band) is attributable to the dye molecules which penetrate into interlayer space.

Thus from the above studies of visible spectra and X-ray diffraction data on sorption of trimethyl propyl thionine by montmorillonite it may be inferred that the metachromasy is initiated when adsorbed cationic dye is located in the interlayer space as a monolayer with the aromatic rings parallel to the aluminosilicate layer causing π interactions between the oxygen plane of the clay and the aromatic dye.

Sorption of trimethyl butyl thionine on Na-montmorillonite

Fig. 108 depicts the changes noticed in the visible spectra between 500 nm and 700 nm for Na-montmorillonite-TMBT complexes formed when TMBT and Na-montmorillonite (0.01%) are mixed in proportions corresponding to 6.5 meq, 13 meq, 24 meq, 32 meq and

64 meq of THBT per 100 gm of Na-montmorillonite. The λ_{max} values are summarized in Table 26. The band shift remains constant beyond an adsorption value of 26 meq/100 gm. The gradual decrease of the α-band intensity as the amount of THBT sorption is increased, is noticeable here as in the case of Trimethyl propyl thionine mentioned earlier (No J-band).

X-ray diffraction measurement: The values of basal spacings of Na-montmorillonite-THBT mixed in varying proportions and dried under two different conditions, are shown in Table 31. The d_{001} values of 25%, 35%, 50% and 100% THBT exchanged Na-montmorillonite after heating to 120°C are 15.505, 15.505, 15.642 and 15.781. As in the cases of Trimethyl propyl thionine (TMPT), here also a single layer is formed, at least upto 25% sorption of the dye, in the interlayer space with the aromatic rings parallel to the aluminosilicate layer and so the metachromasy is caused by π interactions between the oxygen plane of the aluminosilicate and the aromatic dye rings.

Sorption of Trimethyl butyl thionine on H-montmorillonite:

At low adsorption of THBT viz. 8 meq/100 gm by H-montmorillonite a spectrum is obtained in which the α-band is only a shoulder whereas the β band stands out in sharp proportion (Fig. 112 and table 29). A similar behaviour was noted earlier with TMPT and H-montmorillonite systems (page 111). The substrates, without prior coverage of the edges directly enter into the interlayer space in H-montmorillonite (10). In the lower exchange levels a monolayer of the dyes is situated in the inter-space while at higher exchange levels a bilayer or tilting of the cationic dye relative to the aluminosilicate can be furnished. In the former case metachromasy cannot be attributed to polymerisation of TMBT in the clay interlayer but is due to π interactions between the oxygen plane of the clay and the aromatic dye.

Sorption of Diethyl methyl propyl thionine and Diethyl methyl butyl thionine on Na-montmorillonite and H-montmorillonite:

The spectral shifts due to adsorption of varying amounts of DEMPT and DEMBT by Na-montmorillonite and H-montmorillonite are shown in Figs. 109, 110, 113 and 114. The λ_{max} values are recorded in Table 26 and 29. Unlike in Na-montmorillonite and TMPT and TMBT system metachromasy is apparent here even at low sorption level of Dye and the intensity of the β peak is also greater.

Metachromasy due to Sorption of TMPT, TMBT, DEMPT and DEMBT by Vermiculite

The experimental details of the preparation of samples for spectral recordings are already described in Chapter - III page 46.

Sorption of Trimethyl propyl Thionine on Na-vermiculite and H-vermiculite:

The spectral shifts due to adsorption of varying amounts of TMPT by Na-vermiculite and H-vermiculite are shown in Figs. 115 and 119. The λ_{max} values are recorded in Table 27 and 30. Unlike in Na-montmorillonite - TMPT, TMBT, DEMPT and DEMBT systems, metachromasy is apparent here even at low sorption level of TMPT by Na-vermiculite and the intensity of the β-peak is also greater. This may be attributed to the higher charge density of Na-vermiculite, because of which, more intimate π interaction between the oxygen plane of the clay and the aromatic rings of the dye takes place, resulting in the higher intensity of the β-peak even at an early stage of adsorption. Besides, it also appears that the number of negative edge exchange sites in Na-vermiculite is quite small as compared to Na-montmorillonite and thus the interlayer penetration of the dye seems to take place from the very commencement of the sorption process. As a result, metachromasy is exhibited even at very low percentage of the dye sorption in Na-vermiculite. Similar observation has also been made in the sorption of TMBT by H-vermiculite and the same kind of explanation may be offered here also.

Sorption of TMBT on Na-vermiculite and H-vermiculite.

The α and β-band intensities are almost equal even at a low percentage of sorption i.e., 6.5 meq/100 g (Fig. 116) of TMBT by Na-vermiculite. The β band gradually increases in intensity and α band dwindles as the amount of TMBT adsorbed on Na-vermiculite increases. The λ_{max} values of α band and β-band are summarised in Table 27 and 30.

As in H-montmorillonite, here also a dominant β band is noticed even at a very low adsorption value of the dye by H-vermiculite (Fig. 120), suggesting interlayer penetration of the dye from the initial stages of sorption owing to the presence of the electrical double layer at the edges of the crystal.

Unlike in TMPT adsorption by Na-vermiculite, TMBT molecules perhaps do not get a smooth entry into the interlayer space of the mineral because of its much bigger size due to the presence of large side chain (This is also reflected in the lower maximum capacity of this dye on Na-vermiculite, which is compared to the c.e.c. of the mineral, 110 meq/100 gm). The size factor perhaps encourages the dye molecules to be adsorbed onto the exterior edge exchange sites of the mineral first, which explains the difference observed in the intensities of β-band of Na-vermiculite TMPT and Na-vermiculite - TMBT. Once penetration of the interlayer takes place, the effect of high charge density of Na-vermiculite in causing a more intimate interaction between the aromatic molecule and the oxygen plane of the silicate layer becomes operative and is reflected in the higher intensity of β-peak of TMBT in Na-vermiculite complex than in Na-montmorillonite complex.

Sorption of TMBT, DEMPT and DEMBT on vermiculite:

Figs. 116, 117, 118 and 120, 121, 122 represent the spectral changes for varying TMBT, DEMPT and DEMBT saturations on Na-vermiculite and H-vermiculite respectively. As in TMPT and Na-vermiculite interactions, here also metachromasy is apparent even at a low sorption level of the thionine dyes and the intensity of β-peak is greater than that of α-peak in some cases. Similar explanation as in the case of DEMPT - Na-vermiculite complexes may also be offered.

The results of interactions of these dyes with H-vermiculite as depicted in Figs. 120, 121, 122 are very much similar to those observed for H-montmorillonite and may be interpreted in the same manner.

Metachromasy due to sorption of TMPT, TMBT, DEMPT and DEMBT on Na-Laponite:

Experimental details are already discussed in page 47

Sorption of TMPT on Na-Laponite

In contrast to the observations made in montmorillonite and vermiculite systems, the spectra of the dye adsorbed on Na-Laponite suspensions upto about 64 meq/100 gms appear to bear an analogy to those observed for dilute aqueous solutions of the dye (Fig. 123) showing no metachromatic effect. The β-band begins to be visible only on addition of a fairly large amount of dye (90 meq/100 gm and 100 meq/100 gm) to the synthetic hectorite suspension. Vansant and Yariv (22) also did not observe any metachromatic effect when they adsorbed methyl violet onto Na-, K-, or Ca-Laponite. A new band, in the form of shoulder, appears at 606 nm given in Fig. 127.

Sorption of TMBT on Na-Laponite:

Fig. 124 depicts the spectral variations when increasing amounts of TMBT are added to a suspension of Na-Laponite. The shifts in λ_{max} values for α-band and β -band are recorded in Table 28. Metachromasy is observed only after a fairly large amount of the dye has been added (Fig. 128).

Sorption of DEMPT and DEMBT on Na-Laponite.

The changes in the spectra of DEMPT and DEMBT when varying amounts of the dye are adsorbed by a suspension of Na-Laponite, are shown in Fig. 125 and 126. Here also metachromasy is observed when large amounts of the dye (90 meq/100 and 100 meq/100 gm for the dyes) have been adsorbed. Table 28 records the λ_{max} values of the α and β-bands as the amount of the dye sorption is increased.

It is evident from the above observations that Na-Laponite differs widely from Na-montmorillonite and Na-vermiculite in its behaviour towards TMPT, TMBT, DEMPT and DEMBT in respect of metachromasy. Thus these dyes TMPT, TMBT, DEMPT and DEMBT show slight metachromatic behaviour only after sufficient quantity of them has been adsorbed by the mineral and that the α-bands are usually more prominent than the β bands. This failure of the thiazine dyes to exhibit metachromasy at lower adsorption values may, perhaps be attributed to the lower charge density vis-a-vis the higher swelling property of the synthetic hectorite. As a result of high swelling large amount of water will be present in the interlayer space of Na-Laponite which permits the hydration status of the adsorbed dye ions to be similar to that existing in the dilute aqueous solution of the dyes. Aside from this the intercalated dye ions in Na-Laponite cannot approach the oxygen plane of the silicate layer close enough to induce π-electron interaction perhaps because of the low charge density of the synthetic clay. This is also in agreement with the observation that the intensity of the β-peaks of the dye-vermiculite complex is higher than that of the dye-montmorillonite complex for the amount of dye sorption, probably due to the fact that the higher charge density and lower swelling property of the former mineral enhance the π interactions with the oxygen plane of the aluminosilicate layer and the dye, thereby, leading to a greater intensity in the β band. The observation of metachromasy at higher adsorption values of the dyes, however, may be ascribed to the decrease in water content and increased hydrophobic properties of the interlayer space with increasing intercalation of the organic material (23), which results in a situation conducive to π-interaction between the Laponite oxygen sheet and the organic dye ions, required to exhibit metachromasy.

Values of λ_{max} when varying amounts of Dye are sorbed by clay Minerals (Tables 26-31)

Table - 26

(Sorption of Na-montmorillonite)

Name of the dye sorbed	mM sorbed per 100g clay	λ_{max} (in nm)	
		α-band	β-band
TMPT	6.5 meq	661	580
	13 "	655	587
	24 "	660	585
	32 "	652	575
	64 "	645	570
TMBT	6.5 meq	657	565
	13 "	659	572
	24 "	655	574
	32 "	660	572
	64 "	670	570
DEMPT	6.5 meq	657	583
	13 "	655	565
	24 "	653	558
	32 "	655	555
	64 "	650	552
	80 "	652	552
DEMBT	6.5 meq	656	592
	13 "	654	583
	24 "	656	589
	32 "	655	582
	64 "	653	579

Table - 27

(Sorption on Na-vermiculite)

Name of the Dye sorbed	mM sorbed per 100g clay	λ_{max} (nm)	
		α-band	β-band
	6.5 meq	650	580
	13 "	657	575
TMPT	26 "	659	576
	39 "	655	565
	52 "	665	566
	64 "	665	565
	6.5 meq	645	580
	13 "	655	580
TMBT	26 "	655	555
	39 "	675	565
	52 "	675	565
	6.5 meq	652	590
	13 "	654	585
DEMPT	26 "	657	575
	39 "	668	570
	52 "	660	580
	6.5 meq	648	595
	13 "	660	575
DEMBT	26 "	655	582
	39 "	650	576
	52 "	660	580

Table - 28

(Sorption on Na-Laponite)

Name of the Dye sorbed	mM sorbed per 100g clay	λ max (nm)	
		α-band	β-band
TMPT	8 meq	656	605
	16 "	653	605
	32 "	654	605
	64 "	654	606
	90 "	655	575
	100 "	655	575
TMBT	8 meq	655	602
	16 "	648	602
	32 "	649	605
	64 "	649	605
	90 "	650	570
	100 "	650	570
DEMPT	8 meq	658	610
	16 "	658	612
	32 "	660	615
	64 "	660	614
	90 "	660	580
	100 "	660	580
DEMBT	8 meq	655	603
	16 "	655	605
	32 "	655	607
	64 "	655	607
	90 "	660	580
	100 "	660	570

Table - 29

(Sorption of H-Montmorillonite)

Name of the Dye sorbed	mM sorbed per 100g clay	λ max	
		α-band	β-band
TMPT	4 meq	-	576
	8 "	-	576
	16 "	-	583
	32 "	-	570
	64 "	-	578
TMBT	8 meq	-	583
	16 "	-	583
	32 "	-	583
	64 "	-	585
DMPT	8 meq	-	580
	16 "	-	575
	32 "	-	573
	64 "	-	567
DMBT	8 meq	-	590
	16 "	-	588
	32 "	-	584
	64 "	-	580

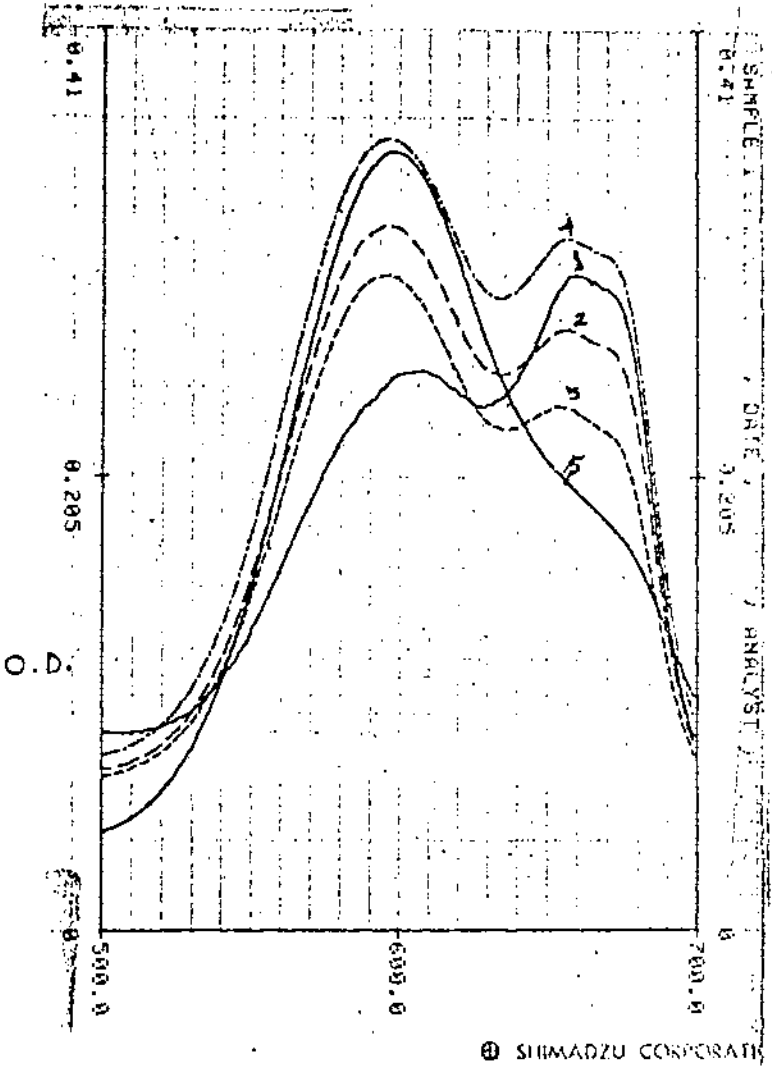
Table - 30
(Sorption on H-Vermiculite)

Name of the Dye sorbed	mM sorbed per 100g clay	λ max (in nm)	
		α-band	β-band
TMPT	8 meq	-	580
	16 "	-	577
	32 "	-	580
	64 "	-	582
TMBT	8 meq	-	555
	16 "	-	555
	32 "	-	555
	64 "	-	556
DEMPT	8 meq	-	595
	16 "	-	595
	32 "	-	601
	64 "	650	605
DEMBT	8 meq	-	575
	16 "	-	570
	32 "	-	575
	64 "	650	570

Table - 31

d_{001} X-ray diffraction values of Na-montmorillonite exchanged with different dyes

Name of the dye	Percentage of the dye adsorbed onto Na-montmorillonite	d_{001}
TMPT	25	12.626
	35	13.505
	50	13.8755
	100	15.37
TMBT	25	15.505
	35	15.505
	50	15.642
	100	15.781
DEMPT	25	13.7035
	35	15.238
	50	15.37
	100	18.034
DEMBT	25	12.7185
	35	12.800
	50	12.999
	100	13.7035



FIG,107 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-MONTMORILLONITE TREATED WITH TMPT. THE SPECTRA 1 ,2 ,3 , 4 AND 5 CORRESPOND TO 6.5 , 13 , 24 , 32 AND 64 meq OF TMPT ADSORBED PER 100g OF Na-MONTMORILLONITE.

