Thermodynamic Limitations for Pigment Adsorption During the Bleaching of Triglyceride Oils

D.M. Chapman* and **E.A. Pfannkoch**
W.R. Grace & Co.-Conn., Washington Research Center, Columbia, Maryland 21044

Triglyceride oils are complex multi-component mixtures, so that the adsorption of chlorophylls is limited by co-adsorption of other components. Efforts to evaluate the effect of co-adsorbates on the capacity of adsorbents for a chlorophyll model compound were undertaken for two-component systems by means of the Ideal Dilute Solution Theory (IDST). Single-component isotherms were measured for adsorption of the model compounds protoporphyrin IX dimethyl ester (PPIX), tripalmitin, trilinolein, stearic acid and linolenic acid onto both acid-activated clay (ABE) and an experimental adsorbent (EXP1) in a non-interacting solvent (CH_2Cl_2). Adsorbent affinities, as qualitatively measured by the initial slope of the isotherms, were in the order porphyrin ($pK_b = 4.8$) >> fatty acid ($pK_b \sim 20.0$) > triglyceride ($pK_b \sim 20.5$) for EXP1, while for ABE the affinities were in the order porphyrin >> fatty acid, triglyceride. These affinities roughly correlate with the adsorbate basicity so that the mechanism of adsorption is acid-base reaction. Isotherms for binary mixtures of PPIX with the other adsorbates were calculated from single-component isotherm data by using IDST. Calculated isotherms for the adsorption of low concentrations of prophyrin in the presence of higher concentrations of triglyceride or fatty acid dramatically demonstrate the ability of these co-adsorbates to suppress the adsorption of porphyrin. Thus, competitive adsorption has a predominant effect on the behavior of adsorbents in the edible oil application. Improvements in adsorbent selectivity or the removal of co-adsorbing components are necessary to substantially improve bleaching performance.

KEY WORDS: Adsorbent selectivity, bleaching earth, chlorophyll adsorption, isotherms.

The removal of pigments and various other trace constituents from triglyceride oils by adsorption is one of the most important steps in the processing of edible oils. In spite of this importance, the physical and chemical adsorbent properties that determine adsorbent efficacy are poorly understood. However, identification of these properties and determination of their relative impact on performance are essential for the design of improved adsorbent systems.

Several possible factors limit the ability of solid adsorbents to remove pigments, notably chlorophylls, from triglyceride oils. These factors include thermodynamic, mass transfer-kinetic and sorption-kinetic limitations. Adsorbent performance is limited thermodynamically by competition for the adsorbent surface. In commercial practice, pigment removal often requires high adsorbent dosage levels, and adsorption of triglycerides onto the adsorbent surface (as well as entrainment in adsorbent pores) is responsible for "neutral oil loss". An ideal adsorbent should therefore have high affinity for components to be removed and essentially no affinity for other components. The objective of this study is to determine the significance of competitive adsorption equilibria on adsorbent performance.

Several studies have addressed the importance of physical and chemical properties of adsorbents for the removal of trace contaminants from edible oils, and some have suggested that competitive equilibria are important. Palaniappan and Proctor (1) showed that both isopropanol and water lowered the capacity of rice hull ash for lutein and that triglycerides also had some affinity for the ash. The results suggested that competitive adsorption limited lutein adsorption. Davies *et al.* (2) concluded that chlorophyll removal from rapeseed oils is a competitive process, influenced by the presence of other impurities (notably phospholipids) in the oil. Taylor *et al.* (3) evaluated an extensive series of layered minerals for chlorophyll and carotene removal from refined soy oil to correlate physical and chemical properties of the adsorbents with performance. Their results showed that "strong" surface acidity (moles of acid sites with $pK_a < -3$) coupled with high pore volume in the 50–200 Å range correlated well with adsorbent capacity. However, not one of these studies attempts to determine either the impact of competitive adsorption equilibria on adsorbent performance or the relative affinities of various adsorbates for the adsorbent.

In the present work, two approaches were evaluated for the prediction of the effect of co-adsorbates on the adsorption of a porphyrin pigment. The theory developed by Snyder (4) to predict multi-component equilibria for elution chromatography was of limited utility as a result of the assumptions that the adsorbate distribution coefficient is a constant and that selective chemisorption does not contribute to adsorption. The Ideal Dilute Solution Theory (IDST) (5) is useful for predicting two-solute adsorption from single-solute adsorption data, provided that the solutions are dilute. In the present case, the theory was used to illustrate the large impact that competitive adsorption equilibria have on porphyrin adsorption over realistic adsorbents.

