An Infrared Spectroscopy Study of Lipid Adsorption from Hexane onto an Acid-Activated Bleaching Clay

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ABSTRACT: The mode of adsorption of oleic acid (OA) (0.05 M), triglyceride (TG) (0.05 M) and phosphatidylcholine (PC) (0.5 mM) from hexane solution onto 0.5 g of an acid-activated bleaching clay was investigated using diffuse reflectance Fourier transform infrared spectroscopy. OA was mostly weakly adsorbed by bound water, with some OA adsorbed to silanol sites through carboxyl carbonyl groups. TG was hydrogen- bonded to surface silanol groups through ester carbonyl groups. The CH_2 stretches indicated that TG was oriented perpendicular or at an angle to the surface. PC phosphate groups were bound by the surface moisture with little interaction with silanol groups. The adsorption mechanism of these lipids contrasts with the adsorption of carotenoid and chlorophyll under the same conditions. These pigments are bound by chemisorption, with catalytic modification often occurring before adsorption.
JAOCS 74, 1265–1268 (1997).

KEY WORDS: Hexane, oleic acid, phosphatidylcholine, triglyceride.

Bleaching by adsorption is an important step in the commercial refining of triglyceride (TG) vegetable oils. This is traditionally accomplished by adsorbing pigments on acid-activated montmorillonite aluminosilicate clay. The adsorption occurs at 100°C under low pressure when carotenoid and chlorophyll pigments and residues of previous refining steps, such as phospholipids and fatty acids, are bound by the clay surface (1). Morgan *et al.* (2) described the adsorption of β-carotene from vegetable oil onto clay surface cations as a chemisorbed complex. The pigment then can undergo reaction with the clay's surface protons, formed previously by acid activation. Brønsted acid centers are formed if surface metal ions cause dissociation of chemisorbed water.

Feuge and Janssen (3) investigated the use of bleaching clay to adsorb pigments from vegetable oil in hexane solution at ambient temperature, i.e., miscella refining, to allow bleaching at lower temperatures. The mechanism of binding of carotenoids and chlorophylls from organic solvents at ambient temperatures has been reported (4–6). Sarier and Guler (4) reported that adsorption of β-carotene by acid-activated clay from benzene solution shifted absorbance peaks from 464 to 454 nm and from 490 to 480 nm. This was caused by β-carotene reacting with clay acid sites. Sarier and Guler (5) suggested that β-carotene was adsorbed from benzene solution onto activated montmorillonite in the form of a carbonium ion by hydrogen bonding to Brønsted acid sites or by coordination with Lewis acid sites. Chlorophyll adsorption from hexane solution to acid-activated clay is also reported to occur on Brønsted acid clay sites (6).

While much work has been done in studying carotenoid binding to bleaching clay from organic solvents, the nature of binding of other minor crude oil components, also removed from oil during adsorption bleaching, has not been studied. Recently, diffuse reflectance Fourier transform infrared spectroscopy (FTIR) has been useful in determining the adsorption mechanisms for binding of oleic acid (OA) (7,8), TG (9), and phospholipid (10) onto silica from hexane solution.

The objective of this study was to use diffuse reflectance FTIR to examine the mode of adsorption of OA, TG, and phosphatidylcholine (PC) onto a commercial bleaching clay from hexane solution at room temperature.

MATERIALS AND METHODS

Lipids, solvents, and adsorbents. OA (Sigma Chemical Co., St. Louis, MO), PC (Sigma Chemical Co.), refined soy TG oil (Procter & Gamble, Cincinnati, OH), high-performance liquid chromatography (HPLC)-grade hexane (Fisher Scientific Co., Fairlawn, NJ), and an acid-activated bleaching clay (BC), F-160, 4% moisture (Engelhard Catalysts and Chemicals Division, Jackson, MS) were used.

Adsorbent structure. A Mattson FTIR instrument (Mattson Instruments Inc., Madison, WI) with a diffuse reflectance unit 0300-002 (Barnes Analytical, Stanford, CT) was used. A hundred scans were co-added with a resolution of 4 cm^{-1} (7–10). The spectral data were interpreted by examining the literature values of infrared absorption (11,12). This procedure for obtaining diffuse reflectance FTIR data was used throughout this study. A diffuse reflectance FTIR spectrum of BC was determined, which was used to subtract from spectra of adsorption experiments.

