♣β-Carotene Adsorption on Acid-Activated Montmorillonite

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The adsorption of β-carotene from solution in benzene on acid-activated Canakkale montmorillonite of Turkey has been investigated. The adsorption isotherm had two steps. The first step was of the Langmuir type, and the isosteric heat of adsorption corresponding to this step was equal to -193.514 kJ/mol. The decrease in the total number of acid sites of the clay surface was determined to be 0.45×10^{-4} mol/g clay by nonaqueous titration with diethylamine. The phenomenon seems to be mainly a chemisorption stemming from the interaction of β-carotene with acid sites. Also, the activated clay acts as an oxidation catalyst on the β-carotene left in the solution.

Several ideas have been proposed about the bleaching of vegetable oils with an activated clay (1-3). It is not certain whether the adsorption is a physical process (4) or a chemical one (5,6). With the aim of elucidating the function of the activated clay during bleaching, the adsorption of β-carotene from benzene solution by acid activated montmorillonite was studied.

EXPERIMENTAL

The β-carotene (Merck) solutions were prepared with anhydrous benezene (Merck). The activated clay used as adsorbent was prepared from montmorillonite mineral of Canakkale reserve of Turkey (7). The clay mineral was activated with concentrated sulphuric acid at an acid/clay (mg/g) ratio of 0.2 and temperature of 150 C followed by a drying process (8). The product was mixed with water while hot, filtered, and washed to a pH of 3.0-3.5. The filtercake was dried overnight at 110 C, ground to -50 microns and stored in a desiccator.

Experiments were carried out under a nitrogen atmosphere at a flow rate of 30 ml/min. To establish the thermal equilibrium and remove the free oxygen from the system before adsorption, the solutions were allowed to stand 10 min in the flask at a constant temperature under nitrogen atmosphere; the activated clay at 2% of solution weight was then added to the solution. The contents of the flask were stirred continuously at 250 rpm for 30 min. After the adsorption, the solution-adsorbent mixture was permitted to settle one min, and a few milliliters of the supernatant solution were pipetted out and diluted to the appropriate concentration if it was necessary. Then, the absorption spectrum was obtained immediately using a Pye-Unicam SP 800 UV-Vis. spectrophotometer with the reference of pure benzene. The amount of β-carotene in the supernatant solution was determined from an absorbance-concentration calibration curve.

The concentrations of β-carotene solutions were in the range of 50-2,000 ppm. Experiments were repeated at 30 C, 35 C and 40 C. Adsorption isotherms were plotted with the help of Genstat Statistical Computer Program.

RESULTS AND DISCUSSION

Reaction in solution. The absorption spectrum of β-carotene in benzene solution which is ruby in color appears in the visible region and gives a maximum at 464 nm with two shoulders at 490 nm and 440 nm (Fig. 1). After adsorption on clay, the solutions which had initial concentrations of 250 ppm or greater turned light yellow. The absorption peaks at 464 nm and 490 nm shifted 10 nm lower, respectively, to 454 nm and 480 nm and decreased in intensity (Fig. 1). Also, the shoulder at 440 nm disappeared completely. When the initial solution had a concentration smaller than 250 ppm, no distinct absorption spectrum could be obtained, because almost all of the carotene was adsorbed from solution by activated clay. On the other hand, the activated clay which originally was white turned to a grey-blue color. After filtration, the adsorbent was dried at room temperature and washed with solvents of β-carotene such as benzene, carbon tetrachloride and acetone but its new color did not change; also, the solvents did not gain any spectrophotometrically observable color. Hence, β-carotene adsorbed under these conditions is chemisorbed.