EXPERIMENTAL PROCEDURES

Model-compound adsorption isotherms were measured for protoporphyrin IX dimethyl ester (Sigma Chemical Co., St. Louis, MO, 95%, designated PPIX), tripalmitin (1,2,3-trihexadecanoylglycerol, Sigma, 99%), stearic acid (octadecanoic acid, Sigma, 99%), trilinolein {1,2,3-tri[(*cis,cis*)-9,12-octadecadienoyl]glycerol, Sigma, 99%} and linolenic acid (9,12,15-octadecatrienoic acid, Sigma, 98%) from CH_2Cl_2 (J.T. Baker, Phillipsburg, PA, Spectrophotometer grade, 0.02 wt% H_2O). Methylene chloride was chosen as the solvent to minimize strong and specific solvent-adsorbent interactions that would severely limit adsorbate uptake (*e.g.*, as might occur for methanol solvent) and because the above adsorbates all were suitably soluble in it. Adsorbents studied included a commercially available acid-activated montmorillonite clay (Filtrol F160, referred to as ABE) and an experimental adsorbent designated EXP1.

Characterization data for the adsorbents are given in

---

*To whom correspondence should be addressed at W.R. Grace & Co.-Conn., Washington Research Center, 7379 Route 32, Columbia, MD 21044.

TABLE 1

Adsorbent Physical Properties[a]

	ABE	EXP1
Surface area, m^2/g	297	544
Moisture loss @ 1,000°F	18%	6%
Pore volume, cc/g	0.5	1.1

[a]ABE, filtrol F160, a commercially available acid-activated clay; EXP1, an experimental adsorbent.

Table 1. No attempt was made to exclude moisture or ambient air from either the solvent or the adsorbents prior to use. For the isotherm studies, mixtures were allowed to react to equilibrium at ambient temperature (22 ± 3°C) with varying amounts of adsorbents by stirring at ambient temperature overnight in sealed Teflon containers that were protected from light. After reaction, the adsorbents were separated from the solutions either by filtration or by centrifugation with care to minimize solvent evaporative losses. Entrained solvent was removed from the adsorbent by evacuation at ambient temperature for 10 min. These conditions were found to be adequate to remove solvent but not incipient moisture. The amount of adsorbate removed from the solution was then determined by measurement of the total carbon content of the adsorbent with a Perkin-Elmer 2400 Elemental Analyzer (Norwalk, CT) with frontal chromatography detection of CO_2. For studies with PPIX, solution concentrations were quantitated by optical spectroscopy of the 406-nm transition (ε = 150,000 L/mole•cm) in a Perkin-Elmer Lambda 3A spectrophotometer with 3600 Data Station.

Isotherms were also measured for pheophytin A (prepared from chlorophyll A, Sigma, "free of chlorophyll B") adsorption onto EXP1 from Wesson Oil (refined soy bean oil) and mineral oil (Aldrich, Milwaukee, WI, certified for Nujol mulls) as solvents. The viscosities of these two solvents at 100°C are comparable so that diffusional effects could be neglected. (Viscosities were determined with a Brookfield LVT Thermosel System (Stoughton, MA) and were 14.2 cps and 11.3 cps for the Wesson oil and mineral oil, respectively.) Adsorption reactions in the oil solvents were carried out at 100°C for 30 min with stirring in open containers. Pheophytin A concentrations were determined by a reversed-phase high-performance liquid chromatography (HPLC) method with ultraviolet (UV/vis) detection (6) and by Tintometer (Lovibond AF960).

