The Mechanism of β-Carotene Adsorption on Activated Montmorillonite

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The variations in the structure of mineral during adsorption have been examined comparing the results of X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TG) and infrared (IR) spectroscopy of the acid activated montmorillonite clay mineral before and after adsorption of β-carotene. Based on the results, it was concluded that β-carotene attaches to the clay surface in the form of carbonium ions either by forming hydrogen bonds with Brönsted sites or by forming coordination bonds with Lewis sites of the activated clay mineral.

Acid activated montmorillonite type clay minerals are used as bleaching agents in processing edible oils (1, 2). In the previous paper (3), we studied the adsorption of β-carotene on activated clay from solutions in benzene, in order to understand the nature of bleaching which takes place in vegetable oils. It was observed that the white color of activated clay turned grey-blue immediately upon contact with the β-carotene solution. After filtration, the adsorbent was dried at room temperature and then washed with solvents of β-carotene such as benzene, carbon tetrachloride and acetone, but the grey-blue color of the adsorbent did not change and no coloring was observed in the liquid phases. This situation implied that a chemical reaction occurred on the clay surface during adsorption. Adsorption isotherms were characterized by the presence of two steps. The first step was of the Langmuir type, and the isosteric heat of adsorption corresponding to this step was found to be -193.514 kJ mol^{-1}. Furthermore, at the end of the adsorption, only a very small number of points on the clay surface gave an acidic color with a Hammett indicator, namely p-dimethylaminoazobenzene; the total number of acid sites on the surface decreased from 4.10×10^{-4} mol g^{-1} clay to 1.00×10^{-4} mol g^{-1} clay. In light of these results, it was concluded that the adsorption of β-carotene on the acid sites of the activated clay surface was probably chemical in nature.

In this study, the variations in mineral structure during adsorption have been examined by comparing the XRD, DTA-TG and IR results of the activated mineral before and after the adsorption of β-carotene, and the adsorption mechanism of β-carotene on activated clay surface is discussed.

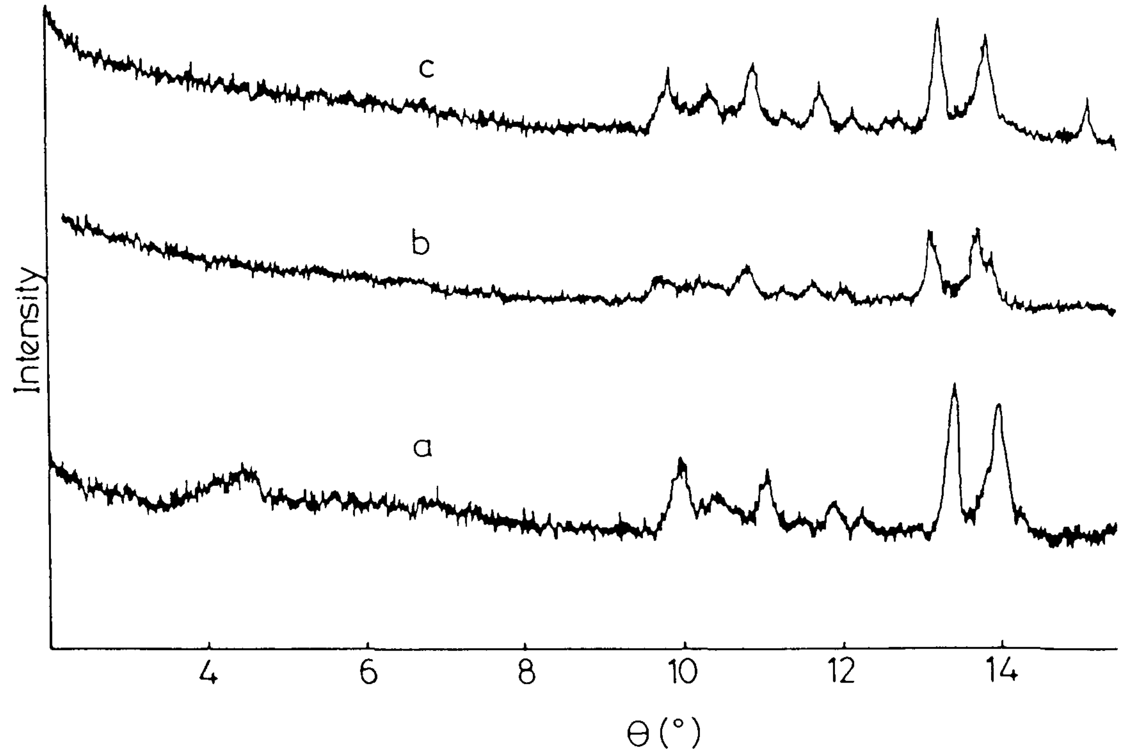

FIG. 1. XRD traces of (a) natural clay mineral of Çanakkale reserve; (b) activated mineral; (c) activated mineral after β-carotene adsorption.