After adsorption, the variations in both the absorption spectrum of the supernatant solution and the color of the adsorbent show that two events happen during the adsorption of β-carotene on the activated clay. Although β-carotene is adsorbed on the clay surface by some chemical interactions, β-carotene which remains in solution is affected by clay and takes on a new form. This new form appears to be due to oxidation (5) of β-carotene.
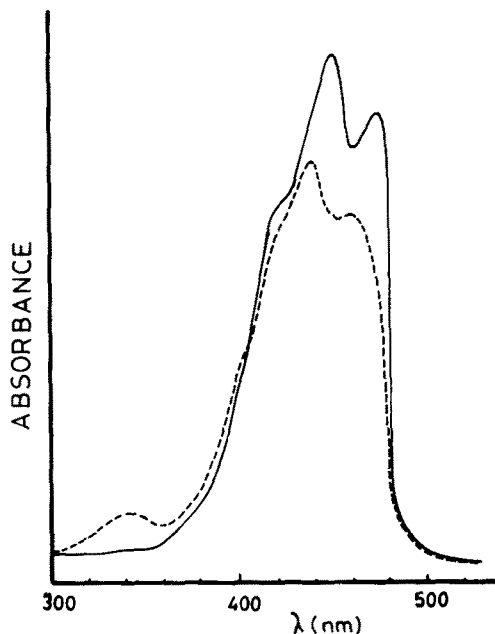

FIG. 1. Absorption spectrum of (a) β-carotene in benzene before adsorption, supernatant solution of β-carotene after adsorption at (b) 30 C, (c) 35 C, (d) 40 C.

In order to understand the type of conversions in the solution during adsorption, the following experiments were made: β-carotene in benzene solution of 200 ppm was prepared and held at room temperature in the presence of oxygen in the dark for 24 hr. The solution turned greenish yellow. In the absorption spectrum, the positions of the peaks at 464 nm, 490 nm and 440 nm didn't vary, but the intensities of them decreased. In the meantime, four new peaks at 405 nm, 350 nm, 335 nm and 280 nm appeared (Fig. 2). When the same 200 ppm solution was left in the presence of O_2 for 48 hr, the peaks in the range of 490-440 nm, characteristic of β-carotene, changed and their intensities decreased rapidly. On the other hand, the new peaks which appeared at 405 nm, 335 nm and 280 nm became more distinct and their strength increased (Fig. 2). It is known that β-carotene easily converts to an aldehyde as a result of oxidation, and new peaks appear around 405 nm and 335 nm in its absorption spectrum (9). Also, the carbonyl group has a chromophore that appears at 280 nm (10). Therefore, it can be concluded the new peaks mentioned above were due to the oxidation of β-carotene in the presence of oxygen. If β-carotene in supernatant solution is oxidized during adsorption, the adsorption spectrum will be similar to the spectrum in Figure 2. However, immediately after the adsorption, in the absorption spectrum of the supernatant solution
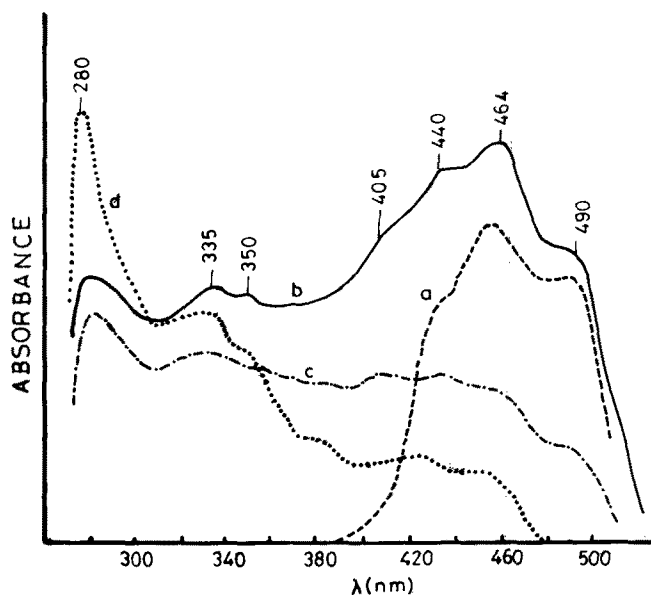