Isotherms were plotted as moles adsorbate per gram (anhydrous basis) of adsorbent *vs.* molar concentration at equilibrium. Experimental equilibrium single-solute isotherms data were fit by least-squares minimization to the expression $Y = A \cdot B \cdot x^c/(1 + B \cdot x^c)$ given by Sips (7) or to a straight line, where y represents moles adsorbate/g anhydrous adsorbent, and x represents moles adsorbate/L solution. Numerical integration of these functions for calculation of binary adsorption isotherms by IDST was accomplished by using Simpson's rule. Adsorbed-phase mole fractions were calculated with IDST by iteration with minimization of the difference in spreading pressures. Binary-adsorption isotherms were calculated for PPIX with the above triglycerides and fatty acids as co-adsorbates at two different concentrations. The porphyrin equilibrium concentration range evaluated was $1.0 \cdot 10^{-7}$ *M* to $1.0 \cdot 10^{-6}$ *M*, which corresponds roughly to the concentration range of 60 ppb to 600 ppb chlorophyll in edible oils. The two equilibrium concentrations of co-adsorbate were $1.0 \cdot 10^{-5}$ *M* and $1.0 \cdot 10^{-4}$ *M*. Thus, while the calculations involved dilute solutions, the triglyceride and fatty acid co-adsorbates were present at orders of magnitude higher than the porphyrin concentration. All calculations were performed with a Vax 7620 computer.

RESULTS AND DISCUSSION

To determine the relative affinities of triglycerides, fatty acids and porphyrins for ABE and EXP1, single-component isotherms were measured for the model compounds PPIX, tripalmitin, trilinolein, stearic acid and linolenic acid. The experimental isotherms are shown in Figures 1–4, and included in the Figures are curves fitted to the data as described in the Experimental Procedures section. Parameters for the fitted curves are given in Table 2. It can be seen qualitatively from the initial slopes of the isotherms (which are proportional to the distribution coefficients for Langmuir isotherms) that, for EXP1, affinities for the adsorbates decrease in the order PPIX >> fatty acid > triglyceride. For ABE, fatty acids and triglycerides had roughly the same affinities for the adsorbent. These qualitative observations were confirmed by fitting the initial slopes of the isotherms to a straight line, as also shown in Table 2. The relative basicities, measured as pK_b in water, are 4.8 (8), ~ 20.0 (9) and ~ 20.5 (9) for PPIX, carboxylic acid and ester, respectively. Since the basicities of the compounds correlate with their affinities for the adsorbents, the predominant mechanism of adsorption is acid-base reaction.

To calculate the effect of competitive equilibria on the adsorption of PPIX, IDST was employed. IDST enables the calculation of multi-component adsorption equilibria with only data from single-solute isotherms. Furthermore, it is valid as long as the solutions are dilute and the adsorbed phase forms an ideal solution (adsorbed solute-solute interactions can be neglected), and these criteria should be satisfied in the present application (see Experimental Procedures section).

Shown in Figure 5 is the experimental single-component isotherm for PPIX adsorption onto EXP1 (solid curve) and the calculated curve for PPIX adsorption in the presence of 1.0×10^{-5} *M* tripalmitin at equilibrium (dotted curve). Obviously, the presence of tripalmitin has a dramatic impact on the amount of PPIX adsorbed, in spite of the greater affinity of the latter for the adsorbent surface. Shown in Figure 6 is the experimental single-component isotherm for PPIX adsorption onto F160 (solid curve) and the calculated curve for PPIX adsorption in the presence of 1.0×10^{-5} *M* stearic acid at equilibrium (dotted curve). Again, the presence of stearic acid has a dramatic impact on the amount of PPIX adsorbed, in spite of the greater affinity of the latter for the adsorbent surface. Calculated curves for PPIX adsorption in the presence of the other adsorbates were qualitatively similar for both of the adsorbents. Thus, while the adsorbents have a high affinity for porphyrin compared to triglyceride and fatty acid, the relatively high concentrations of the latter shift the adsorption equilibria strongly toward adsorption of the component present at the highest concentration.