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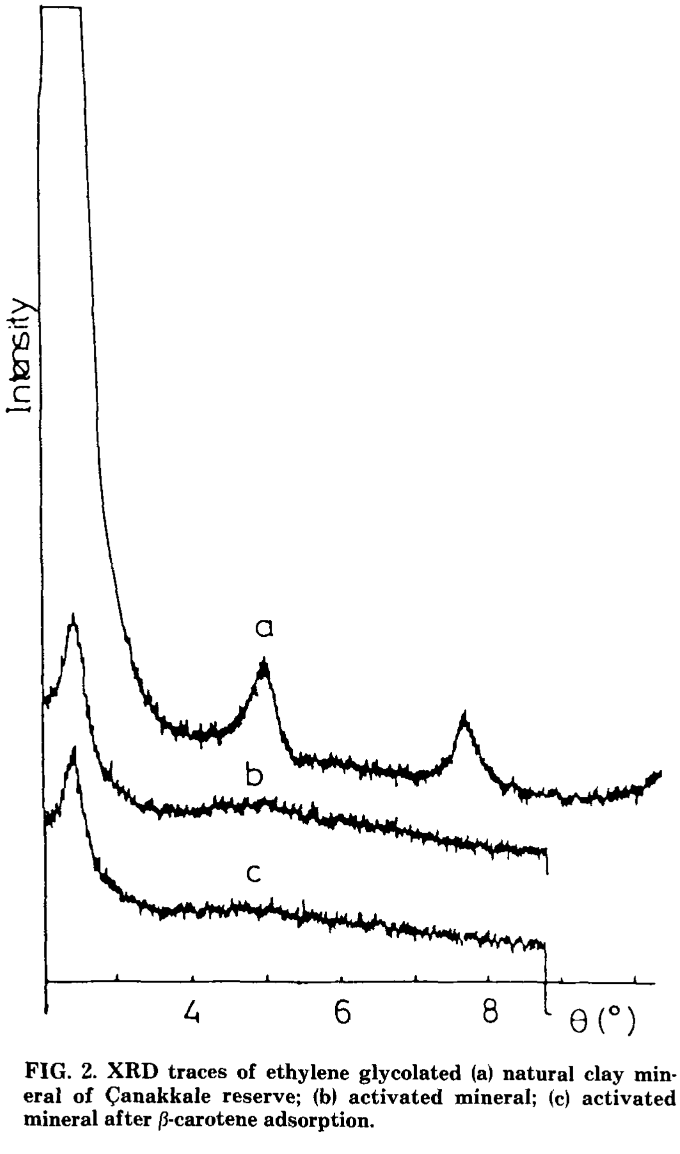


FIG. 2. XRD traces of ethylene glycolated (a) natural clay mineral of Çanakkale reserve; (b) activated mineral; (c) activated mineral after β-carotene adsorption.

EXPERIMENTAL

β-Carotene (Merck) solution was prepared with anhydrous benzene (Merck). The clay mineral of Çanakkale reserve of Turkey was activated with concentrated sulfuric acid at an acid/clay (ml/g) ratio of 0.2 at 150°C, followed by a drying process (4), and then it was used as an adsorbent (3).

X-ray diffraction patterns of the samples were recorded on a JOX-8P Jeol Diffractometer using Cu K_α radiation at 40 kV and 20 mA. Scanning was made in a 2θ range of 4–64° at a speed of 1° min^{-1}. The termal analyses were performed in a Netzsch DTA-TG instrument at a heating rate of 10 K min^{-1} and a paper speed of 120 mm hr^{-1}, using kaoline heated to 1200°C as inert material. The amount of sample was kept constant at 130.00 mg, and the temperature range investigated was from ambient to 1000°C.

For IR experiments, the sample was mixed with spectroscopic KBr (Merck) at a ratio of 0.02 and ground in an agate mortar. Then, ca. one g of this mixture was placed in a 15-mm die chamber, evacuated by means of a vacuum pump and pressed for 15 min under a pressure of 10 ton $inch^{-2}$; a transparent pellet was obtained. IR spectra of the pellets were taken using a Perkin Elmer Model 598 spectrophotometer.

