♣Adsorption of Lutein from Soybean Oil on Silicic Acid II. Kinetics

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Adsorption kinetics of lutein on silicic acid from a crude soybean oil miscella were first order with respect to lutein at small pigment concentrations but zero order above 15 μM. Lutein adsorption was first order with respect to silica. Triglyceride adsorption was first order with respect to triglyceride concentration and adsorbent dose. The adsorption rate constant of lutein was reduced by increasing the triglyceride concentrations relative to that of lutein. Both lutein and triglyceride were reversibly bound. The kinetic data indicated competition between lutein and triglyceride for adsorption sites.

In refining crude soybean oil for use by consumers, pigments are removed by adsorption on bleaching earths (1,2). Although the preponderant pigment in soybean oil is lutein (3,3′dihydroxy α-carotene) (3), many of the previous studies on bleaching have used β-carotene as the experimental pigment. Khoo et al. (4) found β-carotene was physically adsorbed on silica but was chemically transformed to a green pigment by bleaching earths. They attributed the change to iron bound to the bleaching earth. Bleaching earth activity depends on moisture and acid activation, and these characteristics have been studied (5). The kinetics of pigment adsorption have not been studied extensively, but Brimberg concluded that the kinetic pattern meant that a particulate or colloidally dispersed pigment system exists in vegetable oils (6).

The adsorption of lutein on bleaching earths conforms to a Freundlich isotherm (7). Proctor and Snyder (8) showed that adsorption of lutein on silicic acid from a crude soybean oil miscella results in different Freundlich-type isotherms, depending on the amount of adsorbent used. Normally, changing the amount of adsorbent gives a new point on the same isotherm. They also demonstrated that lutein and triglyceride compete for adsorption sites (8).

The purpose of this investigation was to study the kinetics of the adsorption of lutein and triglyceride on silicic acid from a soybean oil miscella, to obtain an understanding of the multiple isotherm phenomena. In addition, this study enabled further exploration of the interaction between lutein and triglyceride during adsorption. The long term objective is to examine the feasibility of establishing an energy-saving soybean oil refining process based on adsorption. Such a process also might improve oil quality relative to conventional high temperature refining practices.

MATERIALS AND METHODS

Oil, solvents and adsorbents. Crude soybean oil was obtained from a commercial extraction and stored at 4 C. Crude soybean oil miscellas were prepared by diluting the oil in HPLC grade hexane.

Bio-SilA (100-200 mesh silicic acid, Bio Rad Laboratories, Richmond, California) was used for all adsorption experiments. The terms silicic acid and silica are used interchangeably. All experiments were done at room temperature, about 22 C.

Lutein measurement. Concentrations of lutein were measured by optical absorbance at 445 nm, the wavelength of maximum absorbance of lutein in hexane (9), using the appropriate $E\ ^{1\%}_{1\,cm}$ (3). A varian 634S spectrophotometer was used for all absorbance measurements.

Lutein adsorption kinetics. The initial rate of adsorption of lutein on silica from a soy oil miscella was monitored by measuring the decline in absorbance at 445 nm. This was done by continuously pumping the miscella in Tygon tubing F-4040A (Cole Parmer Instrument Co., Chicago, Illinois) by means of a Masterflex Speed Controller Pump into a spectrophotometric flow-through cell. The decline in absorbance was recorded with a Recordall Series 5000 chart recorder (Fisher Scientific, Fairlawn, New Jersey). The miscella was then pumped back into the reaction vessel. The initial rate of adsorption was calculated from the recorder trace, and this was plotted versus initial lutein concentration.

All kinetic experiments were done with 200-ml volumes of miscella, which were mixed with a magnetic stirrer and pumped at a speed of 13 ml/min. Silica was retained in the reaction vessel by a filter at the end of the tubing used to remove the solvent.