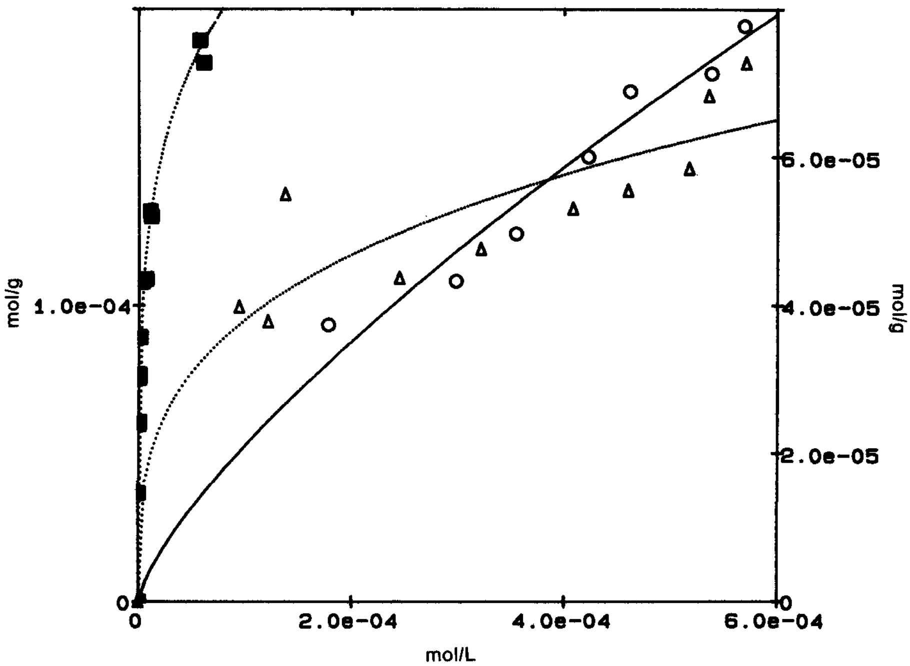

FIG. 1. Experimental single-component adsorption isotherms for protophyrin IX dimethyl esters, 95% (PPIX) (filled squares, dotted line, left ordinate), stearic acid (open circles, solid line, right ordinate) and linolenic acid (open triangles, dotted line, right ordinate) on EXP1 (an experimental adsorbent) from CH_2Cl_2.

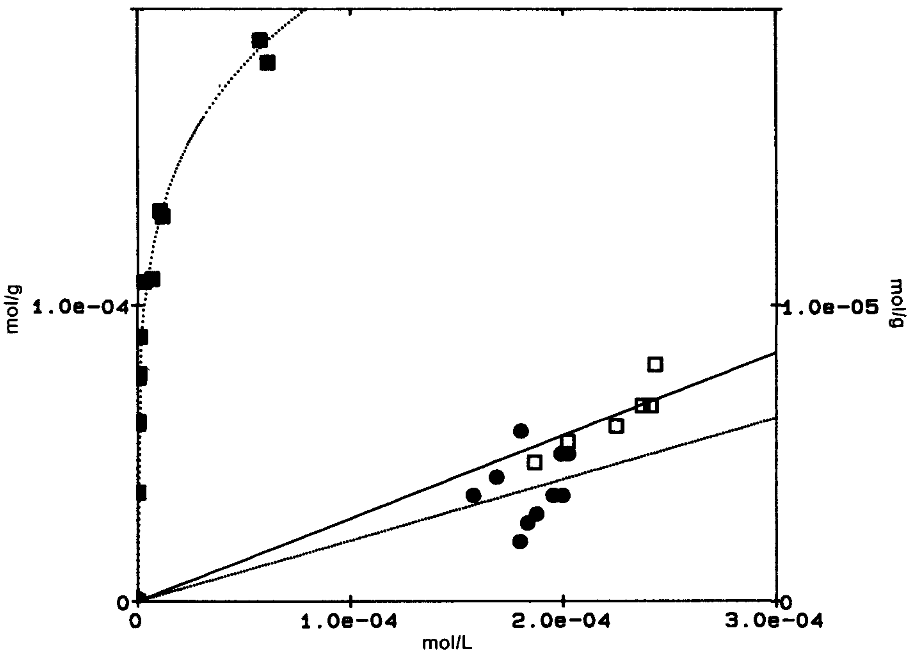

FIG. 2. Experimental single-component adsorption isotherms for PPIX (filled squares, dotted line, left ordinate), tripalmitin (open squares, solid line, right ordinate) and trilinolein (filled circles, dotted line, right ordinate) on EXP1 from CH_2Cl_2. Abbreviations as in Figure 1.