RESULTS AND DISCUSSION

The clay mineral of Çanakkale reserve of Turkey can be defined as a mixed-layer illite-montmorillonite according to its XRD traces (Figs. 1a and 2a). In mixed-layer structures the basal reflections are composites of adjacent reflections of the same order of which the intensities vary with relative abundances of different individual layers (5, 6, 24–26). The first observed reflection is a composite of (001) of both layers at about 9.939 Å. The other reflections are a composite of (020) and (110) at 4.463 Å, (111) layer of illite, montmorillonite and quartz. A strong reflection appears at 3.315 Å. This reflection is a composite of third order of (006)

TABLE 1

θ Angles, d Spacings and I Values of Natural, Acid Activated and β-Carotene Adsorbed Clays[a].

Natural clay				Acid activated clay			β-Carotene adsorbed on clay		
θ(°)	d(Å)	I		θ(°)	d(Å)	I	θ(°)	d(Å)	I
4.45	9.939	1.3	I+M	—	—	—	—	—	—
9.95	4.463	2.1	I+M	9.70	4.577	1.0	9.85	4.507	1.8
10.42	4.264	1.2	I+M+Q	10.8	4.116	1.2	10.30	4.312	1.4
11.05	4.023	1.8	Cr	—	—	—	10.90	4.077	1.9
11.90	3.739	1.0	M	11.60	3.835	0.7	11.70	3.802	1.6
12.25	3.630	0.8	M	—	—	—	13.25	3.364	3.1
13.45	3.315	4.1	I+M+Q	13.10	3.403	2.0	13.85	3.221	1.2
14.00	3.187	3.6	M+F	13.75	3.245	1.9	15.10	2.959	1.2

[a] M, montmorillonite; I, illite; Q, quartz; Cr, crystobalite; F, feldspar.

layer of illite, (102) layer of quartz and montmorillonite. The results of XRD traces of powdered samples have been given in Figure 1 and Table 1.

The X-ray diffraction pattern of an ethylene glycolated sample provides a strong reflection composite of (001) of both layers at 18.041 Å and a broad reflection peak composite of (003) and (002) layers at 5.756 Å. These results are shown in Figure 2 and Table 2.

As a result of acid activation, the layered structure of mineral has been partly broken down; consequently, the 18.041-Å reflection of ethylene glycolated sample weakens. Furthermore, the 8.846-Å and 5.756-Å reflections disappear completely (Fig. 2b and Table 2). Moreover, some of the metal ions in the octahedral layer have been removed from the lattice during the acid leaching of mineral (5). Consequently, the reflections that characterize the individuality of mineral (6) decrease considerably in intensity (Fig. 1b).

When the XRD trace of the sample with adsorbed β-carotene is compared with the XRD trace of the same sample before adsorption (Figs. 1b and 1c), it can be said that the physical adsorption of β-carotene in the interlayered space does not happen. If the long-chain β-carotene molecule was adsorbed between the layers, the lattice would expand in the direction of the c-axis; so, in the XRD trace of the powdered sample, a peak at a high (Å) value could be observed. Such a reflection was not observed. Furthermore, the positions and intensities of the characteristic hk-bands of the mineral (Fig. 1c) and of the 18.041-Å reflection of the ethylene glycolated sample (Fig. 2c) remained almost unchanged.

The DTA curves and the data obtained from TG of the natural clay, the activated clay before and after β-carotene adsorption are shown in Figures 3-5 and Table 3, respectively. Comparison of the DTA peaks of natural clay with the DTA peaks of the acid activated clay shows that after acid activation the third endothermic peak shifted from 855°C to 890°C. This means there is some illite layer in the clay mineral (22, 23). In the DTA and TG curves of the sample with adsorbed β-carotene, the magnitude of the first endothermic peak increased at an important degree and the weight lost corresponding to this peak rose from 1.846% to 4.153%. Taking into consideration that the grey-blue color of the adsorbed sample did not change at this temperature, it might be said that the increase in magnitude of the first endothermic peak was due to the desorption of benzene, which was adsorbed in the pores of the clay during heating. While the sample was being heated, the adsorbed β-carotene exothermally decomposed with a maximum at 300°C. This exothermic peak appeared as a result of the oxidation of adsorbed β-carotene. During the exothermic reaction, the oxidation of hydrogen to water and of carbon to "pe-

TABLE 2

θ Angles, d Spacings, I and I/I_0 Values of Treatment of Natural, Acid Activated and β-Carotene Adsorbed Clays with Ethylene Glycol