Triglyceride adsorption kinetics. The initial rate of triglyceride adsorption onto silica was determined by using the continuous flow system described above. The rate of adsorption was measured as the decline in absorbance at 210 nm of a refined soybean oil/hexane miscella. Silica doses were 0.25, 0.50, and 1.0 g.

Lutein triglyceride ratio. A blend of refined and crude oil (1:1) was made to decrease the lutein:triglyceride ratio. The initial rate of lutein adsorption was determined using a miscella prepared from this blend and one g of silica.

Two g of silica were mixed with 100 g of crude soy oil for 10 min. Miscellas were prepared from the oil recovered, and the initial rate of adsorption of the remaining pigment on 1.0 g of silica was determined.

Lutein desorption kinetics. One- and two-g quantities of silica were stirred with miscellas of various crude soybean oil concentrations. The amount of lutein adsorbed was found by the change in pigment concentration of the miscella. The initial rate of lutein desorption from the silica was measured by monitoring the increase in absorbance at 445 nm when the adsorbent with bound lutein was agitated with refined soybean oil miscella. Initial triglyceride concentration of the refined soybean oil miscell was the same as that of the crude soybean oil miscella. Rates of desorption were plotted against the concentration of lutein that would exist in the system if it were fully desorbed.

RESULTS AND DISCUSSION

The rate of adsorption of lutein, as measured by the reduction in absorbance at 445 nm, decreased ex-

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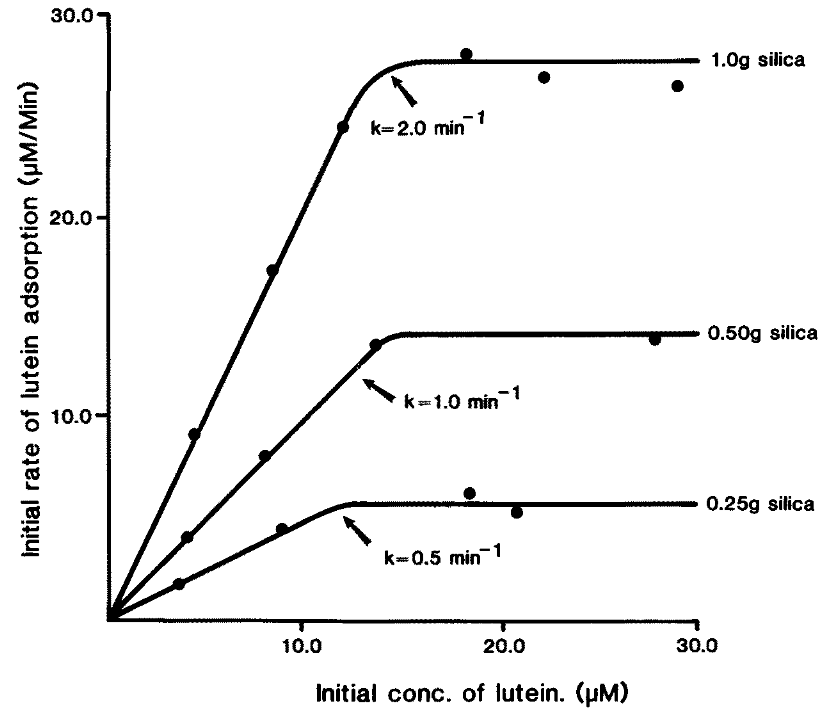

FIG. 1. Initial rates of lutein adsorption determined by measuring the decline of absorbance at 445 nm of 200 ml of a crude soy oil/hexane miscella of variable lutein concentration at 22 C with variable amounts of silica.