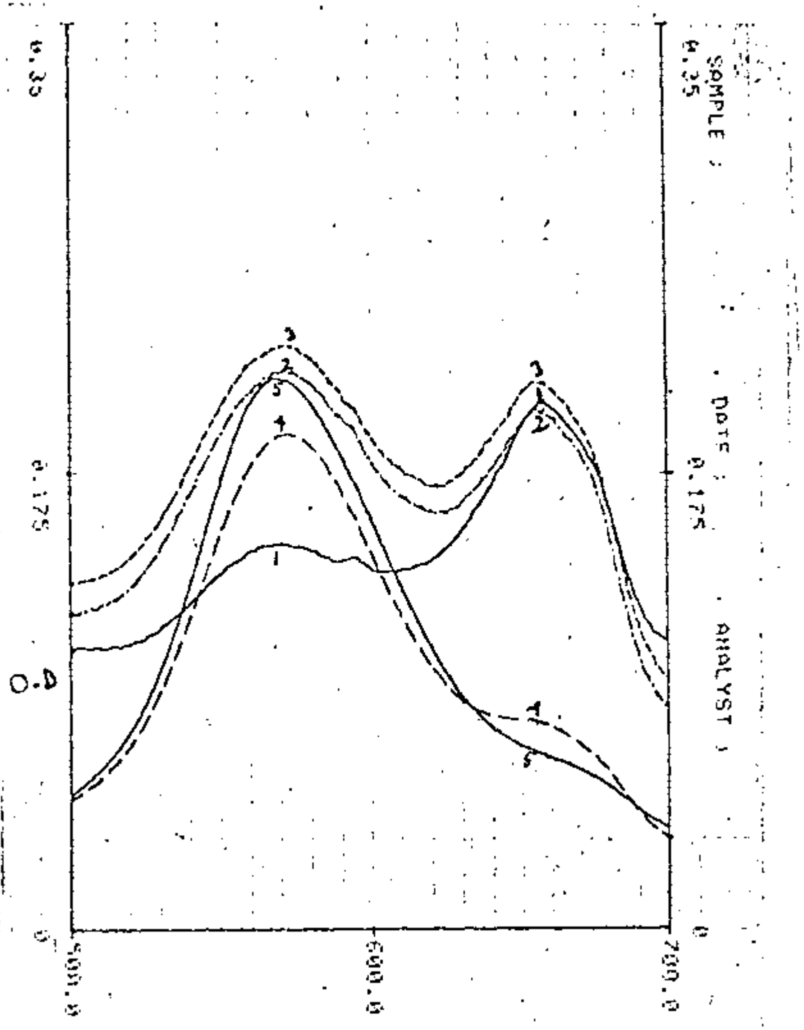


FIG.108 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-MONTMORILLONITE TREATED WITH TMBT. THE SPECTRA 1 , 2 , 3 , 4 AND 5 CORRESPOND TO 6.5, 13 , 24 , 32 AND 64 meq OF TMBT ADSORBED PER 100g OF Na-MONTMORILLONITE.

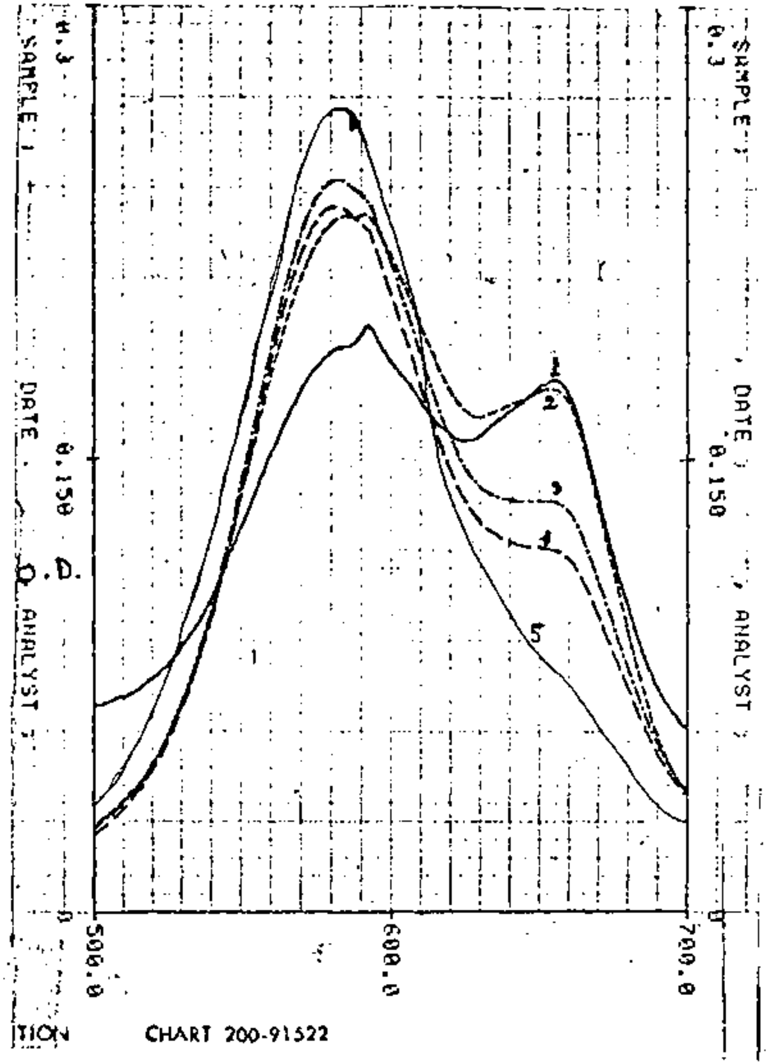


FIG.109 VISIBLE SPECTRA OF AQUEOUS SUSPENTION OF Na-MONTMORILLONITE TREATED WITH DEMBT. THE SPECTRA 1 , 2 , 3 , 4 AND 5 CORRESPOND TO 6.5 , 13 , 24 , 32 AND 64 meq OF DEMBT ADSORBED PER 100g OF Na-MONTMORILLONITE.

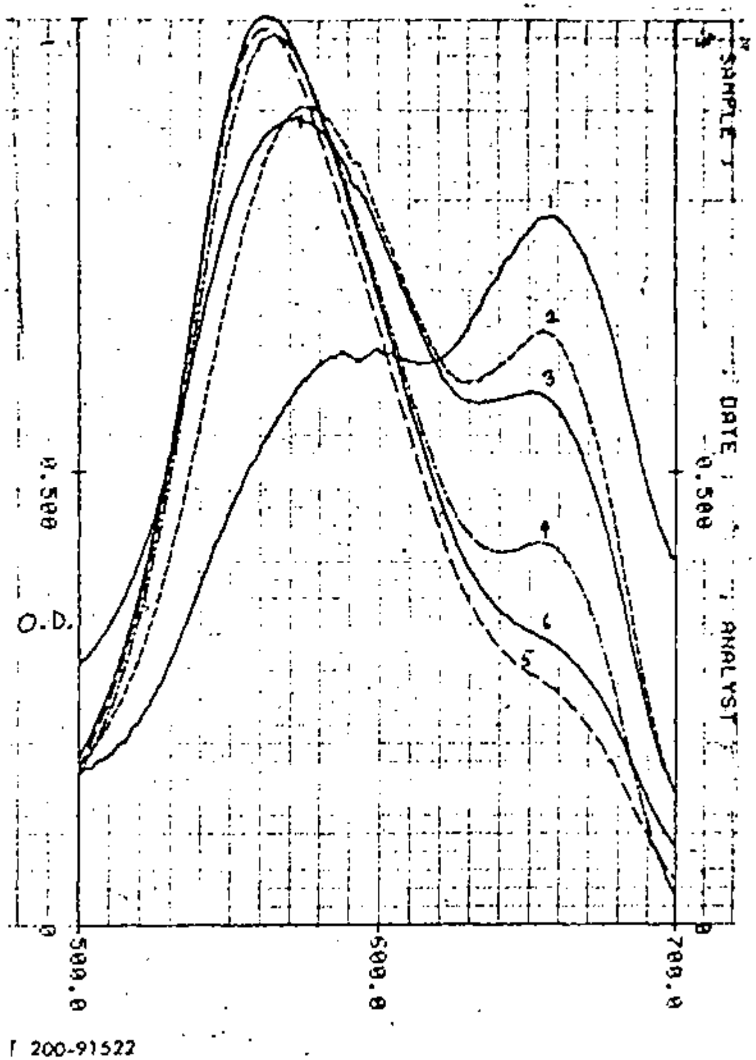


FIG.110 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-MONTMORILLONITE TREATED WITH DEMPT. THE SPECTRA 1,2,3,4,5 AND 6 CORRESPOND TO 6.5,13,24,32,64 AND 80 meq OF DEMPT ADSORBED PER 100g OF Na-MONTMORILLONITE.

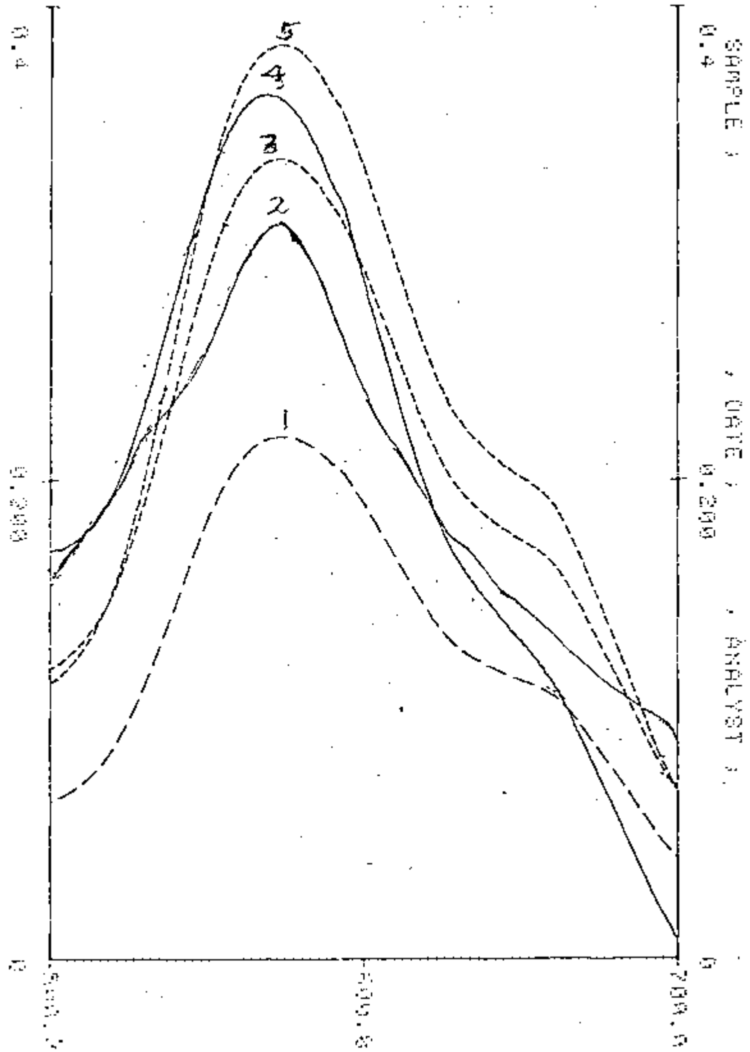


FIG. 111 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H- MONTMORILLONITE TREATED WITH TMPT. THE SPECTRA 1, 2, 3 4 AND 5 OF TMPT ADSORBED PER 100g OF H-MONTMORILLONITE

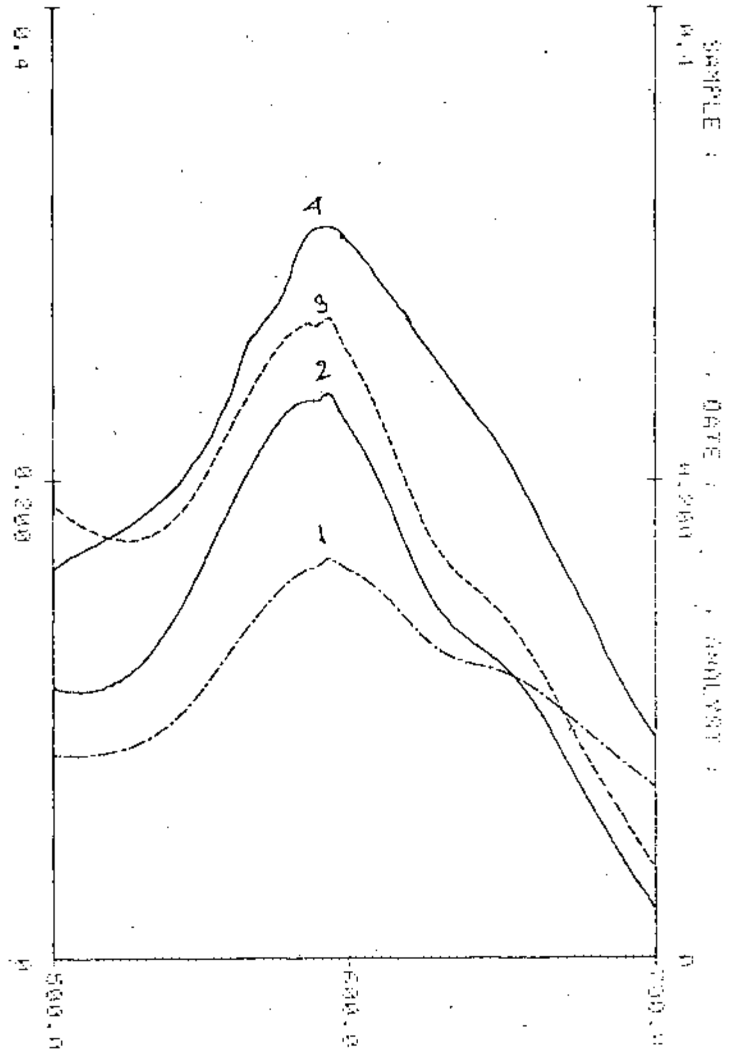


FIG. 112. VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H-MONTMORILLONITE TREATED WITH TMBT. THE SPECTRA 1, 2, 3 AND 4 CORRESPOND TO 8, 16, 32 AND 64 meq OF TMBT ADSORBED PER 100g OF H-MONTMORILLONITE.