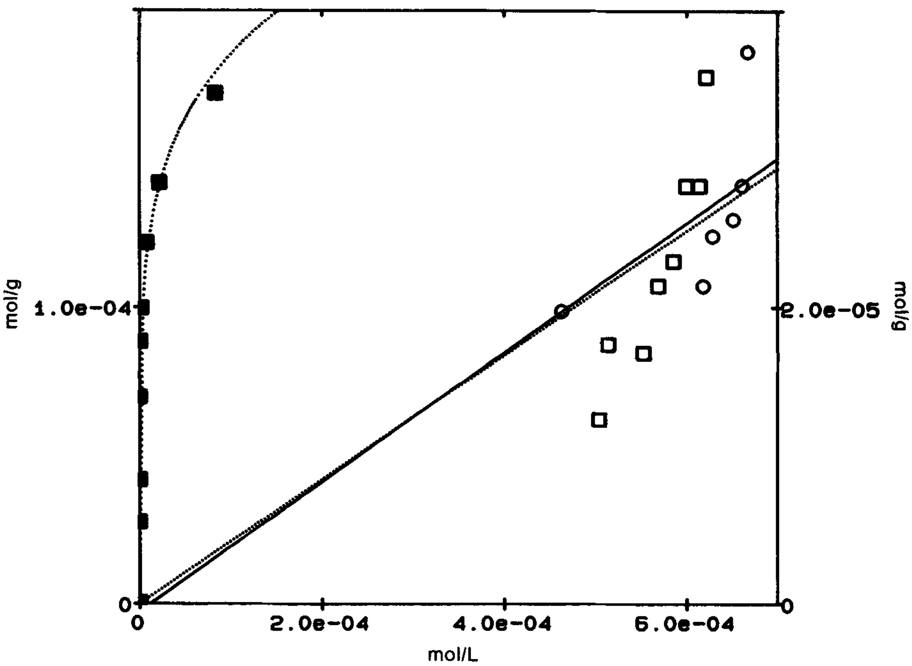

FIG. 3. Experimental single-component adsorption isotherms for PPIX (filled squares, dotted line, left ordinate), stearic acid (open circles, solid line, right ordinate) and linolenic acid (open squares, dotted line, right ordinate) on F160 from CH_2Cl_2. Abbreviations as in Figure 1.

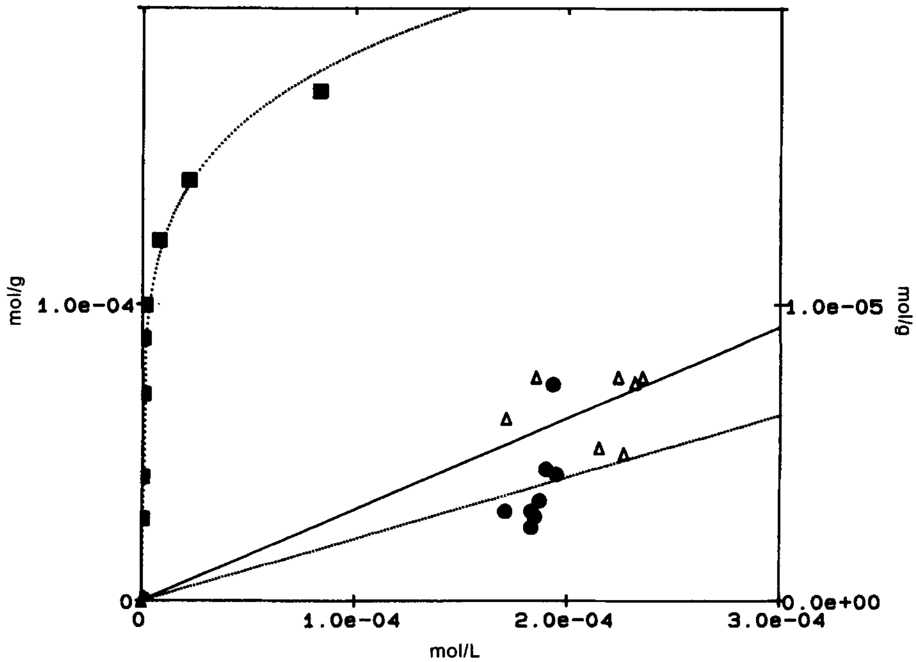

FIG. 4. Experimental single-component adsorption isotherms for PPIX (filled squares, dotted line, left ordinate), tripalmitin (open triangles, solid line, right ordinate) and trilinolein (filled circles, dotted line, right ordinate) on F160 from CH_2Cl_2. Abbreviations as in Figure 1.