Natural clay			Acid activated clay		β-Carotene adsorbed on clay	
θ(°)	d(Å)	I	I	I/I_0%	I	I/I_0%
2.45	18.041	20.0	5.0	25.0	4.5	22.5
5.00	8.848	3.0	—	—	—	—
7.70	5.756	1.5	—	—	—	—

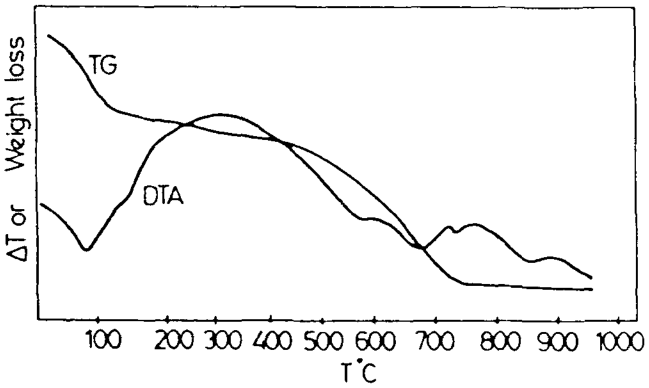


FIG. 3. DTA and TG curves of natural clay mineral of Çanakkale reserve.

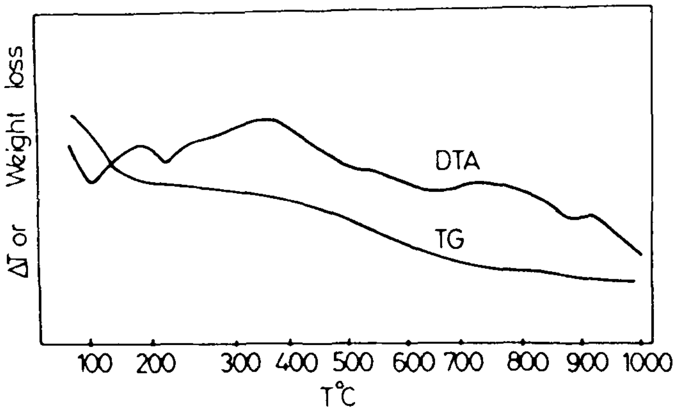


FIG. 4. DTA and TG curves of activated mineral before β-carotene adsorption.

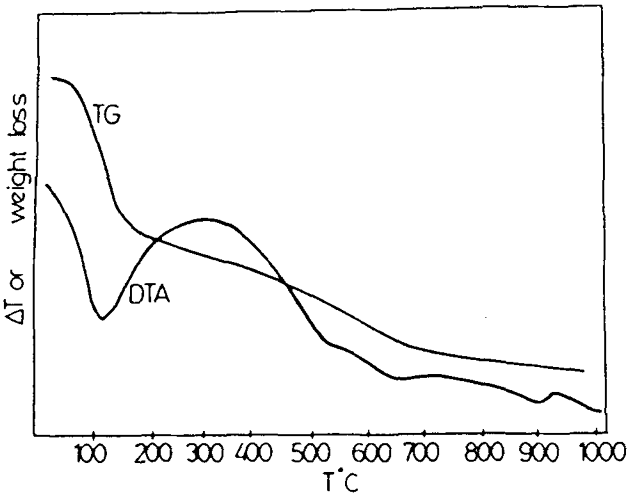


FIG. 5. DTA and TG curves of activated mineral after β-carotene adsorption.

TABLE 3

DTA and TG Results of Natural Clay and Activated Clay Before and After β-Carotene Adsorption

Sample	Peak range (°C)	Peak temp	Kind of reaction	Weight loss (%)
Natural clay	30—175	105	endothermic	1.923
	175—450	300	exothermic	0.846
		570	endothermic	
	450—745	670	endothermic	3.577
		725	endothermic	
	745—900	855	endothermic	0.115
Acid activated clay	30—180	105	endothermic	1.846
	180—475	220	endothermic	0.538
		320	exothermic	
	475—690	515	endothermic	1.577
		655	endothermic	
	690—930		endothermic	0.385
β-carotene on adsorbed clay	30—190	115	endothermic	4.153
	190—385	295	exothermic	0.769
	385—780	515	endothermic	2.308
		655	endothermic	
	780—930	890	endothermic	0.385