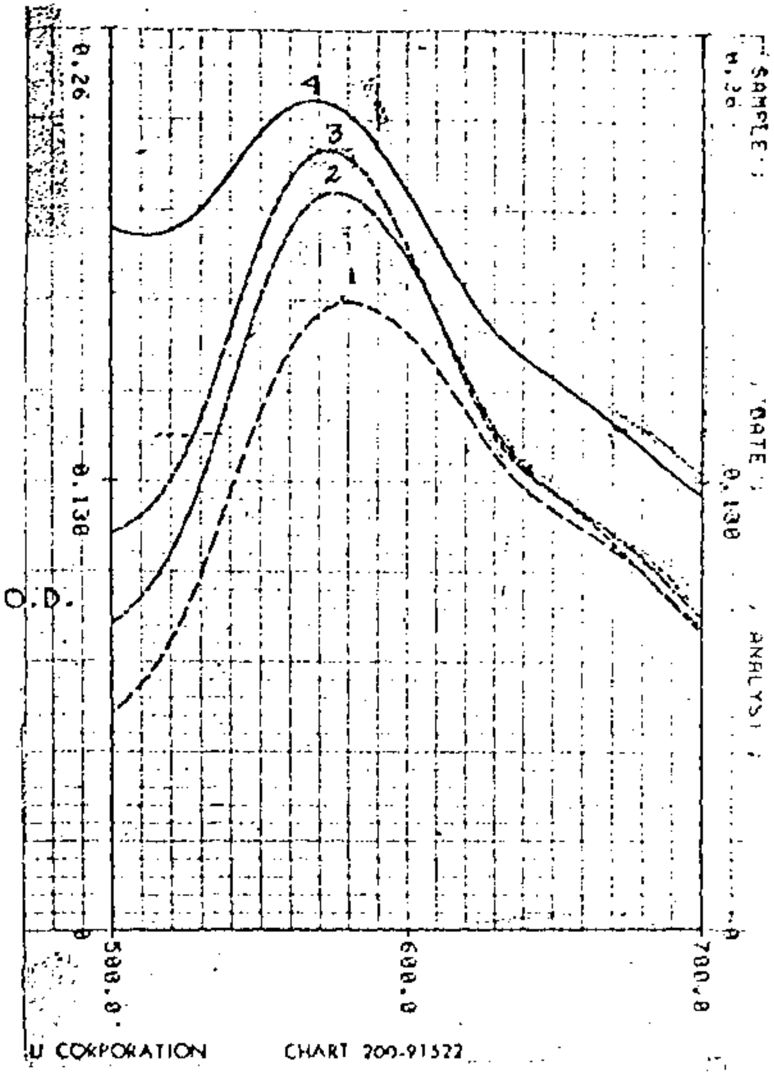


FIG.113 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H-MONTMORILLONITE TREATED WITH DEMPT THE SPECTRA 1 ,2 ,3AND 4 CORRESPOND TO 8 , 16, 32 AND 64 meq OF DEMPT ADSORBED PER 100g OF H-MONTMORILLONITE.

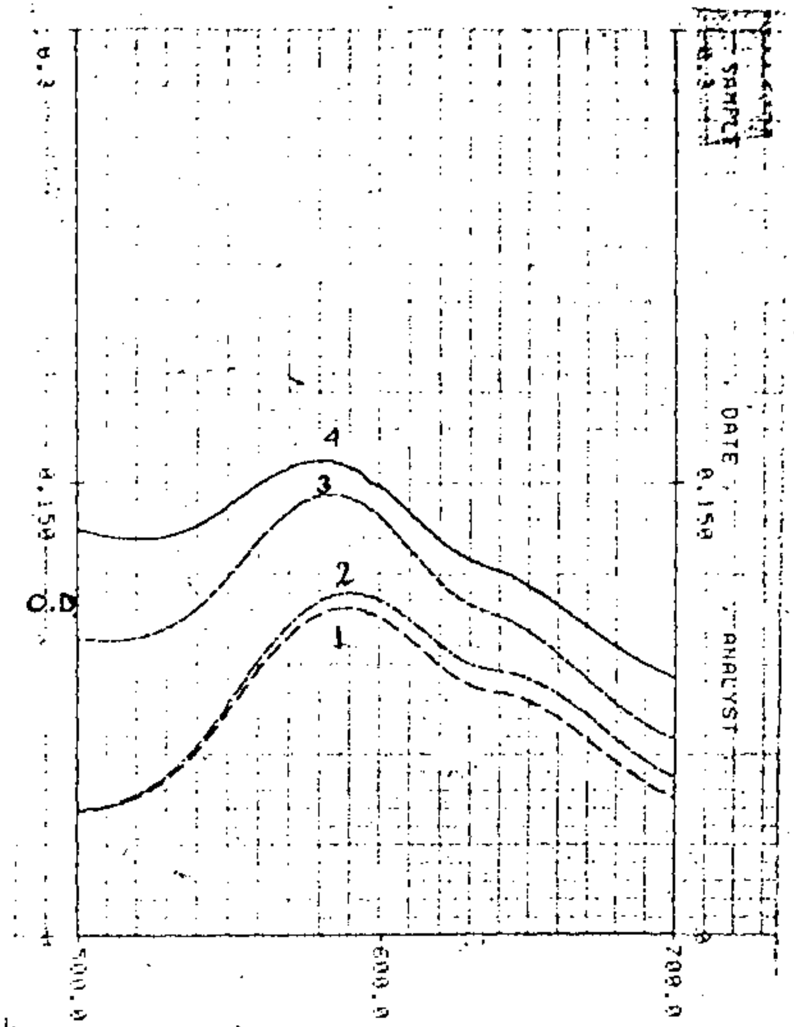


FIG.114 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H-MONTMORILLONITE TREATED WITH DEMBT. THE SPECTRA 1 ,2 ,3 AND 4 CORRESPOND TO 8 , 16 , 32 AND 64 meq OF DEMBT ADSORBED PER 100g OF H-MONTMORILLONITE.

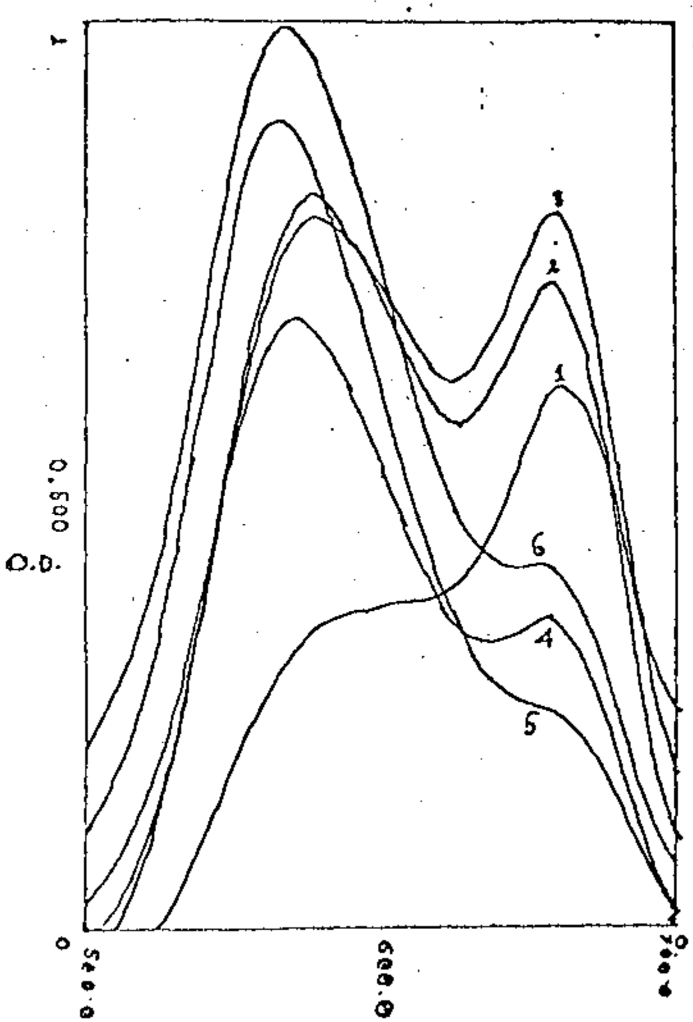


FIG.15 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-VERMICULITE TREATED WITH TMPT. THE SPECTRA 1,2,3,4,5 AND 6 CORRESPOND TO 6.5, 13,26,39,52 AND 78 meq OF TMPT ADSORBED PER 100g OF Na-VERMICULITE.

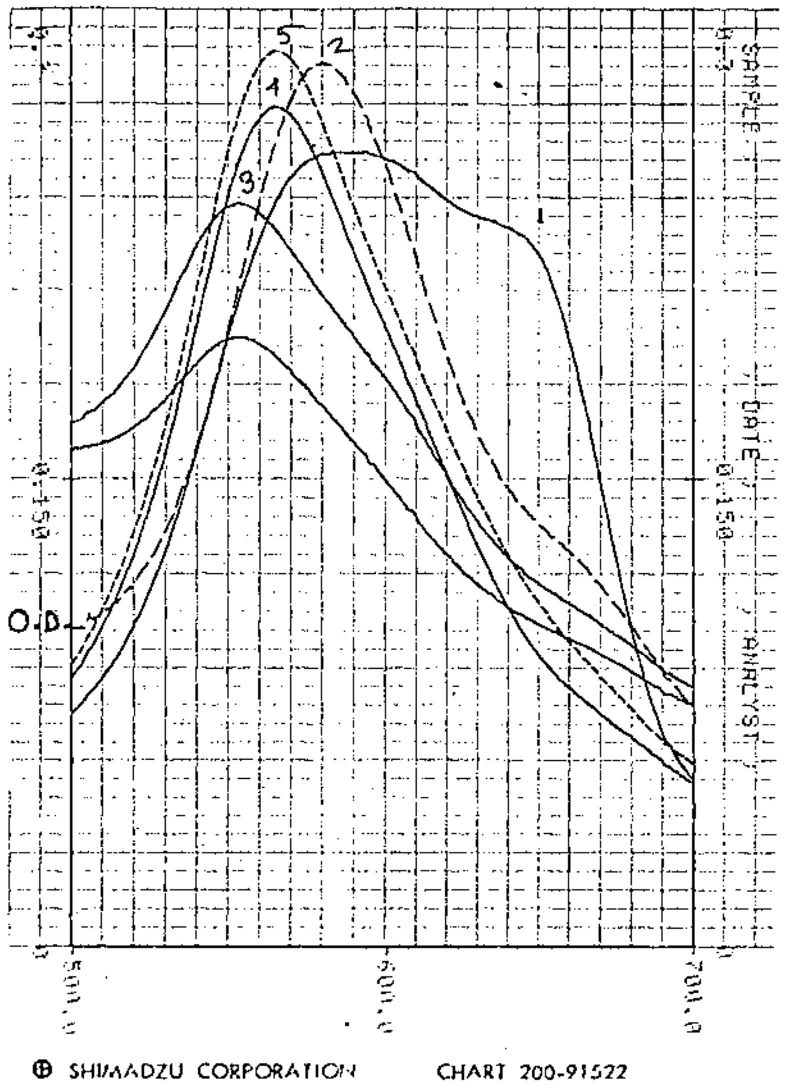


FIG.116 VISIBLE SPECTRAOF AQUEOUS SUSPENSION OF Na-VERMICULITE TREATED WITH TMBT. THE SPECTRA 1,2,3,4 AND 5 CORRESPOND TO 6.5, 13, 26, 39 AND 52 meq OF TMBT ADSORBED PER 100g OF Na-VERMICULITE.