TABLE 2

Parameters for Fitted Curves[a]

	A	B	C	M	M[b]
ABE[c]					
PPIX	0.022	0.046	0.184	—	180
Tripalmitin	—	—	—	0.031	—
Trilinolein	—	—	—	0.021	—
Stearic acid	—	—	—	0.044	—
Linolenic acid	—	—	—	0.042	—
EXP1					
PPIX	0.314	0.005	0.216	—	240
Tripalmitin	—	—	—	0.028	—
Trilinolein	—	—	—	0.021	—
Stearic acid	1.300	0.007	0.655	—	0.14
Linolenic acid	0.101	0.006	0.300	—	0.13

[a] Isotherm data fitted to the curve $y = (A \cdot B \cdot x^C)$ or the the line $y = M \cdot x$.
[b] Initial slopes of isotherms.
[c] Abbreviations as in Table 1. PPIX, protopochyrin IX dimethyl ester, 95%.

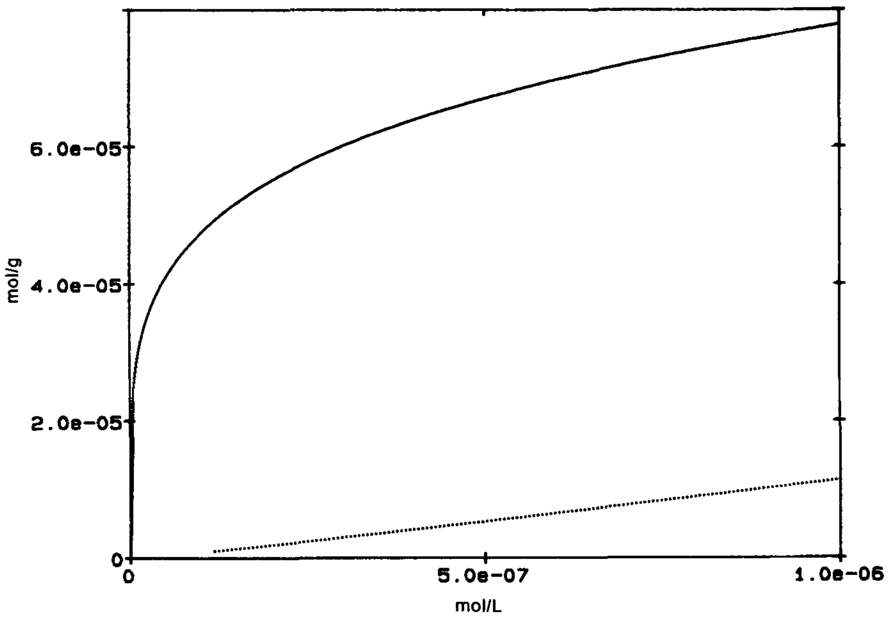

FIG. 5. Effect of tripalmitin on the adsorption of PPIX onto EXP1. Solid curve is best fit of experimental PPIX adsorption isotherm. Dotted line is calculated PPIX adsorption for $1.0 \cdot 10^{-5}$ *M* tripalmitin at equilibrium. Abbreviations as in Figure 1.

The importance of the nature of the co-adsorbing species on the adsorption of the porphyrin pheophytin A (PHEO) onto EXP1 was demonstrated experimentally by the determination of adsorption isotherms from a triglyceride-based solvent (Wesson oil) and an alkane-based solvent (mineral oil). Figure 7 shows that equilibrium adsorbent capacity for PHEO was over an order of magnitude greater for adsorption from the mineral-oil solvent than for adsorption from the triglyceride-oil solvent. For dispersion interactions between adsorbate and adsorbent, both alumina and silica should have much higher affinities for the polar esters, carboxylic acids and amines than for nonpolar paraffins (10). In the present case, acid-base reaction controls adsorption, and the triglyceride esters in the Wesson oil are more basic than the paraffins of the mineral oil. Thus, the latter compete less effectively than the former with the highly basic porphyrin for adsorbent surface.

The calculated ability of weakly adsorbing components (present at high relative concentrations) to suppress adsorption of strongly adsorbing PPIX (present at low concentrations) and the observed difference in adsorbent capacities for PHEO A in triglyceride and paraffin solvents lead to the conclusion that competitive adsorption equilibria play the predominant role in determining adsorbent performance. Thus, for evaluation of the factors that control performance, selectivity must be considered in addition to surface area and pore volume.