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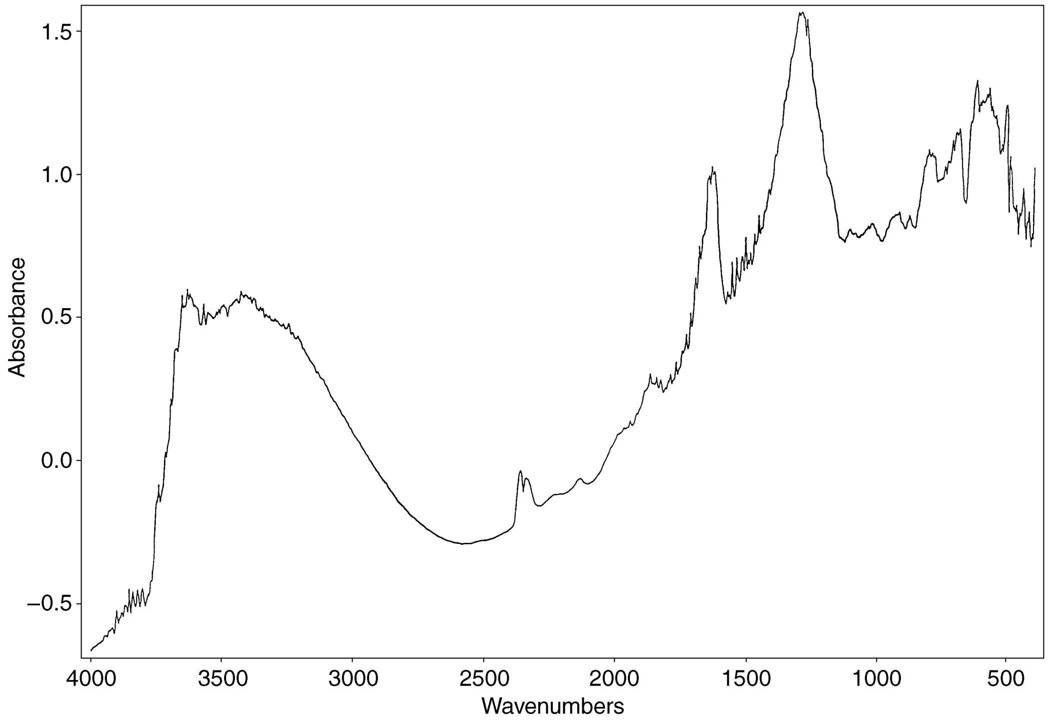

FIG. 1. The Fourier transform infrared spectroscopy spectrum of acid-activated bleaching clay. One hundred scans were co-added with a resolution of 4 cm^{-1}.

Lipid adsorption. The methodology used was that of Adhikari *et al.* (7,8,10). BC (0.5 g) was stirred in 100 mL of either 0.05 M OA, 0.05 M TG, or 0.5 mM PC in hexane solution, in a glass-stoppered flask for 15 min at 22°C. The BC was recovered by decanting and evaporating the supernatant solvent in an air-flow hood for 15 min. The diffuse reflectance FTIR spectrum of each BC sample was obtained, as described earlier, and corrected for the background spectrum of the BC.

RESULTS AND DISCUSSION

Figure 1 shows the diffuse reflectance FTIR spectrum of BC. A broad OH stretch is present between 2800–3800 cm^{-1} and an OH bending vibration at 1634 cm^{-1}. Similar results were observed with bound water adsorbed on silicic acid (7,8). The free OH peak at about 3747 cm^{-1} was similar to that of silicic acid (7,8). Skeletal Si-O and Al-O vibrations were evident below 1300 cm^{-1}, as seen in silicic acid (7,8). There were many similarities between the FTIR spectra of silicic acid and bleaching clay, despite differences in crystal structure and composition.

Figure 2 shows the diffuse reflectance FTIR spectra of OA on BC with the BC spectrum subtracted. The small negative OH peak at 3747 cm^{-1} indicated weak interaction of OA with the free OH peak of BC, as was found with silicic acid (7,8). The breadth of the carbonyl peak at 1712 cm^{-1} provided evidence of carbonyl interaction with surface OH sites. The position and intensity of the asymmetric CH_2 stretch at 2927 cm^{-1} and symmetric stretch at 2856 cm^{-1} remained unchanged relative to unbound OA (7,8), indicating an absence of dipole-dipole coupling.

Figure 3 shows the diffuse reflectance spectra of TG adsorbed onto BC with the BC spectrum subtracted. The negative OH peak at 3739 cm^{-1} illustrates hydrogen bonding to free OH sites. Similar spectra were observed when TG was bound to silicic acid (9). Carbonyl peaks of TG bound to BC were observed at 1745 and 1726 cm^{-1}. The first peak (1745 cm^{-1}) was unmoved relative to TG and showed unbound carbonyls. The second peak (1726 cm^{-1}) was shifted from 1745 cm^{-1}, indicating hydrogen bonding of carbonyls. There was little probability of TG hydrolysis on the adsorbent surface because there was no carboxylic acid carbonyl stretch, which would be at 1712 cm^{-1}. Furthermore, there was no change in the asymmetric and symmetric CH_2 stretch relative to the unbound form (8), indicating that the molecule was not oriented parallel to the surface, but was either perpendicular or at an angle to the surface.