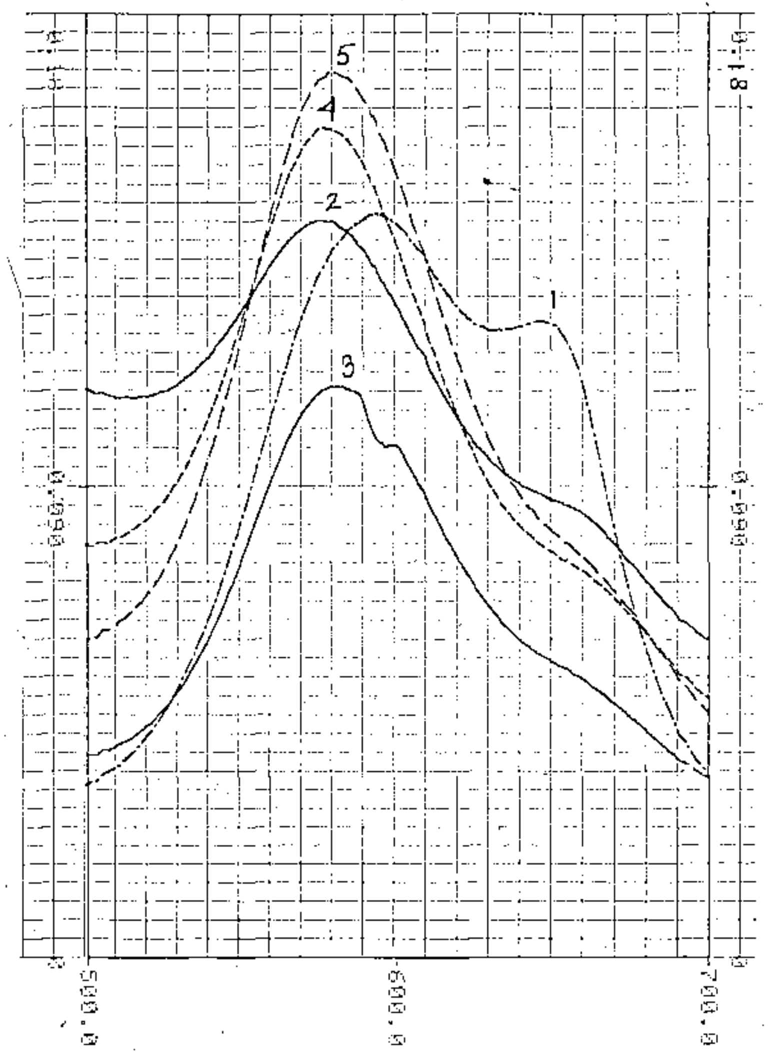


FIG. 118 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-VERMICULITE TREATED WITH DEMBT. THE SPECTRA 1, 2, 3, 4 AND 5 CORRESPOND TO 6.5, 13, 26, 39 AND 52 meq OF DEMBT ADSORBED PER 100g OF Na-VERMICULITE.

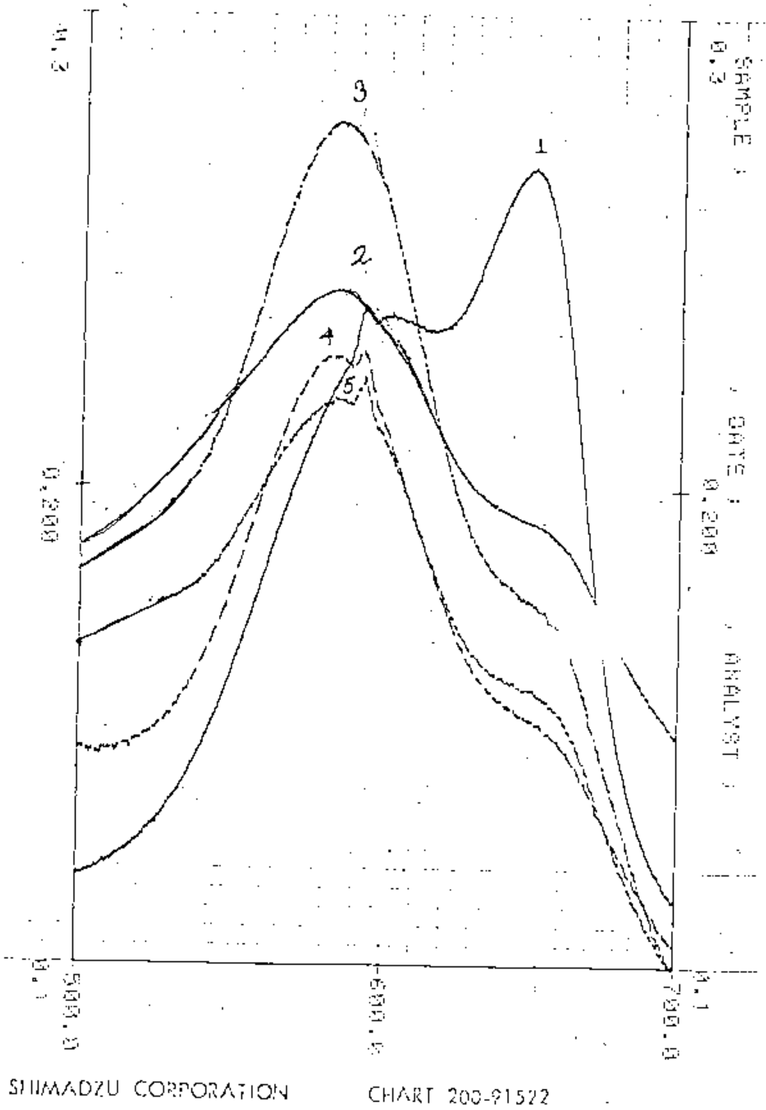


FIG. 117 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-VERMICULITE TREATED WITH DEMPT. THE SPECTRA 1, 2, 3 4 AND 5 CORRESPOND TO 6.5, 13, 26, 39 AND 52 meq OF DEMPT ADSORBED PER 100g OF Na-VERMICULITE

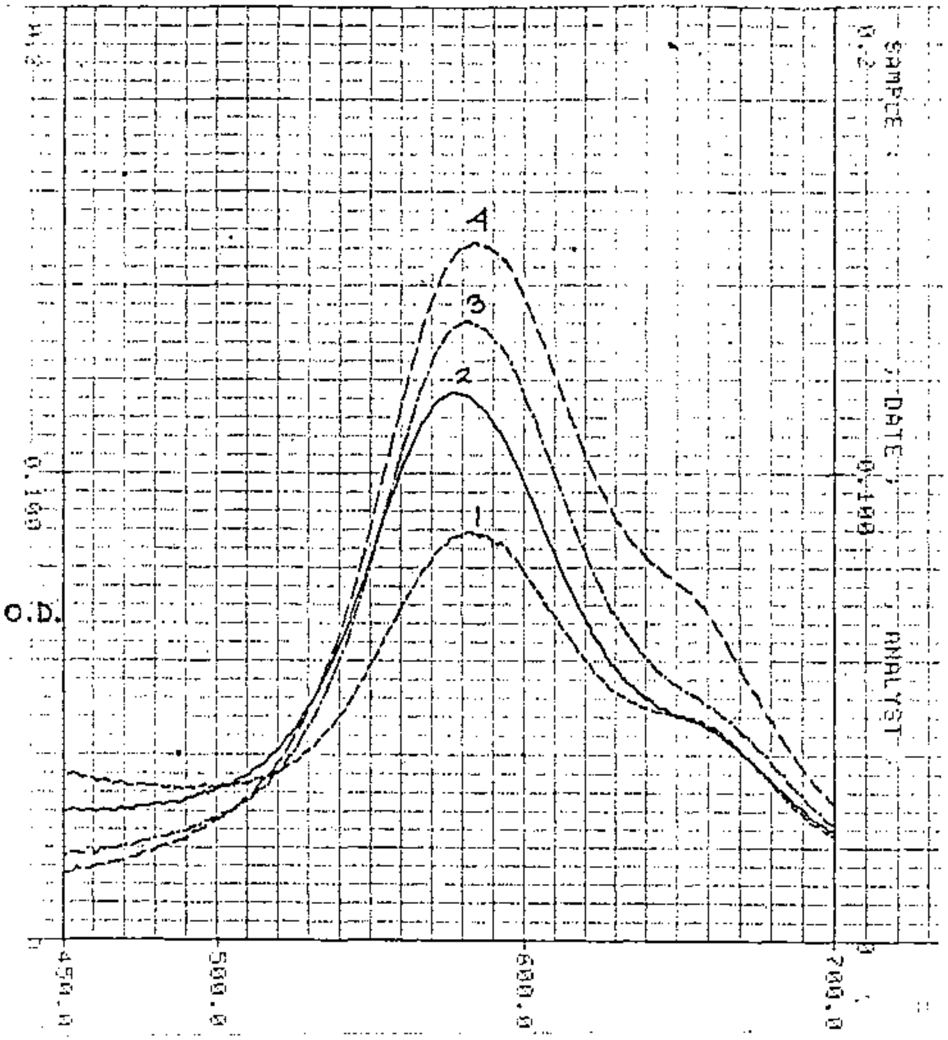


FIG.119 VISIBLE SPECTRA OF AQUEOUS SUSPENSI-ON OF H-VERMICULITE TREATED WITH TMPT. THE SPECTRA 1 , 2 , 3 AND 4 CORRESPOND TO 8 , 16 , 32 AND 64 meq OF TMPT ADSORBED PER 100g OF H-VERMICULITE.

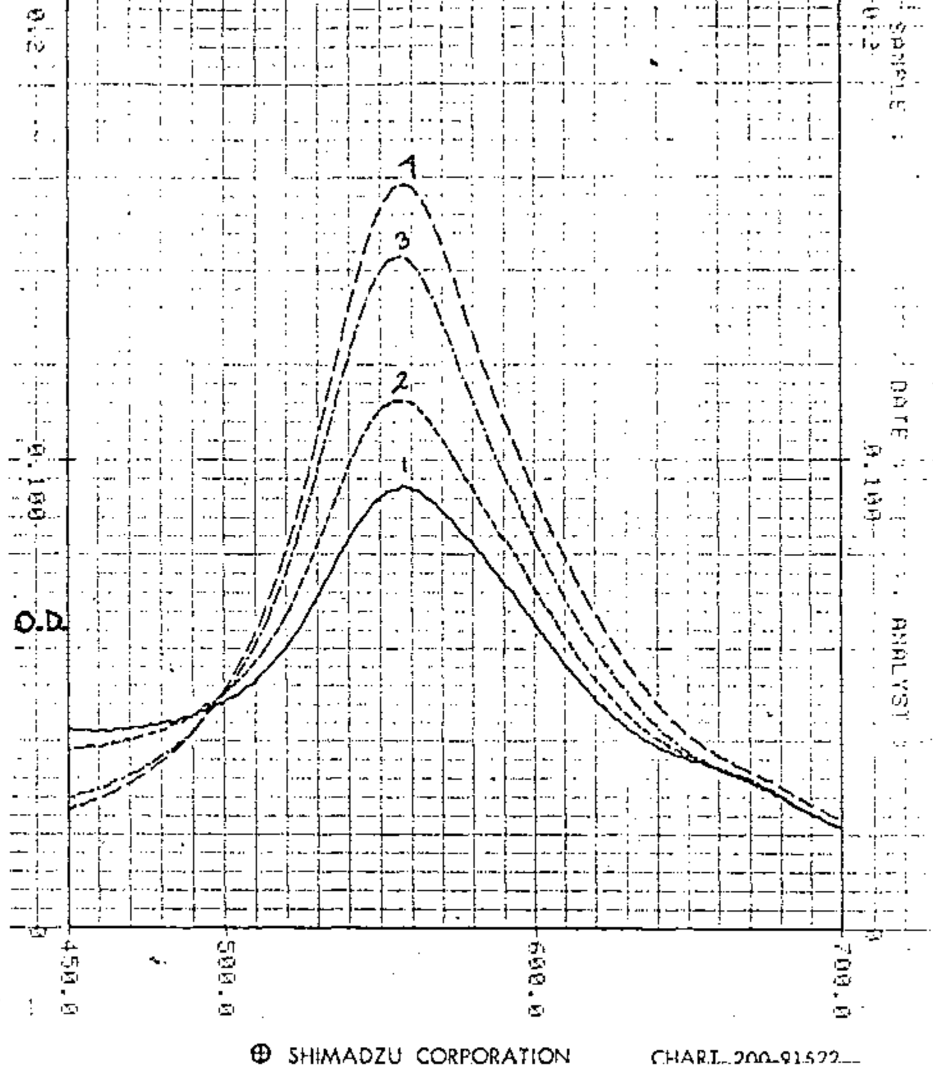


FIG.120 VISIBLE SPECTRA OF AQUEOUS SUSPENSI-ON OF H-VERMICULITE TREATED WITH TMBT. THE SPECTRA 1 ,2 ,3 AND 4 CORRESPOND TO 8 ,16 , 32 AND 64 meq OF TMBT ADSORBED PER 100g OF H-VERMICULITE.

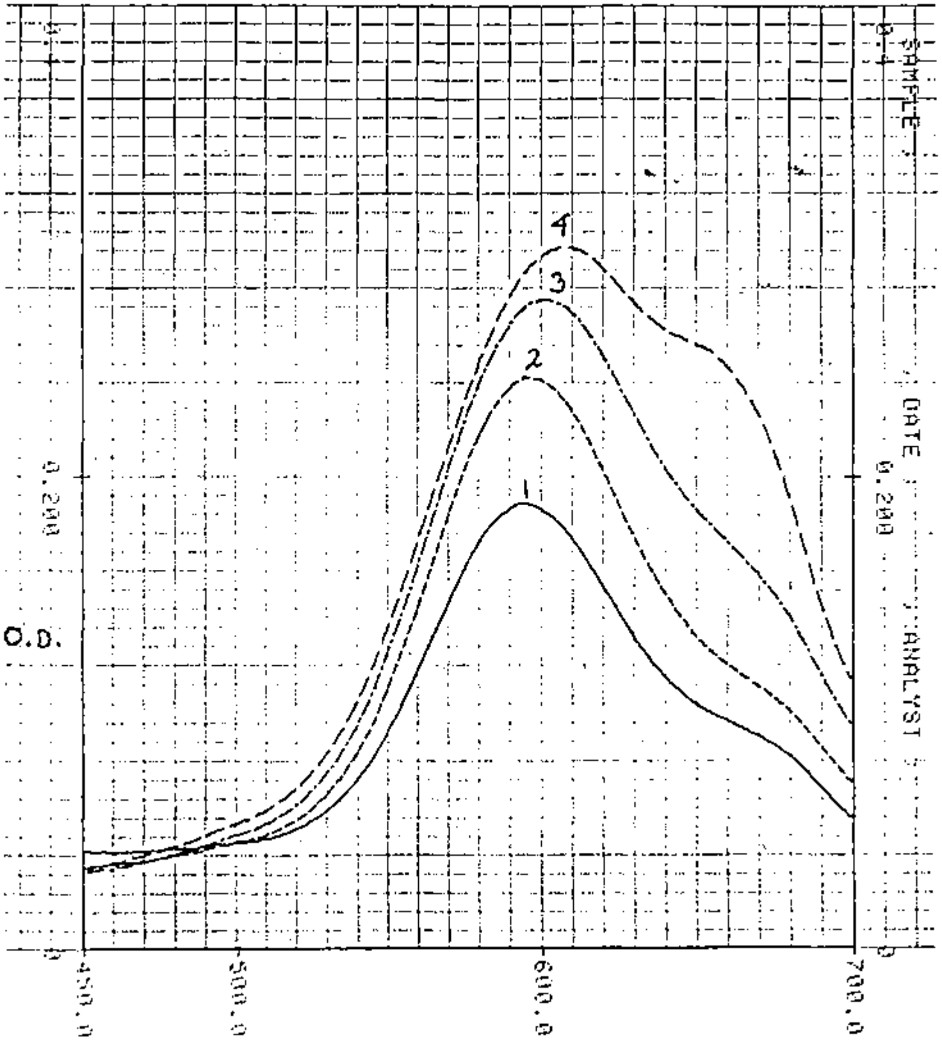


FIG.21 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H-VERMICULITE TREATED WITH DEMPT. THE SPECTRA 1 ,2 ,3 AND 4 CORRESPOND TO 8 ,16 , 32 AND 64 meq OF DEMPT ADSORBED PER 100g OF H-VERMICULITE.