FIG. 2. UV-vis absorption spectrum of (a) fresh β-carotene in benzene solution; (b) β-carotene solution stored 24 hr in oxygen; (c) β-carotene solution stored 48 hr in oxygen; (d) supernatant β-carotene solution stored four hr in a closed flask at room temperature after adsorption at 30 C.
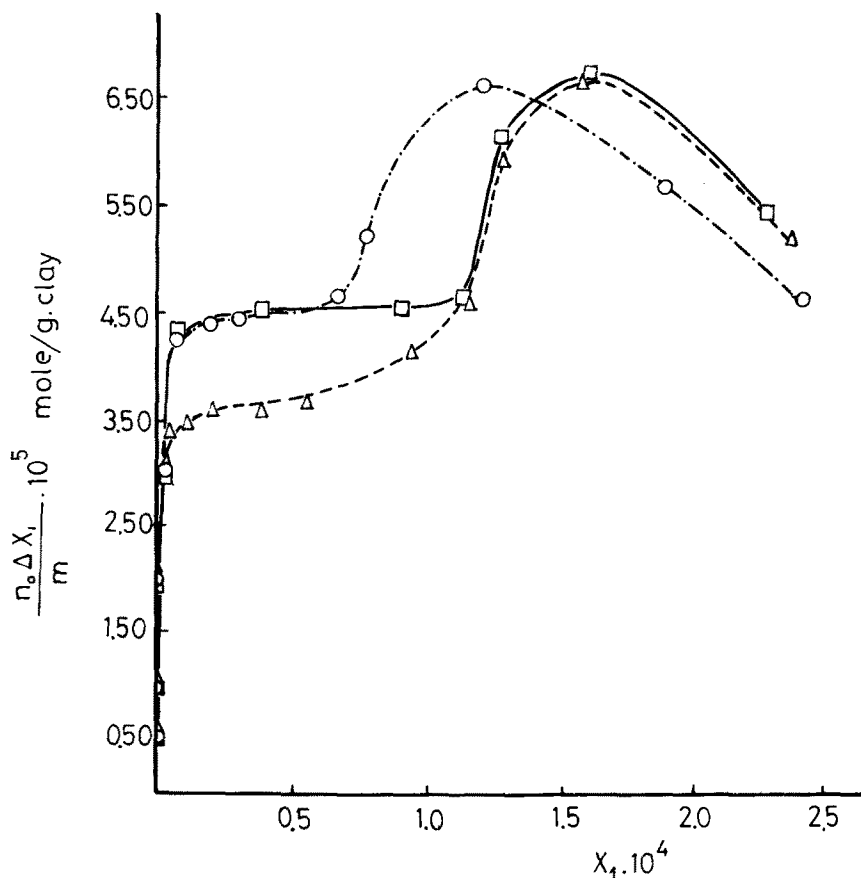

FIG. 3. Apparent adsorption isotherm of β-carotene by activated Canakkale montmorillonite at (O) 30 C; (□) 35 C, and (△) 40 C.

the new peaks mentioned above were not observed. When the same supernatant solution was left four hr in air after adsorption, its absorption spectrum was similar to the spectrum of β-carotene solution left 48 hr in oxygen. In addition, the intensities of the 335 nm and 280 nm peaks of the former were greater than those of the latter (Fig. 2). In light of these results, it is seen that in the absence of oxygen an activated clay has not caused an observable oxidation in β-carotene solution during adsorption; but unadsorbed β-carotene has been oxidized rapidly later on, even more than the solution which stood in oxygen for 48 hr. For this reason, it may be said that the activated clay initiates the oxidation of unadsorbed β-carotene. The oxidative catalyst effect of activated clay in this reaction may arise from its surface acid sites.