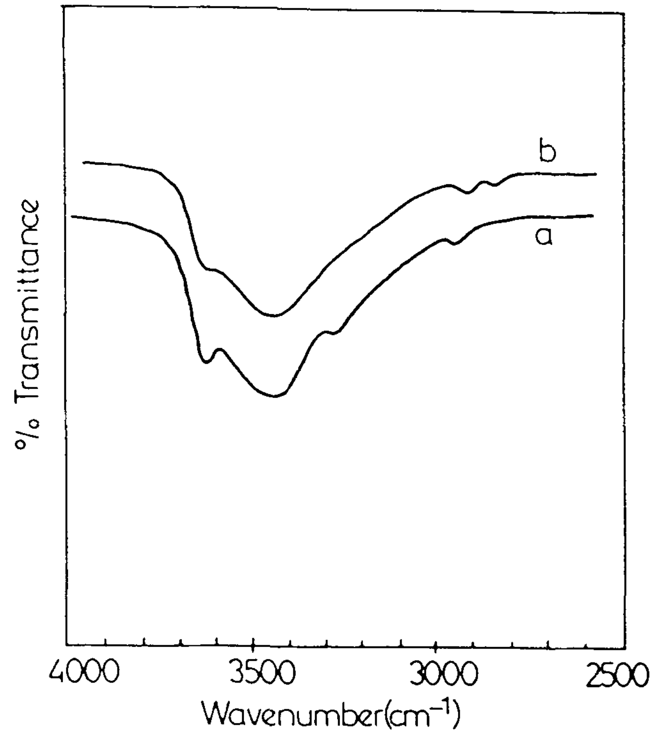


FIG. 6. IR spectra of activated mineral (a) before adsorption, and (b) after adsorption, in 4,000 cm^{-1}—2500 cm^{-1}.

troleum coke" occurred (7), and the color of the sample turned from grey-blue to black. The position and the magnitude of the dehydroxylation peak of the activated clay did not change after the adsorption of β-carotene, but the weight lost corresponding to this range increased from 1.577% to 2.308%. This situation shows that the oxidation of adsorbed β-carotene was completed at a higher temperature than the upper limit of the exothermic peak.

The IR spectra of the initial activated clay and of the clay with adsorbed β-carotene are shown in Figures 6 and 7. In the IR spectrum of acid activated mineral, the band at 3,610 cm^{-1} arises from the stretching vibrations of free hydroxyl groups in the octahedral layer, and the band at 3,400 cm^{-1} is due to the stretching vibrations of the H-bridged SiOH groups and of interlayer water (8, 9). Also, the band at 1,620 cm^{-1} is correlated with the bending vibrations of the latter groups (Figs. 6a and 7a). After the adsorption of β-carotene, the absorption bands in the range 3,700 cm^{-1} —3,200 cm^{-1} became narrow and their intensities decreased (Fig. 6b). Because β-carotene is not adsorbed between the sheets of the mineral, it cannot reach the octahedral layer through the interlayer space. During acid leaching, the cleavages are formed on the edges of the octahedral layer. If β-carotene is adsorbed near these cleavages, it prevents the free vibration of octahedral hydroxyl groups; it appears that the 3,610 cm^{-1} band became smaller as a result of this effect. The band at 3,400 cm^{-1}, which is attributed to the hydrogen-bonded SiOH groups and the interlayer water, shifted to 3,440 cm^{-1}; its magnitude and intensity decreased considerably (Fig. 6b). Also, the 1,620 cm^{-1} band of these groups became smaller (Fig. 7b). These variations suggest that the hydrogen ions of the SiOH groups have reacted with the sorbed β-carotene, and the amount of them in the activated mineral structure has decreased (10).

IR spectra of the activated montmorillonite show the characteristic absorption bands in the range of 1,400 cm^{-1} cm^{-1} 400 corresponding to the Si-O and Si-O-R (R is an ion such as Al^{3+} or Fe^{3+} which the coordinate number is 6) vibrations (8). These bands are broad and strong, due to the decrease in the structural order the destruction of charge balance of mineral, and the formation of Si-OH groups during acid activation (11, 12). At the end of the β-carotene adsorption, the half-widths and the intensities of all those bands have decreased (Fig. 7b). Therefore, it can be said that the mineral lattice has gained a more ordered situation as