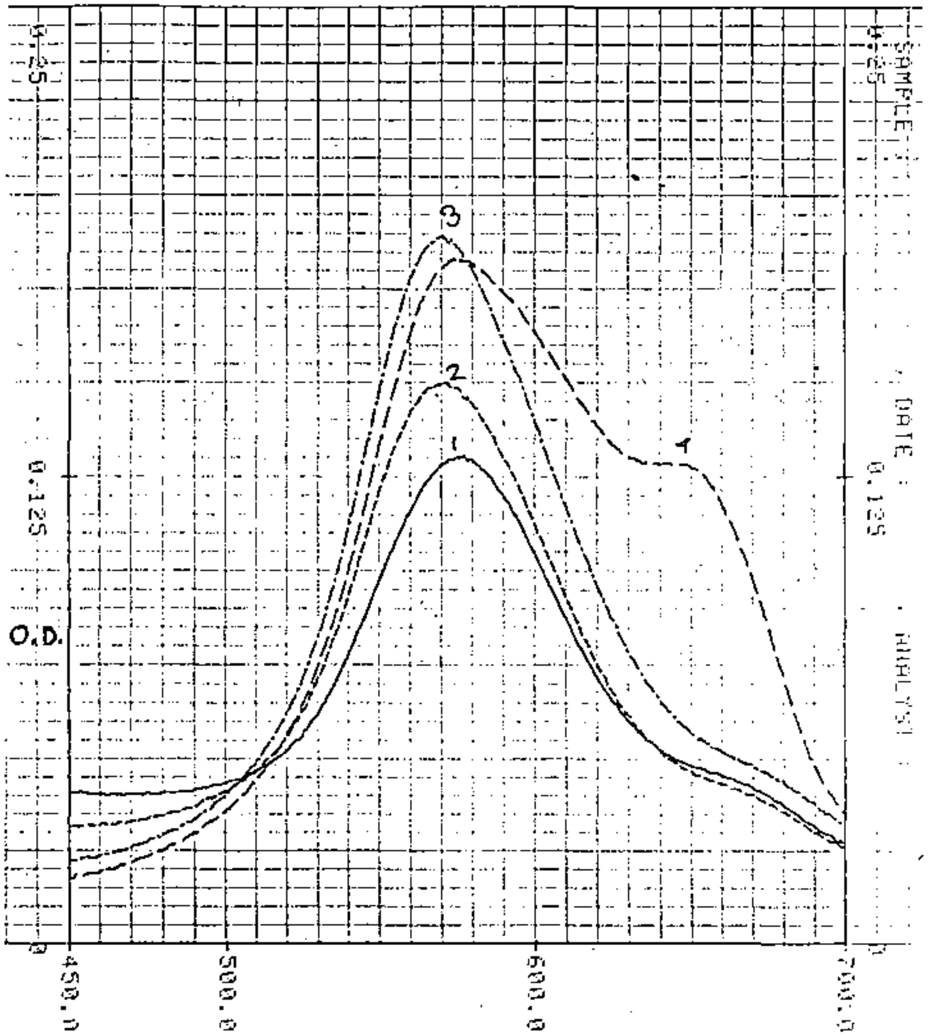


FIG.22 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF H-VERMIGULITE TREATED WITH DEMBT. THE SPECTRA 1 ,2 , 3 AND 4 CORRESPOND TO 8 ,16 , 32 AND 64 meq OF DEMBT ADSORBED PER 100g OF H-VERMICULITE.

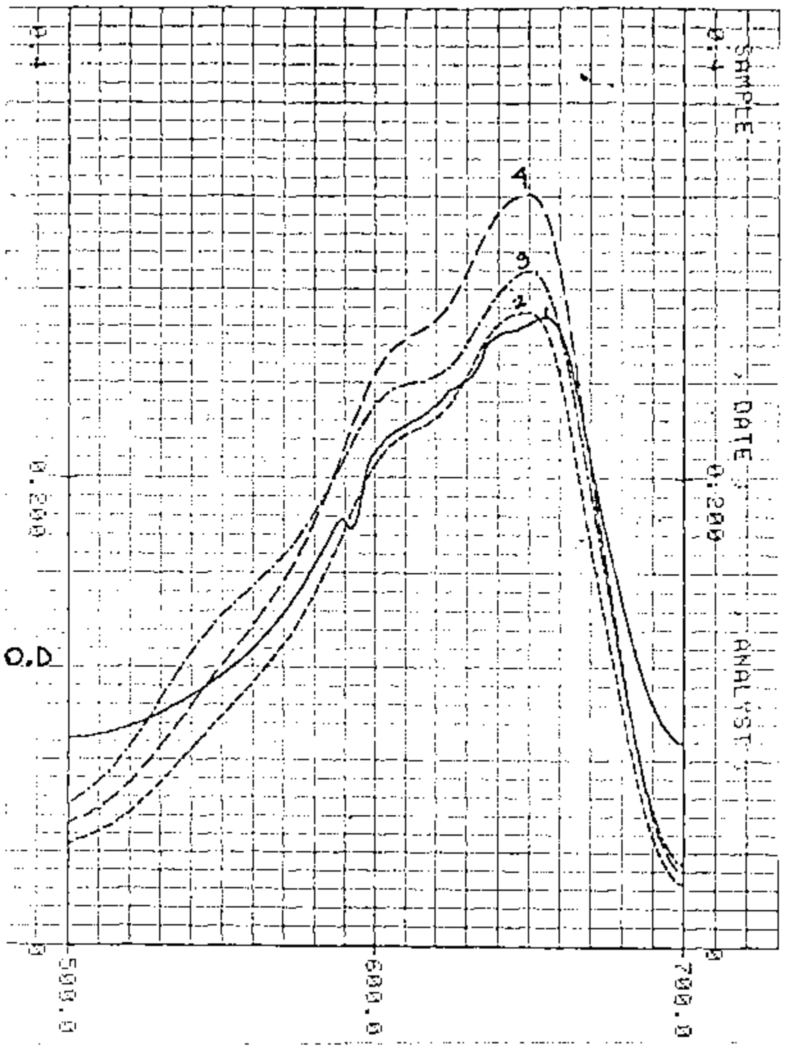


FIG.123 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF NaLAPONITE TREATED WITH TMPT. THE SPECTRA 1,2,3 AND 4 CORRESPOND TO 8, 16 , 32 AND 64 meq OF TMPT ADSORBED PER 100gOF Na-LAPONITE.

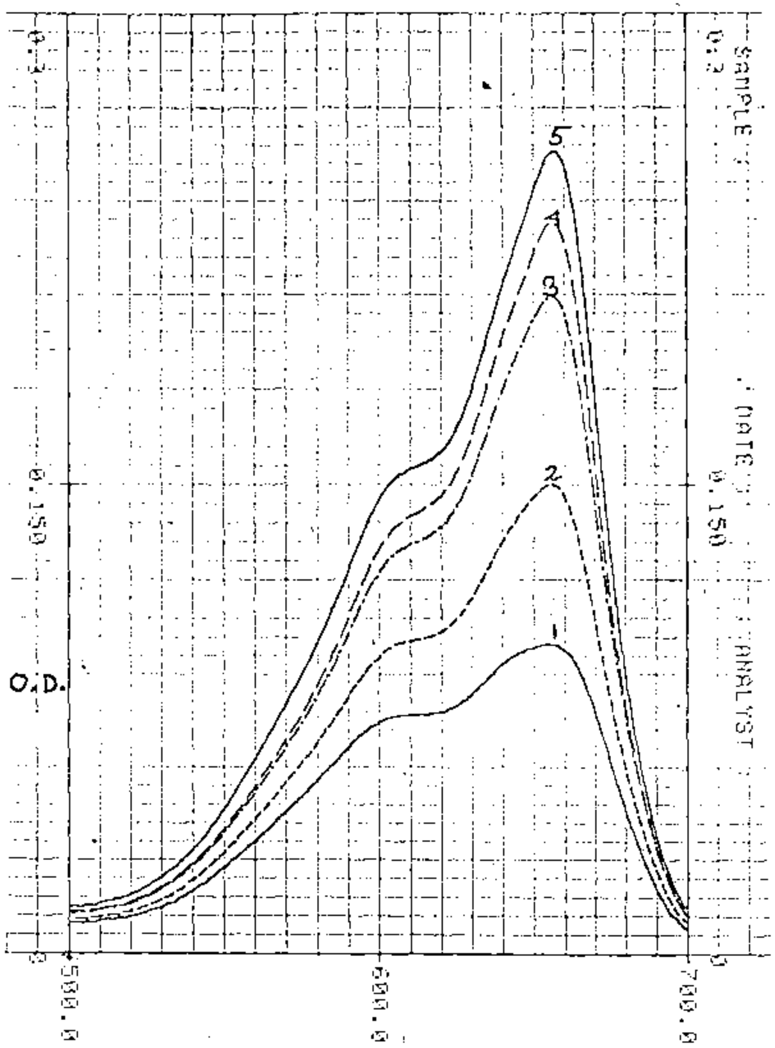


FIG.124 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH TMBT. THE SPECTRA 1,2,3 AND 4 CORRESPOND TO 8 ,16 , 32 AND 64 meq OF TMBT ADSORBED PER 100g OF Na-LAPONITE.

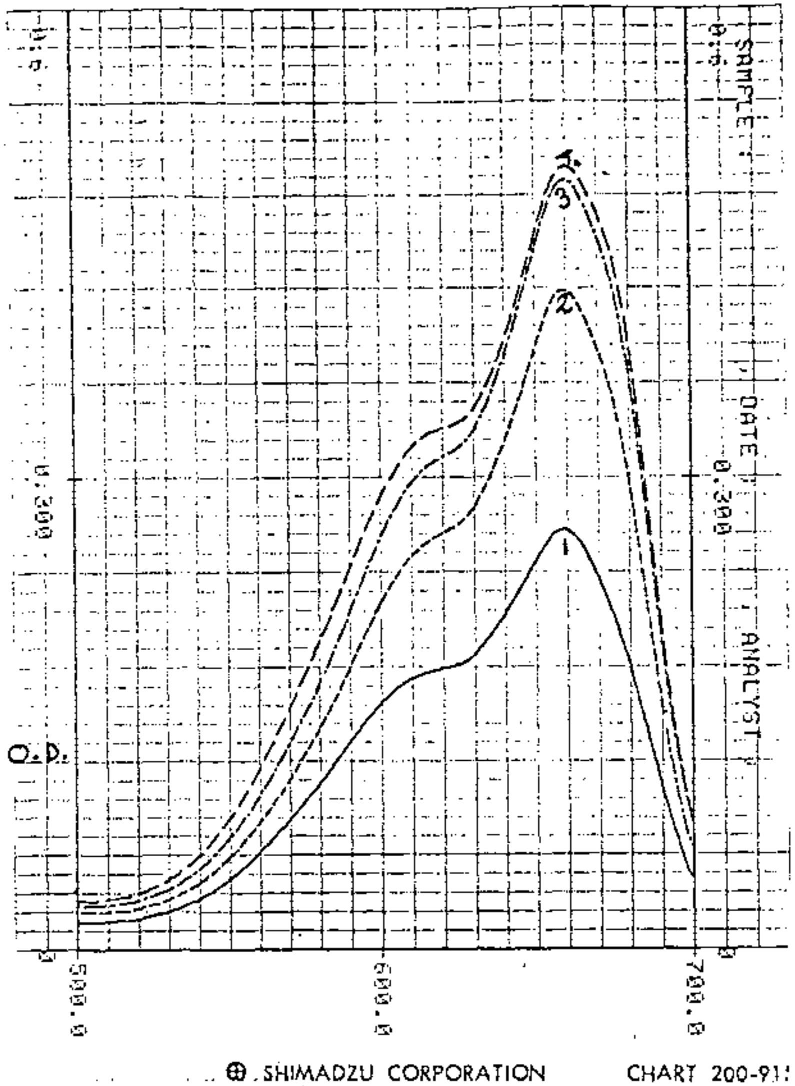


FIG.125 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH DEMPT. THE SPECTRA 1, 2, 3 AND 4 CORRESPOND TO 8, 16, 32 AND 64 meq OF DEMPT ADSORBED PER 100g OF Na-LAPONITE.