Apparent adsorption isotherm. Apparent adsorption curves were obtained by plotting the number of moles adsorbate/g of adsorbent ($n_0 \Delta X/m$) vs the mole fraction of β-carotene in the supernatant fluid (X_1) where n_0 is the total number of moles of initial solution, ΔX_1 is the difference between the mole fraction of β-carotene in solution before and after adsorption, and m is the amount of adsorbent (11). As seen in Figure 3, isotherms are of the high affinity type with a steep initial slope, so that benzene offers no competition for the surface in dilute solution. Adsorption isotherms are characterized by the presence of two stages, indicating that the adsorption goes on after the formation of a monolayer. According to the isotherm, the first stage of adsorption was completed at the solution concentration of about 600 ppm, which is greater than the amount of β-carotene in vegetable oils (3). The first step of isotherm is of the Langmuir type, and this situation implies that the adsorption starts with chemical interactions (12). After a plateau the curves rise suddenly, reach a maximum and then decrease rapidly. This decrease occurs as a result of solute-solvent competition for the surface in concentrated solutions (11).

Isosteric adsorption heat. To determine the isosteric heat of adsorption of β-carotene on activated montmorillonite, van't Hoff's integrated equation can be applied to the adsorption curves (13):

$$\Delta H(iso) = R \, (\ln C1 - \ln C2)/(1/T1 - 1/T2)$$

Where C1 and C2 are the equilibrium concentration of the isotherms at temperatures T1 and T2, corresponding to an equivalent amount adsorbed (C). Results are shown in Table 1. The enthalpy change related to the first stage of adsorption is -193.514 kJ/mol. This value is approximately five times greater than the lower limit of chemisorption, which is 42 kJ/mol (12). In the mean-

TABLE 1

The Isosteric Heats of Adsorption Corresponding to the Two Steps of Adsorption Isotherm in Fig. 3

Adsorbed amount (mol/g clay)	X_1 at 303 K	X_1 at 313 K	ΔH (iso) (kJ/mol)
4.25×10^{-5}	8.30×10^{-6}	9.66×10^{-5}	-193.514
6.50×10^{-5}	1.22×10^{-4}	1.60×10^{-4}	-21.376

time, the apparent activation energy of β-carotene-activated clay reaction was determined as 41.84 kJ/mol (5). The magnitudes of isosteric adsorption heat and apparent activation energy also suggest that the adsorption of β-carotene on activated clay is due essentially to chemical interactions. The heat of adsorption corresponding to the second step of isotherm has been found to be -21.376 kJ/mol, and this implies that the adsorption at this stage is not chemical in character.

Surface acidity. The surface acid strength of the activated clay sample of Canakkale reserve was measured as $H_0 < -0.29$ by using Hammett indicators (14). The total number of acid sites on the surface was determined to be 4.10×10^{-4} mol/g clay by nonaqueous titration with diethylamine (15). The results are shown in Table 2. During the first step of the adsorption, only a very small number of points on clay surface washed three times with benzene before titration gave an acidic color with an indicator, namely p-dimethylamino-azobenzene (pK = +3.30). Since the adsorbed sample had a gray-blue color, the indicators with smaller pK values could not be used. The number of acid sites for p-dimethylaminoazobenzene was reduced to a value of 1.00×10^{-4} mol/g clay. The decrease in the number of acid centers is equal to 0.45×10^{-4} mol/g clay. This value is the same order of magnitude as the amount of adsorbed β-carotene in the first step of adsorption isotherm, which is 0.45×10^{-4} mol/g clay. The surface acidity data suggest that the strongly acid sites on clay surface react with β-carotene during adsorption. As a consequence, it seems that the adsorption of β-carotene on the activated clay is mainly a chemical process stemming from the interaction of β-carotene with the Lewis and Bronsted acid sites of clay, a great majority of which are formed during the acid leaching of the mineral. It also appears that the activated clay affects the β-carotene left in the solution as an oxidation catalyst. Our proposals about the mechanism of chemisorption of β-carotene on activated clay will be discussed later.

TABLE 2

The Numbers of Acid Center of Acid-Activated Clay for Various H_0 Values

H_0	(6.8)-(3.3)	(3.3)-(0.8)	(0.8)-(-0.29)	<-0.29	Total
Acid-activated clay (10^{-4} mol/g clay)	1.45	0.65	1.80	0.20	4.10

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