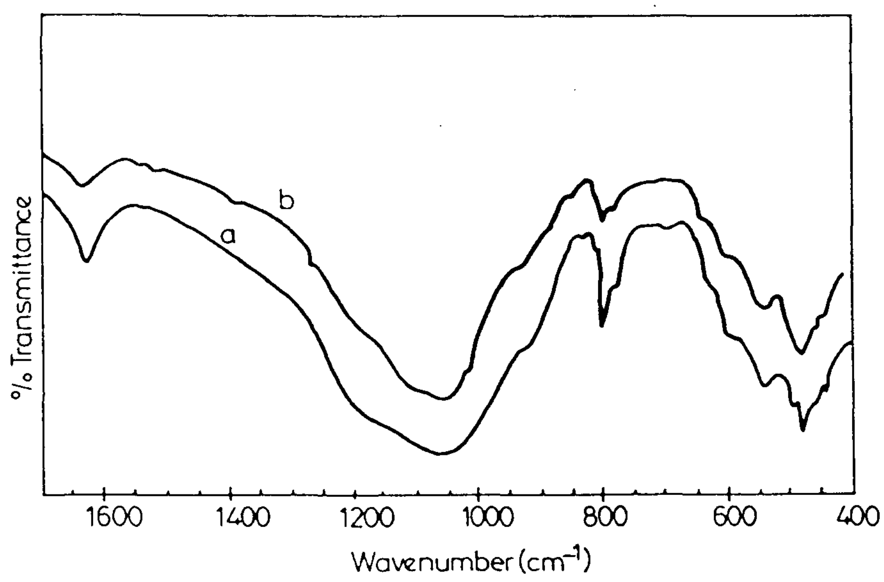


FIG. 7. IR spectra of activated mineral (a) before adsorption, and (b) after adsorption, in 1,600 cm^{-1}—400 cm^{-1}.

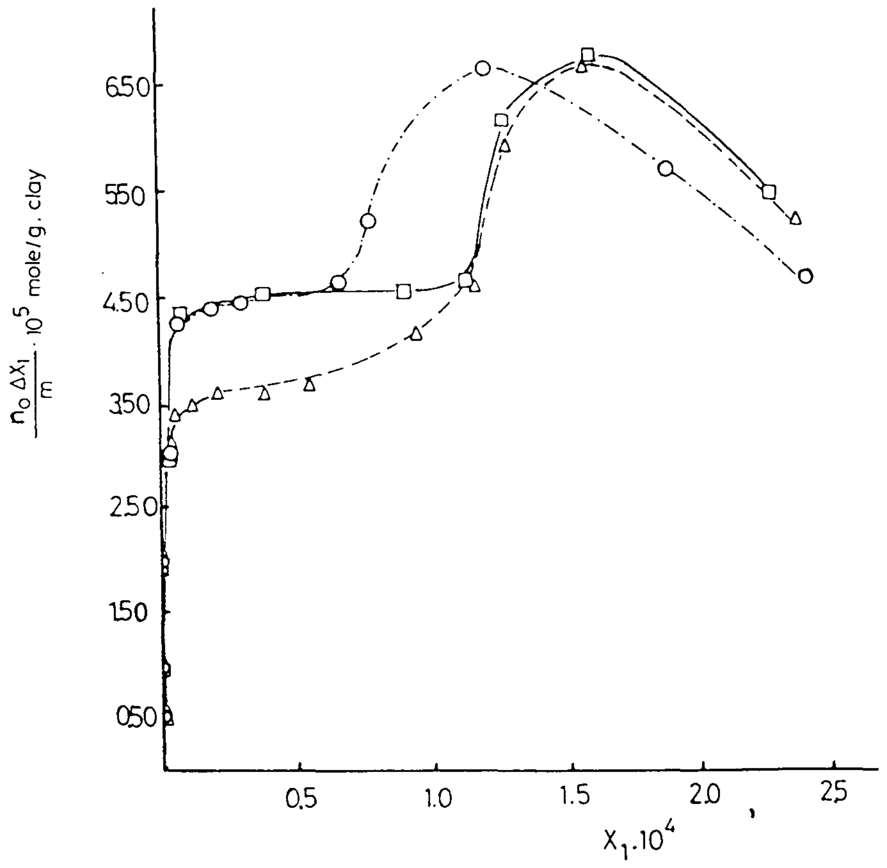
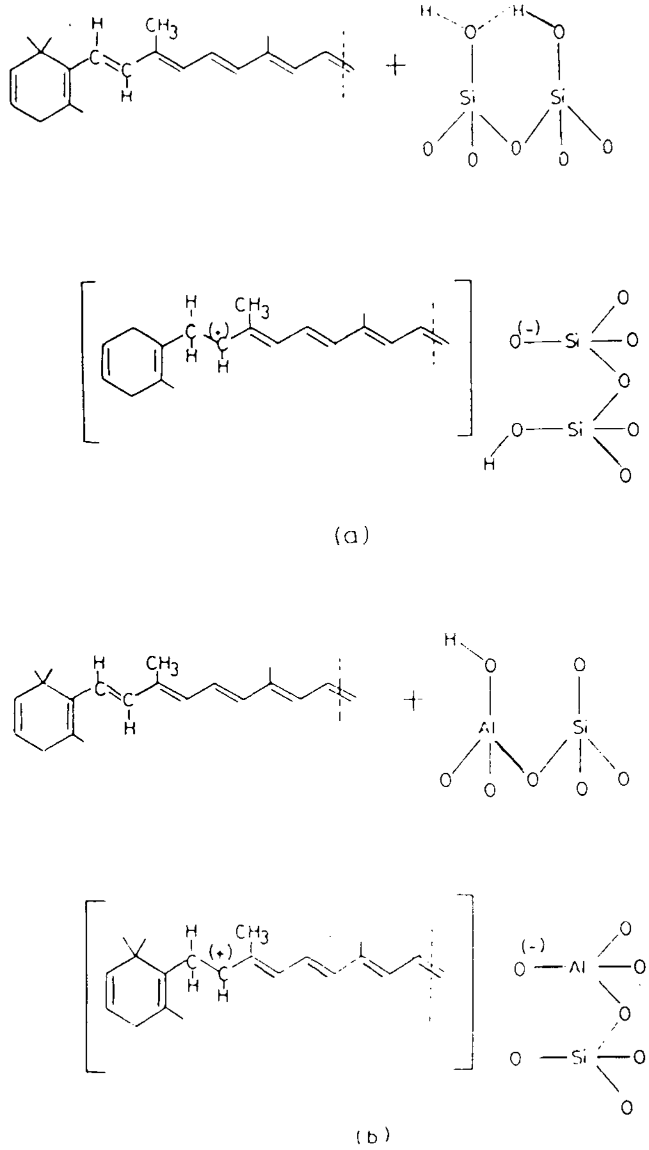