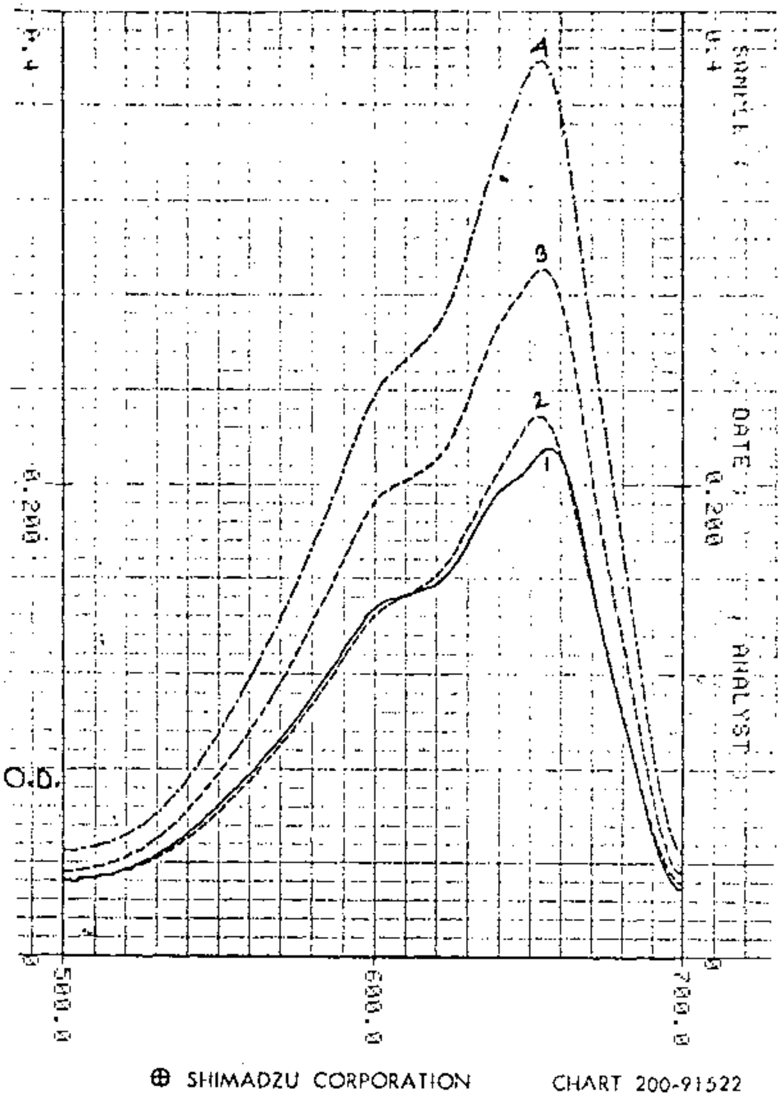


FIG.126 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH DEMBT. THE SPECTRA 1,2,3AND 4 CORRESPOND TO 8, 16, 32 AND 64 meq OF DEMBT ADSORBED PER 100g Na-LAPONITE.

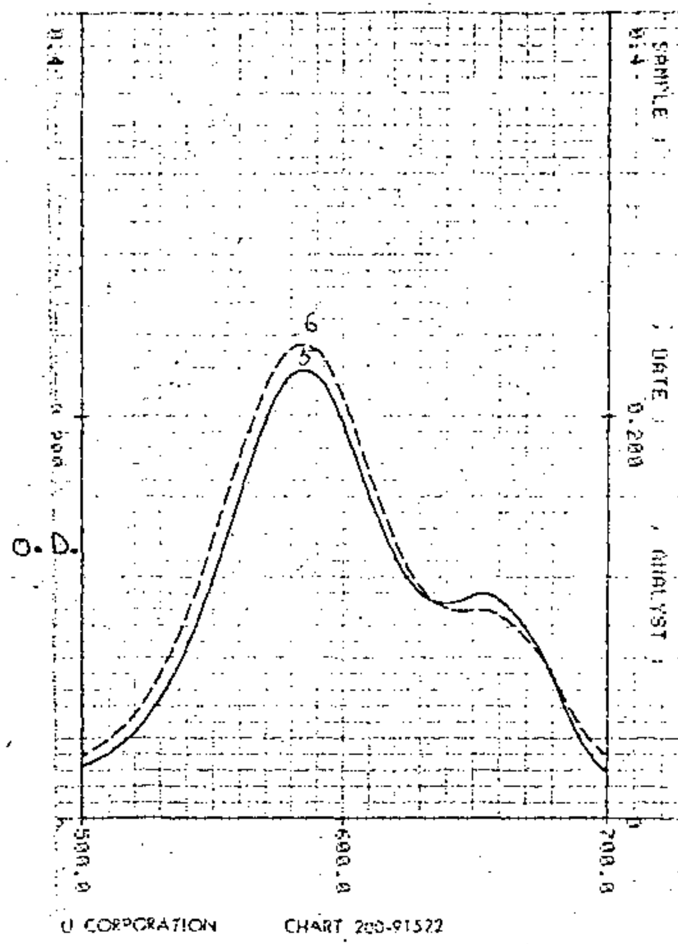


FIG.127 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH TMPT . THE SPECTRA 5 AND 6 CORRESPOND TO 90 AND 100 meq TMPT ADSORBED PER 100g OF Na-LAPONKTE .

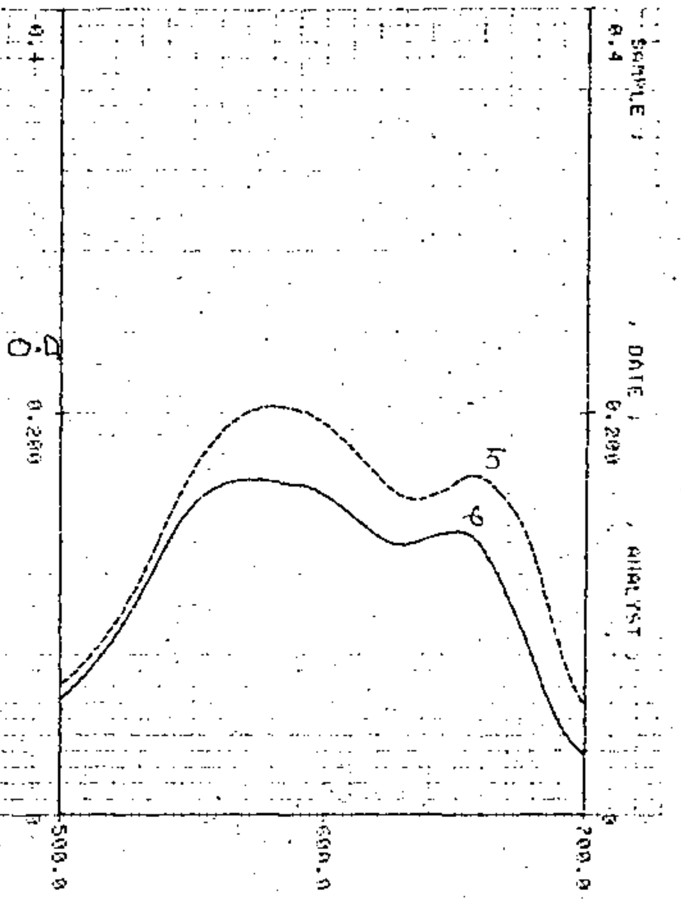


FIG.128 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH TMBT . THE SPECTRA 5 AND 6 CORRESPOND TO 90 AND 100 meq OF TMBT ADSORBED PER 100g OF Na-LAPONITE .

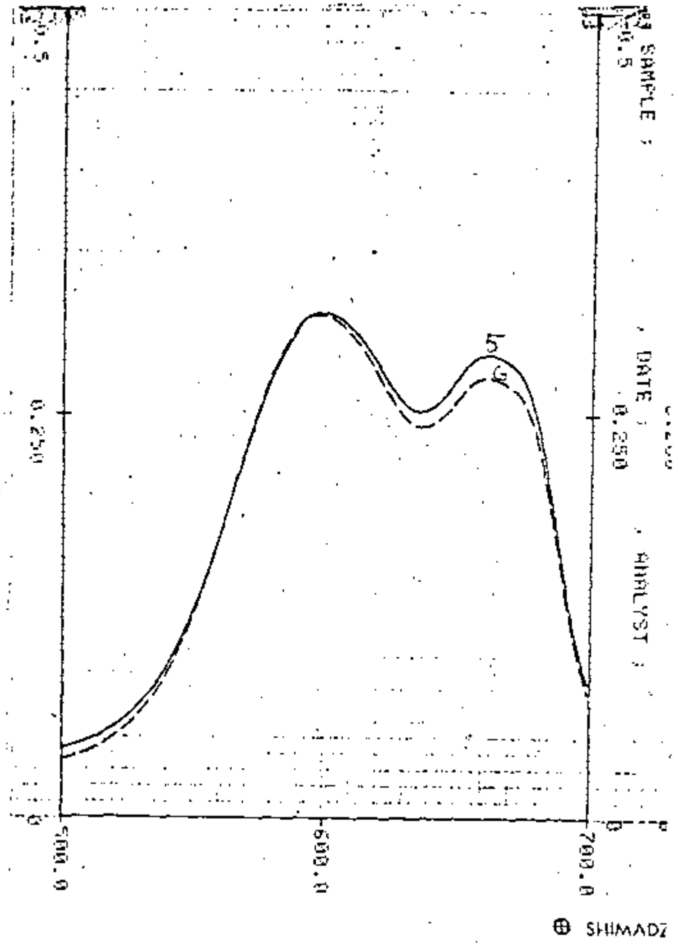


FIG.129 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH DEMPT . THE SPECTRA 5 AND 6 CORRESPOND TO 90 AND 100 meq OF DEMPT ADSORBED PER 100g OF Na-LAPONITE .

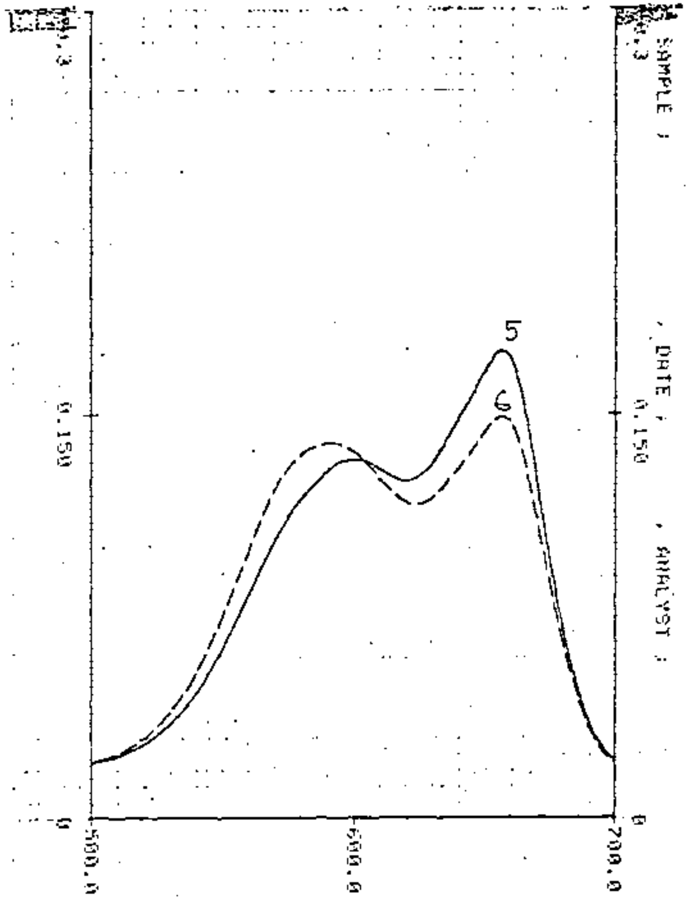


FIG.130 VISIBLE SPECTRA OF AQUEOUS SUSPENSION OF Na-LAPONITE TREATED WITH DEMBT . THE SPECTRA 5 AND 6 CORRESPOND TO 90 AND 100 meq OF DEMBT ADSORBED PER 100g OF Na-LAPONITE .

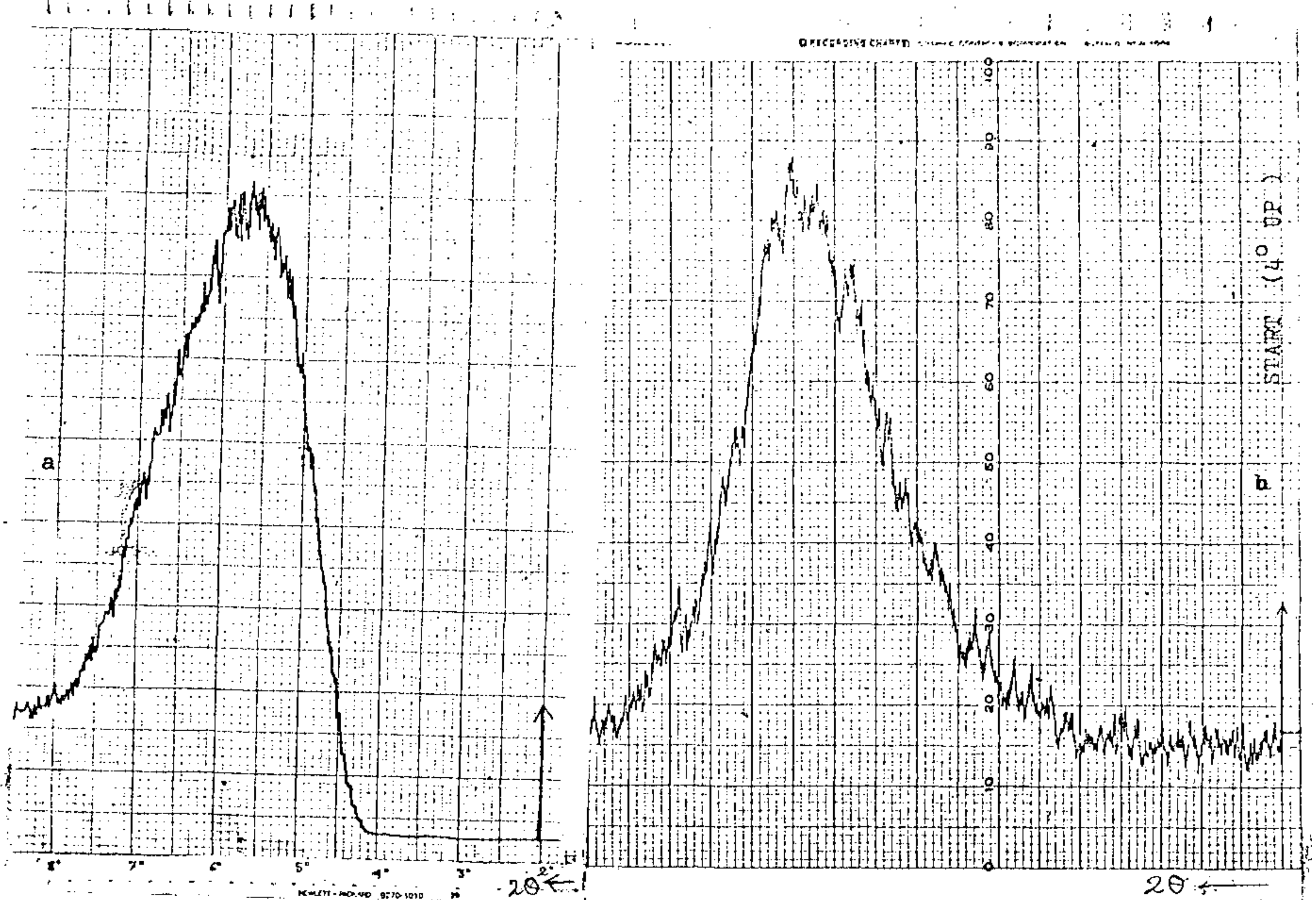


FIG.13: X-RAY DIFFRACTION SPECTRA OF (a) 35% SORBED TMPT ONTO Na-MONTMORILLONITE (b) 25% SORBED TMPT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS ; SCANNING RATE (a) 1° PER MINUTE AND (b) $\frac{1}{4}$° PER MINUTE).