Figure 4 shows the diffuse reflectance FTIR spectrum of PC on BC with the BC spectrum subtracted. The negative silanol peak was small and broad, indicating weak interaction of PC with the silanol groups. The PC carbonyl shifted significantly from 1742 cm^{-1} in the unbound form (10) to 1730 cm^{-1} when adsorbed on BC. The phosphate peaks found in spectra of PC (11) were not evident, most likely because of the strong interaction with the bound moisture on the adsorbent surface, as found with silicic acid (11).

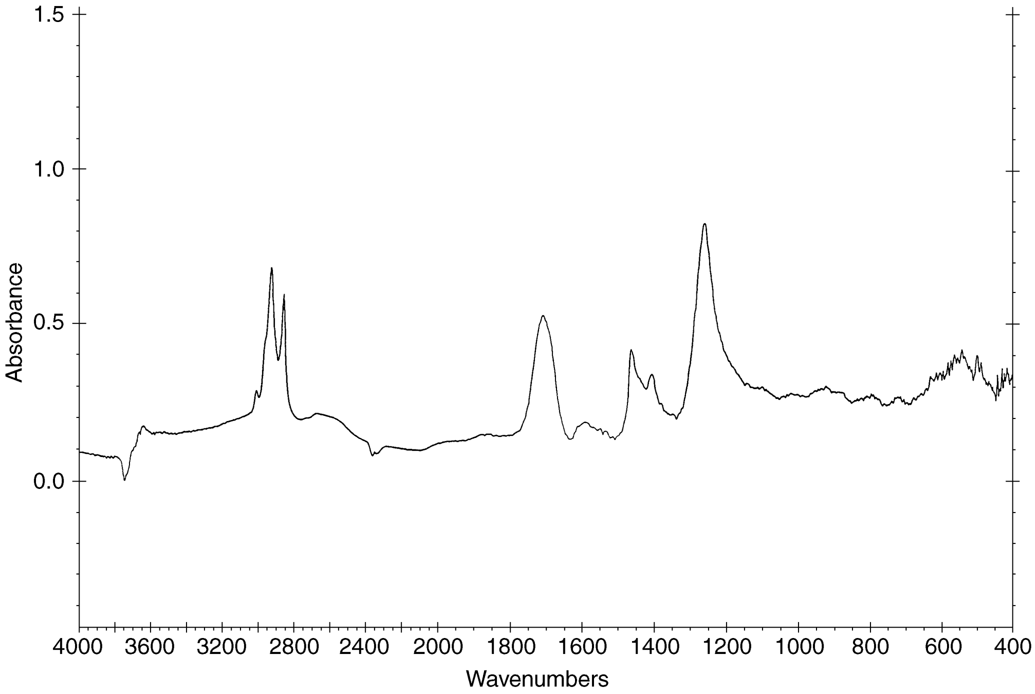

FIG. 2. The Fourier transform infrared spectroscopy spectrum of oleic acid bound to 0.5 g of acid-activated bleaching clay from 100 mL of 0.05 M oleic acid solution in hexane. One hundred scans were co-added with a resolution of 4 cm^{-1}.