FIG. 8. Apparent adsorption isotherm of β-carotene by activated Çanakkale clay mineral at a temperature of 30°C, (○); 35°C, (□); 40°C, (△) (Ref. 3).



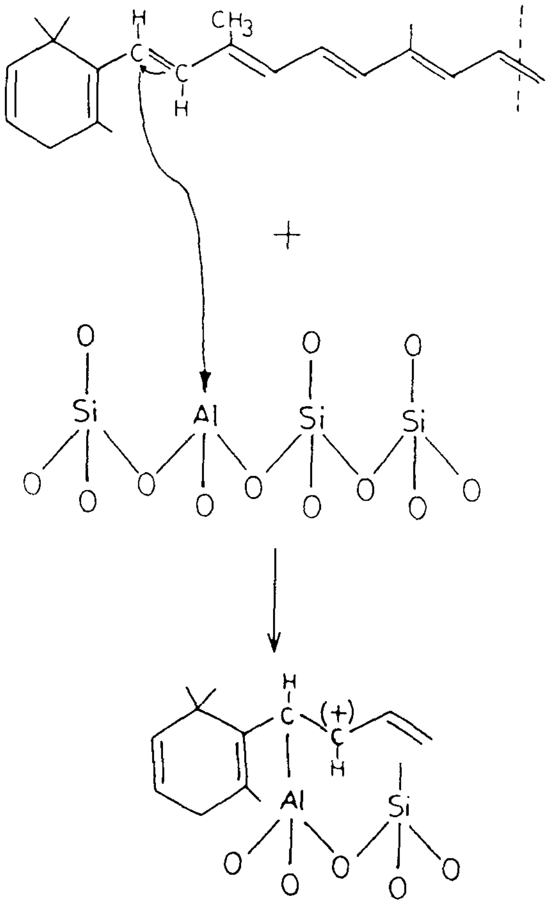
SCHEME 1. The chemisorption of β-carotene on Brönsted acid sites.

a result of β-carotene adsorption. In addition, β-carotene may set up a charge balance in the mineral lattice by reacting with acid sites and silanol groups of the acid activated clay surface.

After adsorption of β-carotene, the surface acidity of activated clay decreases from 4.10 × 10^{-4} mol g^{-1} to 1.00 × 10^{-4} mol g^{-1}, i.e., 75% of the acidity sites have been occupied by β-carotene (5).

Heat of adsorption of β-carotene is −193.514 kJ mol^{-1} (3). Based on these results it can be deduced that β-carotene reacts with Lewis and Brönsted acid sites on the activated clay surface.