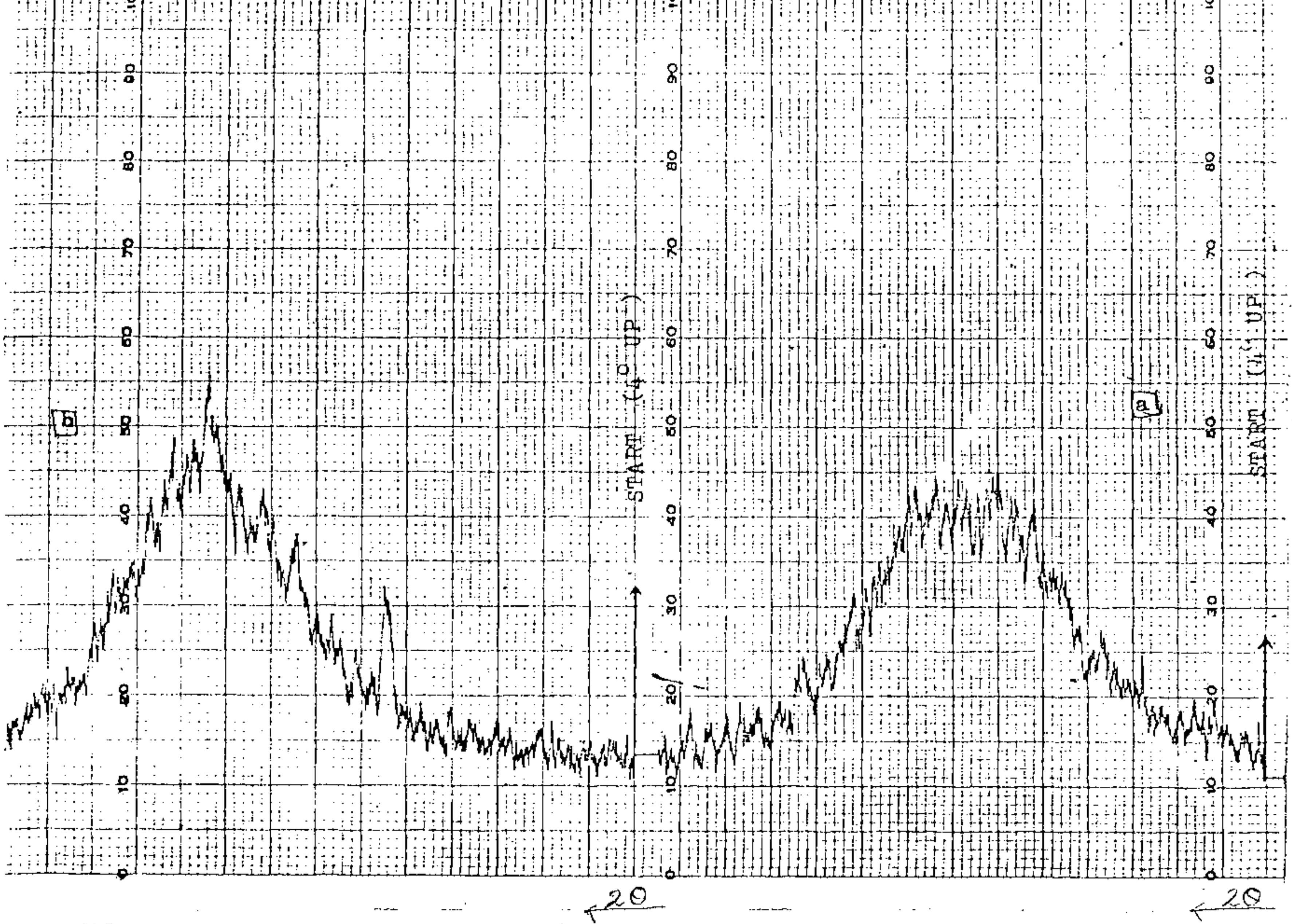


FIG.132 X-RAY DIFFRACTION SPECTRA OF (a) 100% SORBED TMPT ONTO Na-MONTMORILLONITE (b) 50% SORBED TMPT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS ; SCANNING RATE ¼° PER MINUTE).

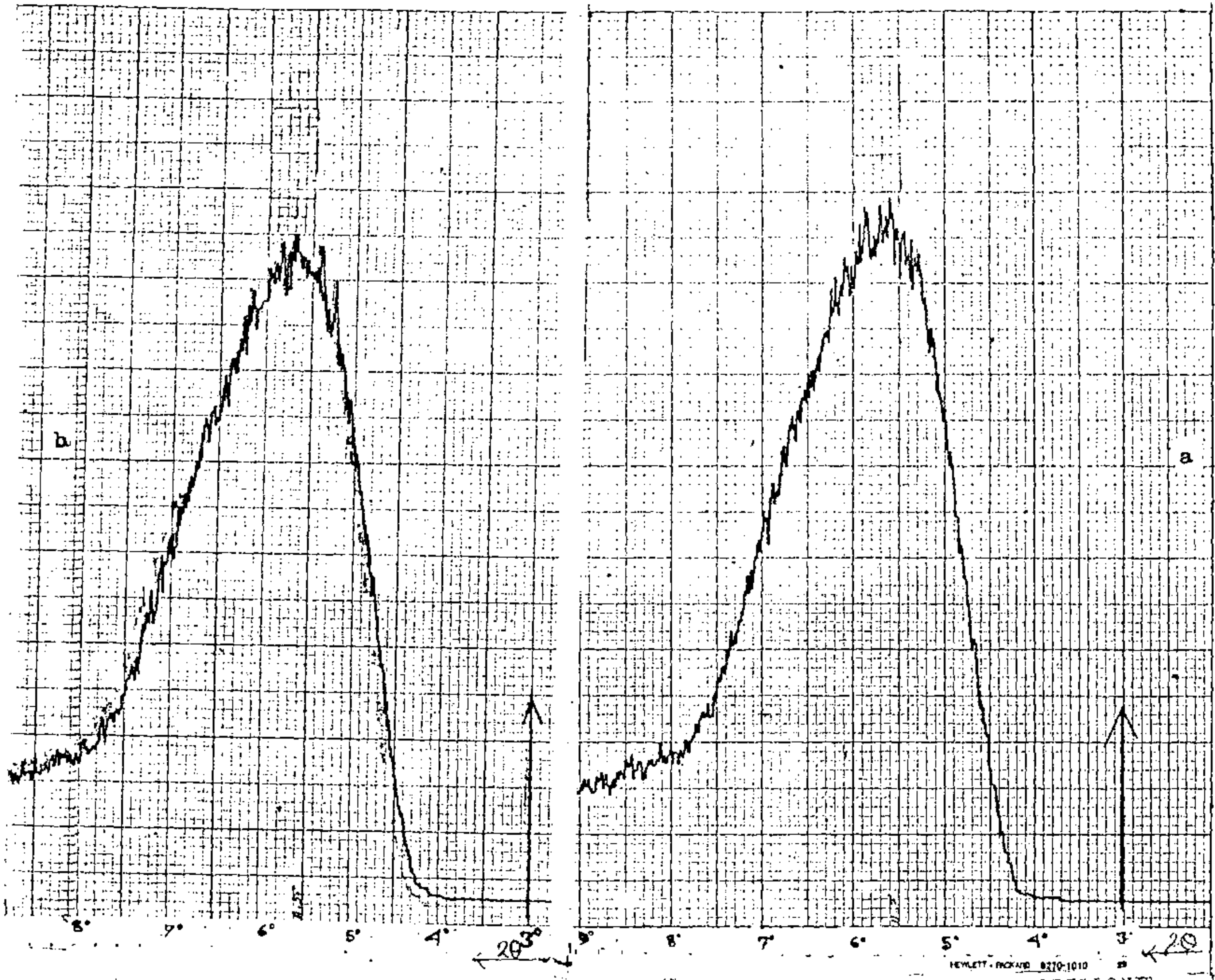


FIG.133 X-RAY DIFFRACTION SPECTRA OF (a) 35% SORBED TMBT ONTO Na-MONTMORILLONITE (b) 25% SORBED TMBT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS: SCANNING RATE (a) 1° PER MINUTE

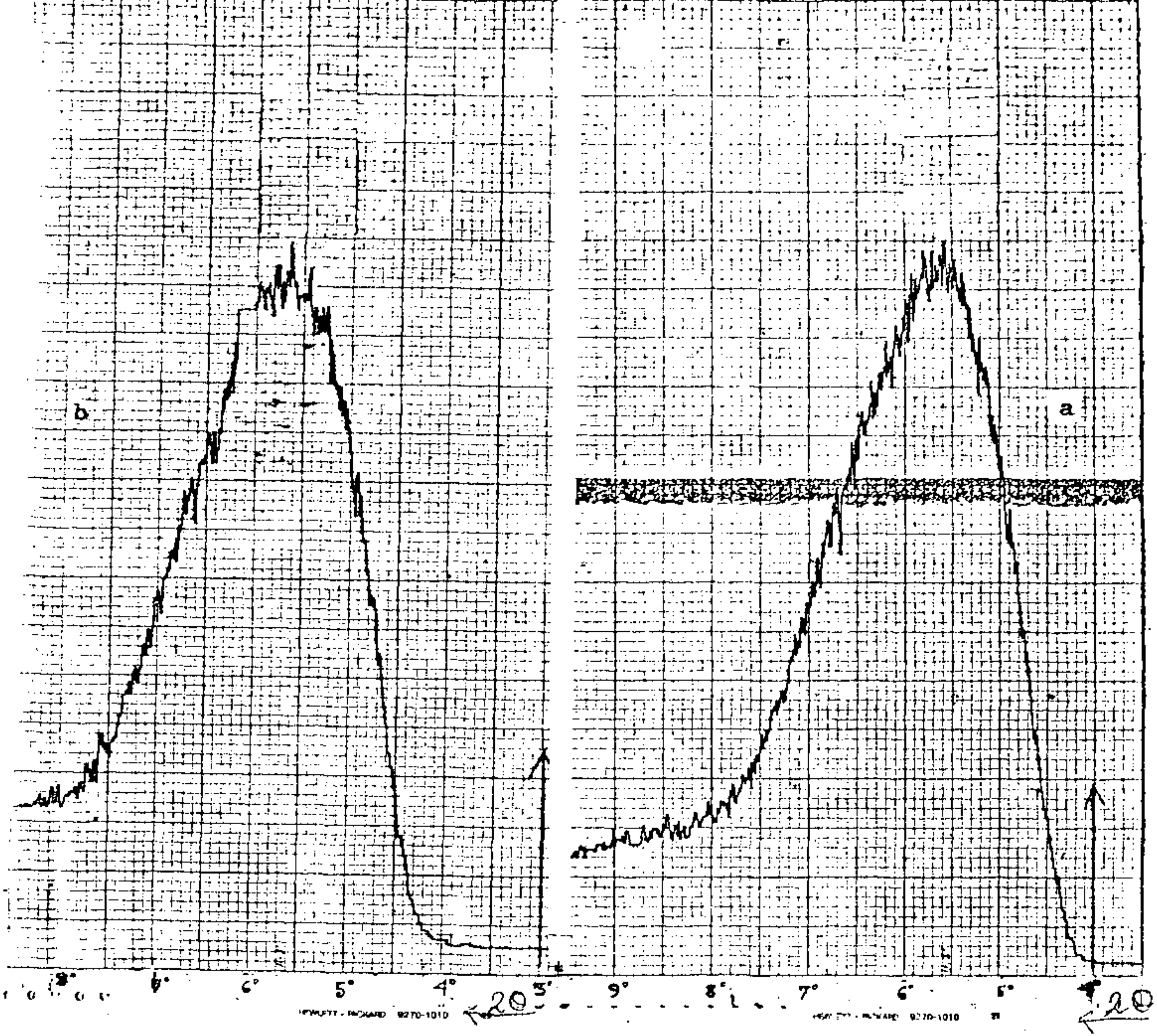


FIG.134 X-RAY DIFFRACTION SPECTRA OF (a) 100% SORBED TMBT ONTO Na-MONTMORILLONITE (b) OF 50% SORBED TMBT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS; SCANNING RATE 1°PER MINUTE).