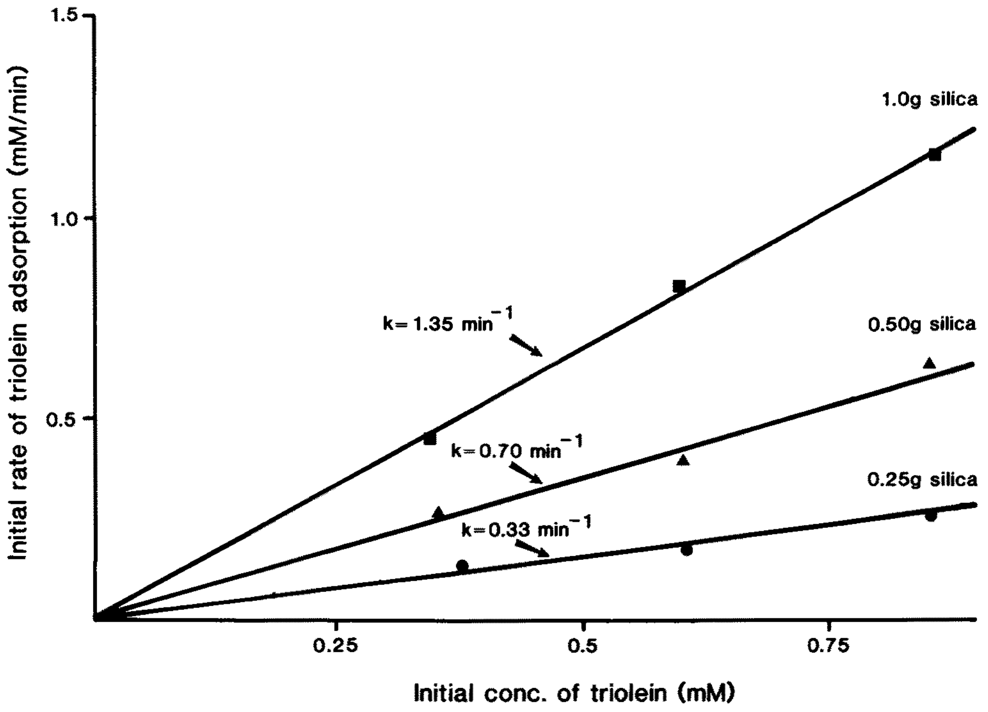

FIG. 2. Initial rates of triglyceride adsorption determined by measuring the decline of absorbance at 210 nm of 200 ml of a refined soy oil/hexane miscella of variable triglyceride concentration of 22 C with variable amounts of silica.

ponentially with time (data not shown). Figure 1 shows that the rate of adsorption was first order with respect to lutein at small lutein concentrations and was first order with respect to silica dose throughout.

Increasing the binding sites by increasing adsorbent would be expected to increase the adsorption rates. No increase in adsorption rate occurred at lutein concentrations exceeding 15.0 μM. At miscella concentrations above 15 μM, triglyceride may compete more effectively with lutein for adsorption sites, thereby keeping the lutein adsorption rate constant. Previous studies have suggested that such competition is an important factor in this adsorption (8).

The rate of triglyceride adsorption, as measured by the decline in absorbance at 210 nm, fell exponentially with time (data not shown). Figure 2 shows that the rate was first order with respect to both triglyceride concentration and silica dose.

The calculated rate of adsorption of triglyceride from a 40% (w/v) miscella on one g silica was 2.2 mM min^{-1}, whereas the calculated adsorption rate of lutein in a similar system was 0.023 mM min^{-1}. Hence, silica has a much greater affinity for triglyceride than for lutein.

To study the effect of an increased ratio of triglyceride:lutein on the lutein adsorption rate constant, crude soybean oil was mixed with refined soybean oil (relatively lutein-free) 1:1. Figure 3 shows that using one g of silica and the concentrated triglyceride mixture caused the lutein adsorption rate to decrease. The calculated rate constant was 1.1 min^{-1} compared to two min^{-1} found for crude soybean oil (Fig. 1).

Initial desorption rates for lutein from silica are shown in Figure 4. The equilibrium constant for lutein (adsorption rate/desorption rate) is 5.9, indicating that the equilibrium greatly favors adsorption. Lutein desorption was found to be zero order with respect to silica. The zero order kinetics with respect to silica were reasonable, because the amount of lutein bound rather than the proportion of silica covered would govern the rate of desorption.