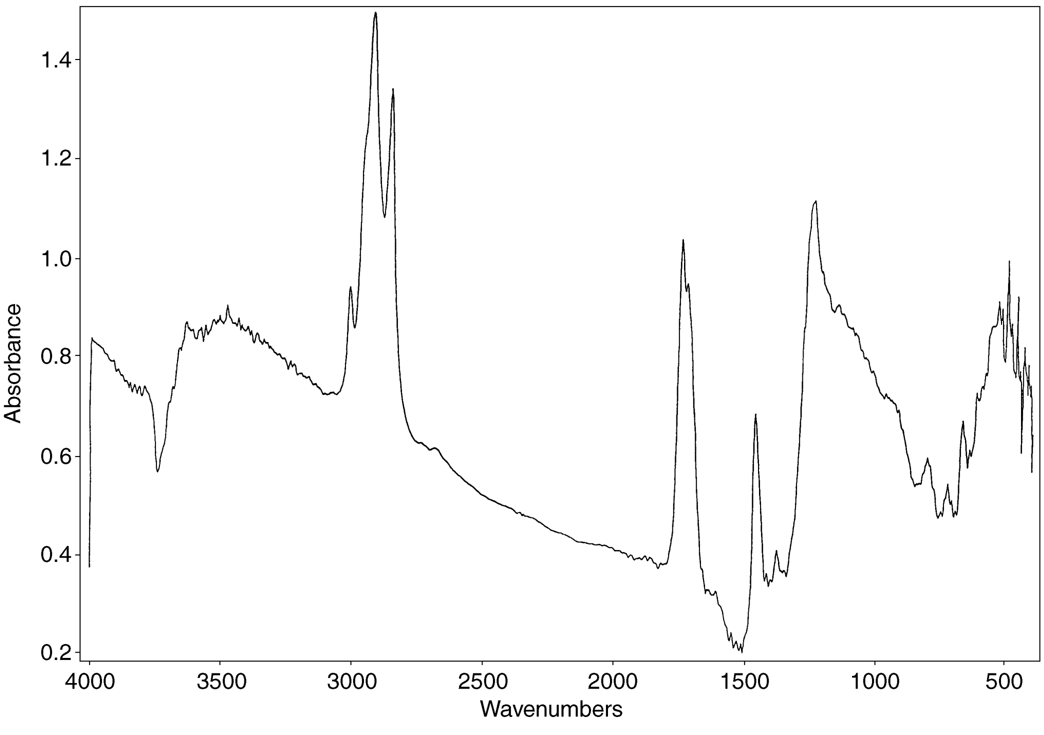

FIG. 3. The Fourier transform infrared spectroscopy spectrum of triglyceride bound to 0.5 g of acid-activated bleaching clay from 100 mL of 0.05 M triglyceride solution in hexane. One hundred scans were co-added with a resolution of 4 cm^{-1}.

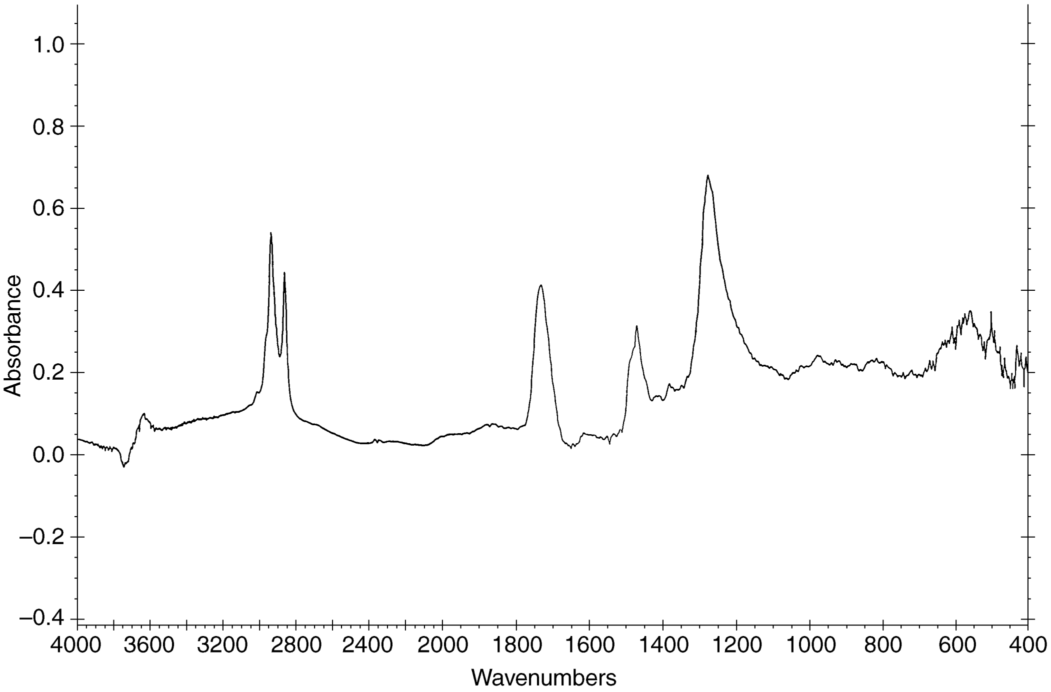

FIG. 4. The Fourier transform infrared spectroscopy spectrum of phosphatidylcholine bound to 0.5 g of acid-activated bleaching clay from 100 mL of 0.5 mM phosphatidylcholine solution in hexane. One hundred scans were co-added with a resolution of 4 cm^{-1}.

The BC lipid adsorption mechanisms from hexane reported in this study contrast with those of carotenoid and chlorophyll pigments, where ionic interaction, catalysis, and chemisorption play important roles (4–6). Lipid adsorption of the selected lipids by BC from hexane was largely by polar interactions to surface OH sites and bound water, which is similar to adsorption of lipids on silicic acid (7–10). OA was weakly bound to the surface water of the adsorbent, some TG bound to BC OH groups, while PC was most probably bound through the phosphate group to bound moisture. When bleaching clay is used commercially at 100°C under reduced pressure, moisture is lost and allows direct contact with the aluminosilicate surface. However, this study indicates the mode of adsorption of lipids from hexane during miscella refining at room temperature (3), which has proved effective as a low-energy adsorption process.

ACKNOWLEDGMENT

This paper is published with the approval of the Director, Arkansas Agricultural Experiment Station.

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[Received October 11, 1996; accepted May 14, 1997]