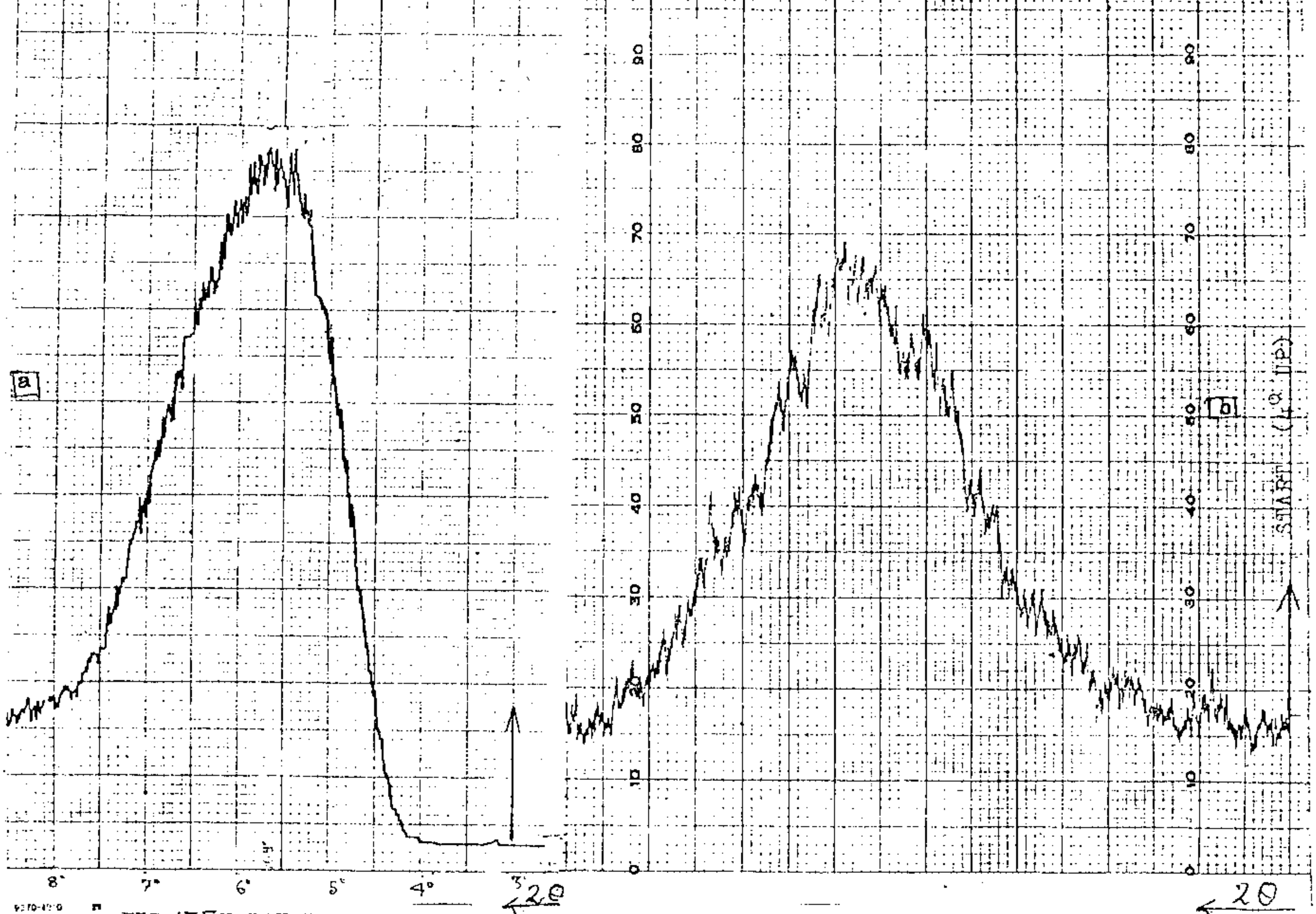


FIG. 135 X-RAY DIFFRACTION SPECTRA OF (a) 35% SORBED DEMPT ONTO Na-MONTMORILLONITE (b) 25% SORBED DEMPT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120°C FOR 24 HRS ; SCANNING RATE (a) 1° PER MINUTE AND (b) ¼° PER MINUTE).

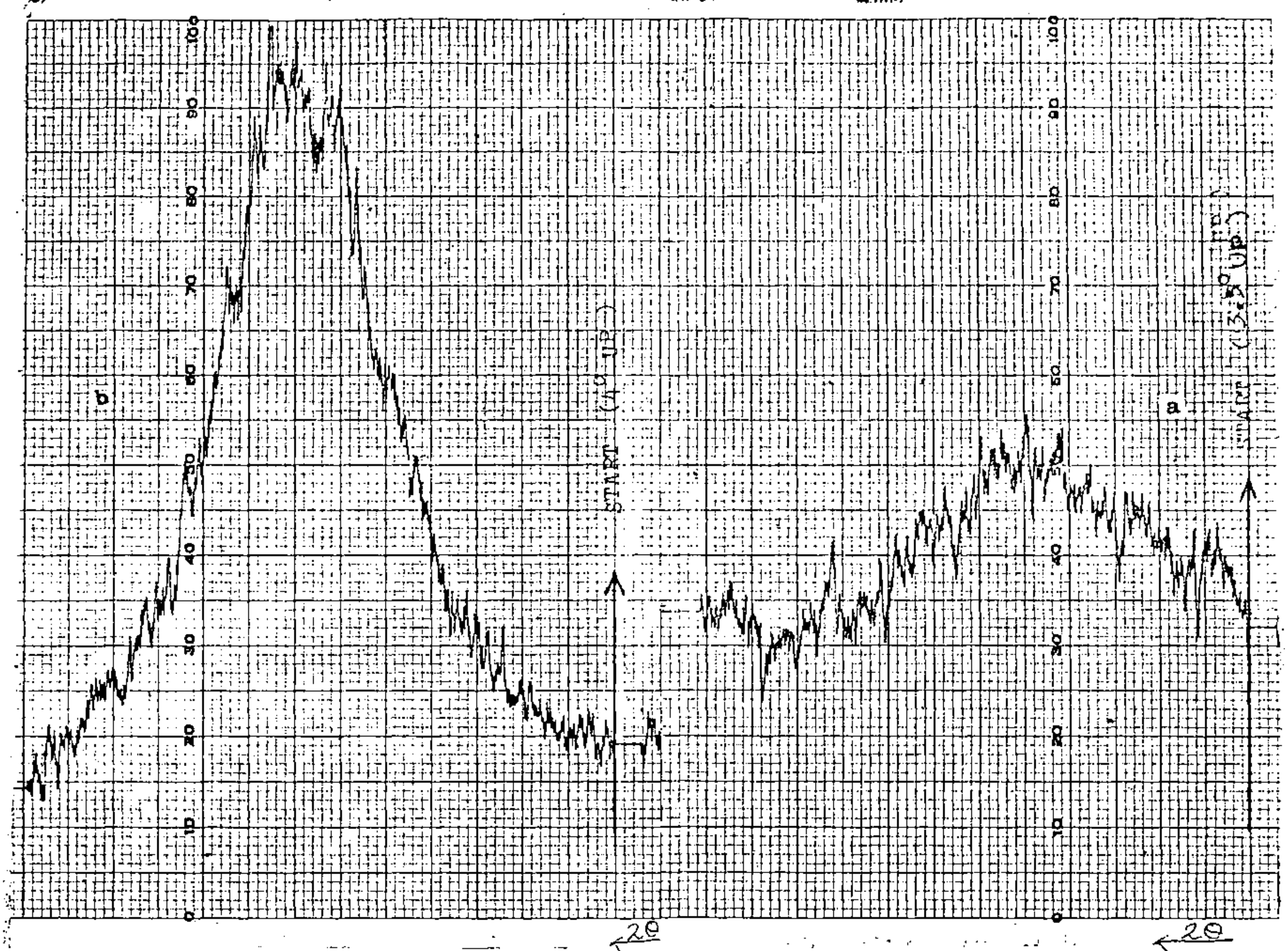


FIG.136 X-RAY DIFFRACTION SPECTRA OF (a)100% SORBED DEMPT ONTO Na-MONTMORILLONITE (b) 50% SORBED DEMPT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS ; SCANNING RATE ¼° PER MINUTE).

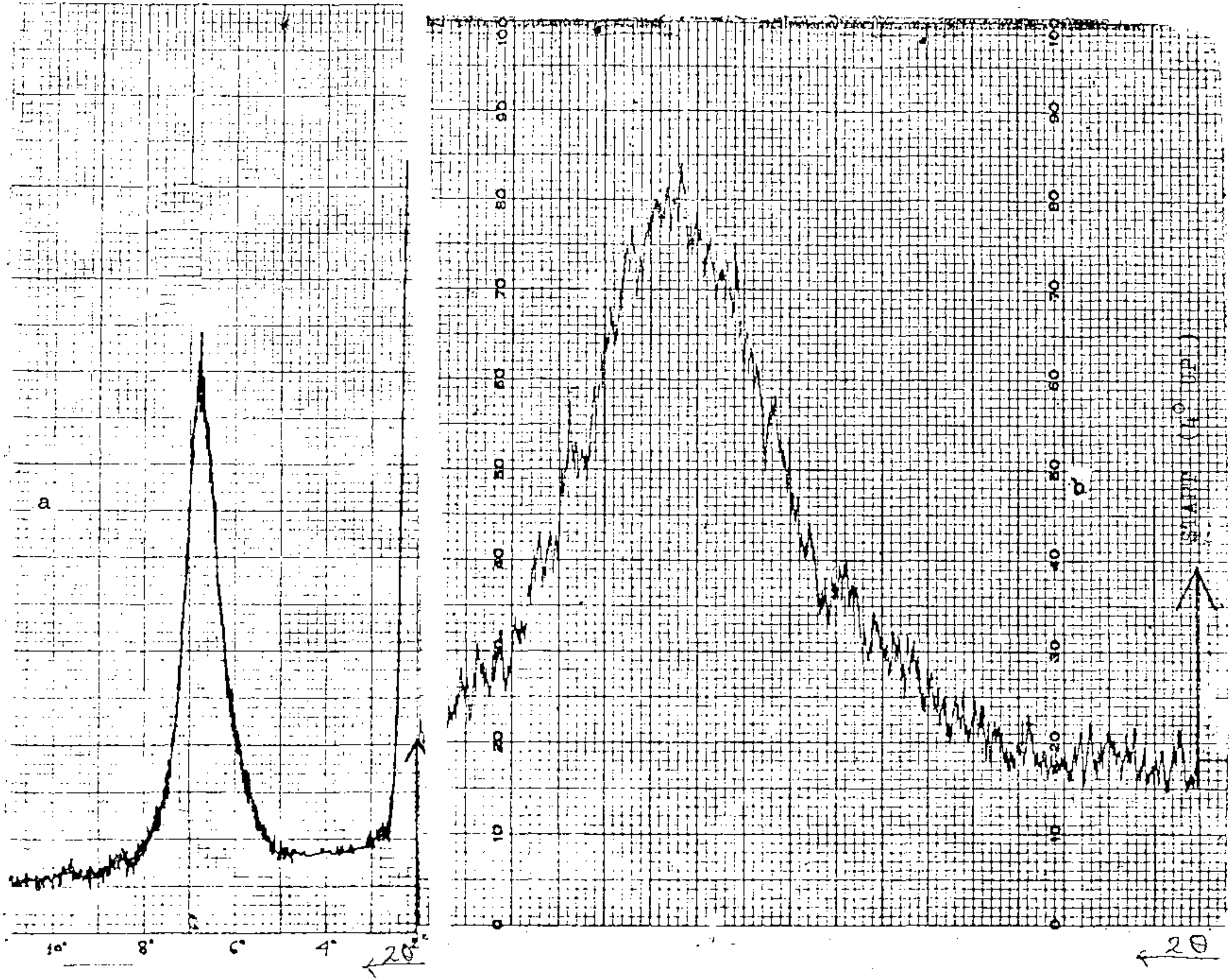


FIG.37X-RAY DIFFRACTION SPECTRA OF (a)35% SORBED DEMBT ONTO Na- MONTMORILLONITE (b) 25% SORBED DEMBT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS ;SCANNING RATE (a) 1°PER MINUTE AND (b) ¼° PER MINUTE).

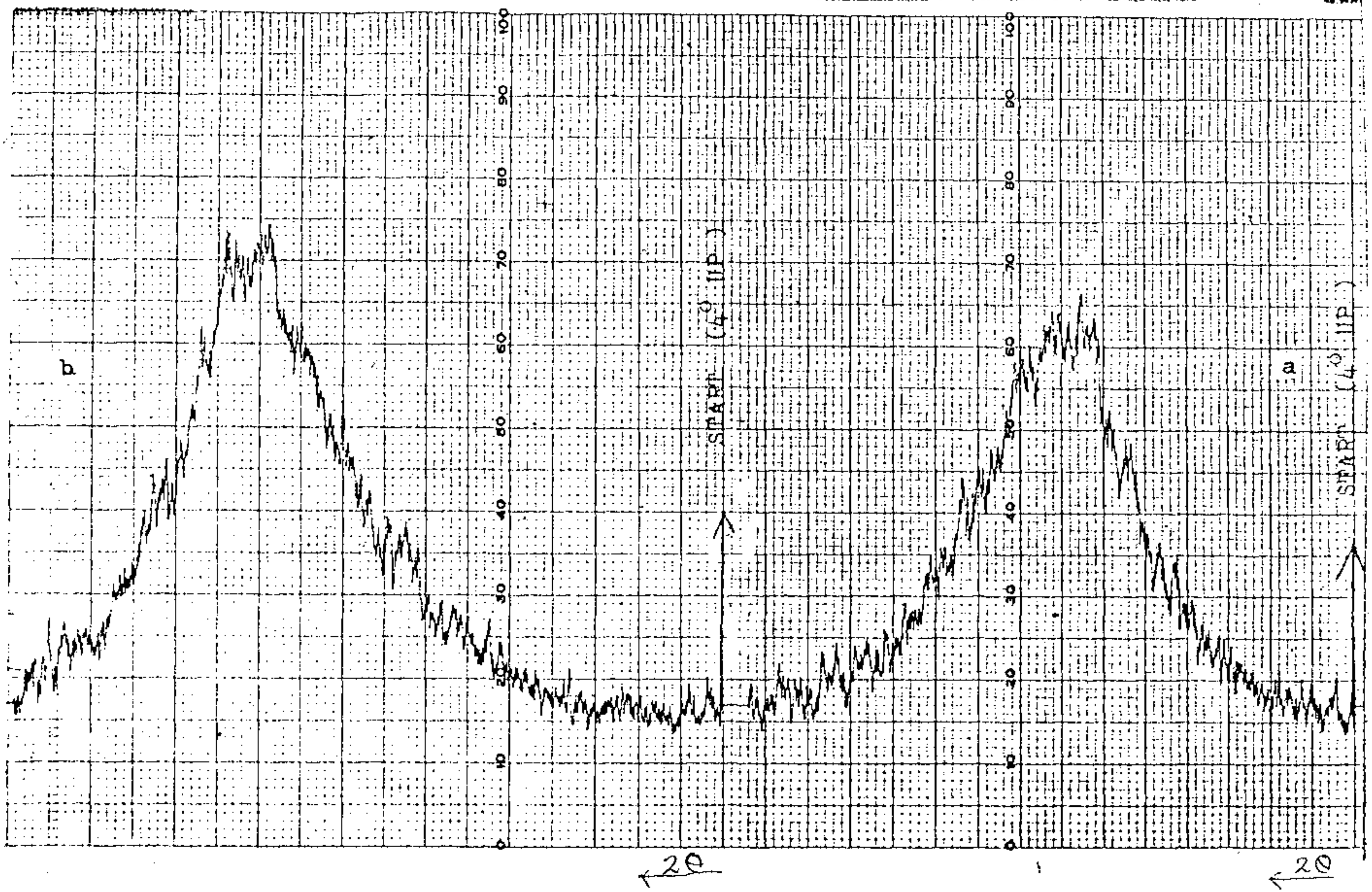


FIG.138 X-RAY DIFFRACTION SPECTRA OF (a) 100% SORBED DEMBT ONTO Na-MONTMORILLONITE (b) 50% SORBED DEMBT ONTO Na-MONTMORILLONITE (AFTER DRYING UNDER VACUUM AT 120° C FOR 24 HRS ; SCANNING RATE ¼° PER MINUTE).