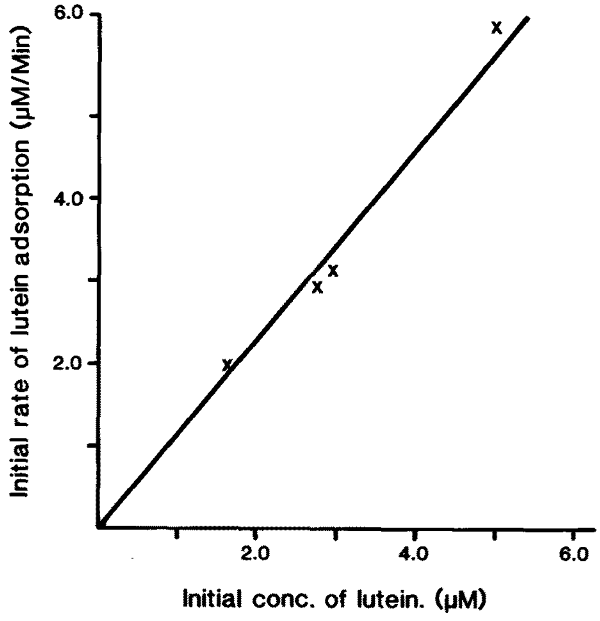

FIG. 3. Initial rates of lutein adsorption of a 1:1 blend of crude and refined soy oil/hexane miscella determined by decline of absorbance at 445 nm and 22 C with one g of silica.

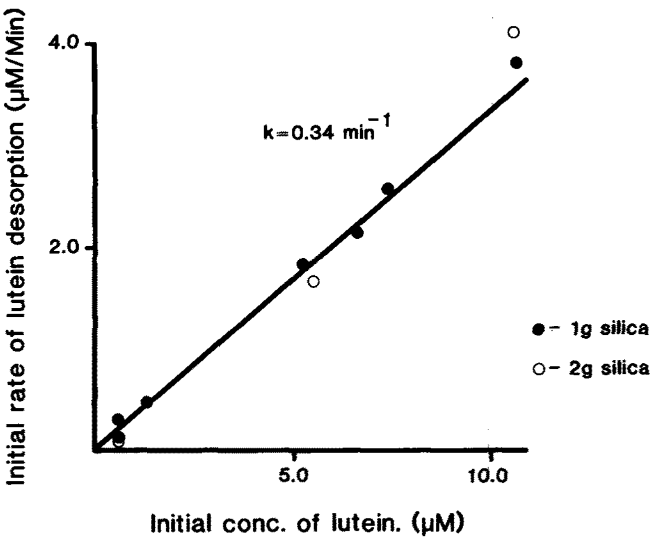

FIG. 4. Initial rates of lutein desorption from one and two g of silica that had been exposed to crude soy oil/hexane miscellas of various lutein concentrations. Desorption was measured by the increased absorbance at 445 nm and 22 C in a refined soy oil/hexane miscella of the same dilution in which adsorption had occurred.

Triglyceride desorption kinetics were not studied because a suitable solvent for desorption was not found. Hexane, which should serve as such a solvent, did not elute triglyceride adsorbed on silica. Radioactively labeled triglyceride could be used to study desorption kinetics, but our laboratory is not equipped to do these studies.

The kinetic data did not satisfactorily explain the anomaly of several adsorption isotherms found when investigating lutein adsorption isotherms (8). However, the adsorption kinetics did strongly support the hypothesis that there is competition between lutein and triglyceride for adsorption sites. Thus, the ratio of lutein to triglyceride could affect both the adsorption kinetics and isotherm behavior. Better understanding of the adsorption of lutein from crude soybean oil will enhance opportunities for improving present practices and for designing new refining procedures.

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