In light of the above reasoning the following reaction mechanisms have been proposed. In β-carotene, energy of the highest occupied molecular orbital is 5.356 kJ mol^{-1}, and the energy of the lowest empty molecular orbital is −12.050 kJ mol^{-1} (13). These values indicate that β-carotene is both an excellent electron donor and an excellent electron acceptor. In addition, it is known that the most reactive bond in β-carotene is the 7-8 double bond, and the main reactive center of the molecule toward any type of attack is the seventh carbon atom according to electrical charge, bond order, free valance and carbon localization energy values of the molecule (13). Therefore, it may be said that β-carotene reacts with acid centers of the activated clay surface by means of its seventh carbon atom. The molecule may be adsorbed on the surface either by forming a hydrogen bond with Brönsted sites (Scheme 1) or by forming a coordination bond with Lewis sites (Scheme 2). Thus, β-carotene attaches to the surface in the form of a carbonium ion. This ion is fairly stable and can be decomposed only when it is heated to 250-300°C (14-19). By taking into consideration that the adsorption isotherm has two steps (Fig. 8), it may be said that when the amount of β-carotene in solution increases, a second layer of β-carotene is adsorbed on the first layer, which is chemi-



SCHEME 2. The chemisorption of β-carotene on Al and/or Si atoms of Lewis acid sites.

sorbed as carbonium ions (3). In this event, β-carotene seems to show a nucleophilic character, and ion-dipole interaction (20, 21) seems to take place between the nucleophilic β-carotene and the carbonium ion layer. Because ion-dipole interactions are stronger than long-range physical bonds (7), it appears that the desorption of the second layer from the surface also is not easy.

Studies on the mechanism of β-carotene chemisorption on the activated clay surface are in progress.

REFERENCES

1. Mag, T.K., *J. Am. Oil Chem. Soc 50*:251 (1973).
2. Richardson, L.L., *Ibid. 55*:777 (1978).
3. Sarier, N., and Ç. Güler, *Ibid, 65*:776 (1988).
4. Heyding, R.D., R. Ironside, et al., *Can. J. Chem. 38*:1003 (1960).
5. Sarier, N., Ph.D. Thesis, Ege University, Izmir, Turkey, 1986.
6. Fang, J.H., and F.D. Bloss, *X-ray Diffraction Tables*, Southern Illinois University Press (1966).
7. Yariv, S., *Thermochimica Acta 88*:49 (1985).
8. Farmer, V.C., and J.D. Russell, *Spectrochimica Acta 20*:1149 (1964).
9. Hair, M.L., *Infrared Spectroscopy in Surface Chemistry*, 79–137, Marcel Dekker Inc., New York, NY, 1967, pp. 79–137.
10. Killmann, E., and M. Bergmann, *Colloid Polym. Sci. 263*:372 (1985).
11. Ovcharenko, F.D., *Kolloidnyi Zhurnal 35*:367 (1973).
12. Mapes, J.D., and R.P. Eischens, *J. Phys. Chem. 58*:1059 (1954).
13. Pullman, B., and A. Pullman, *Quantum Biochemistry*, Interscience Publishers, New York, 1963.
14. Hall, W.K., *J. Catalysis 1*:53 (1962).
15. Leftin, H.P., and W.K. Hall, *Ibid. 65*:1353 (1963).
16. Holm, V.L.F., and A. Clark, *Ibid. 2*:16 (1963).
17. Hirshler, A.E., and J.O. Hudson, *Ibid. 3*:239, (1964).
18. Satterfield, C.N., *Heterogeneous Catalysis in Practice*, McGraw Hill, New York, NY, 1980.
19. Thomas, J.M., and W.J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, London, 1981.
20. Pauling, L., *The Nature of The Chemical Bond*, Cornell University Press, New York, NY, 1960.
21. Martin, M.J.S., and M.S. Camazano, *J. Agric. Food Chem. 32*:720 (1984).
22. Sarier, N., and Ç. Güler, *Thermochimica Acta 119*:293, (1987).
23. Cole, W.F., and J.S. Hoskin, in *The Differential Thermal Analysis Investigation of Clays*, edited by Mackenzie, 1966, pp. 248–274.
24. Weaver, C.E., *Am. Mineralogist 41*:202 (1956).
25. Stout, G.H., and L.H. Jensen, *X-ray Structure Determination*, MacMillan Co., New York, NY, 1968, pp. 31–37.
26. Barhad, I., *Clays and Clay Minerals:* Proc. 7th Natl. Conf. Pergamon Press, London, 1960, pp. 350–363.

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