A rigorous definition of adsorbent selectivity for the various components in an N-component mixture can be defined by using IDST. However, the approach is not feasible for an edible oil because in this case N is large and the assumptions in the theory are no longer valid. However, the above results do have practical ramifications for the development of new adsorbents. For example, the

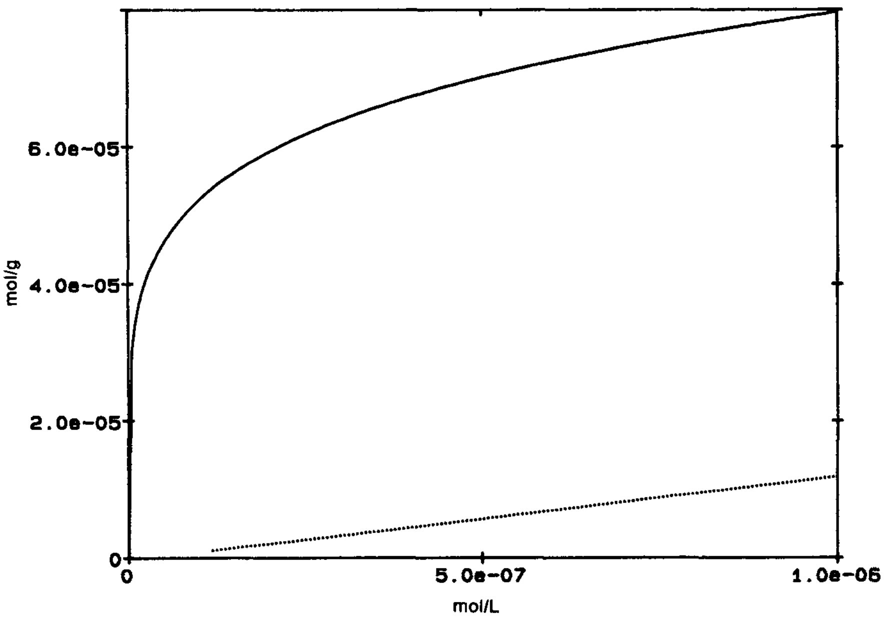

FIG. 6. Effect of stearic acid on the adsorption of PPIX onto F160. Solid curve is best fit of experimental PPIX adsorption isotherm. Dotted line is calculated PPIX adsorption for 1.0 • 10^{-5} *M* stearic acid at equilibrium. Abbreviations as in Figure 1.

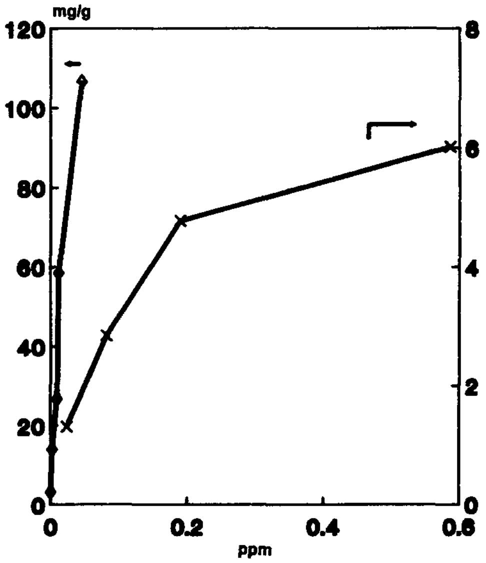

FIG. 7. Adsorption isotherms for pheophytin A at 100°C onto EXP1. Right ordinate, triglyceride-oil solvent; left ordinate, mineral-oil solvent. Abbreviations as in Figure 1.

results suggest that one method of increasing adsorbent efficiency is to tune surface acidity or incorporate selective chemisorption functionalities onto the adsorbent surface. Another method of improving adsorbent efficiency is to remove from multi-component mixtures compounds that will most effectively "poison" the adsorbent.

ACKNOWLEDGMENTS

The authors acknowledge Dr. R.H. Harding, C.J. Sciambi and P.J. Gill for their contributions and thank W.R. Grace & Co.-Conn. for permission to publish this work.

REFERENCES

1. Palaniappan, S., and A. Proctor, *J. Am. Oil Chem. Soc. 67*:572 (1990).
2. Davies, M.E., P.R. Shanks, D.S. Anderson and R.S. Taylor, Poster Presentation at the World Conference on Edible Oils and Fats Processing, Maastricht, The Netherlands, Oct. 1–6, 1989.
3. Taylor, D.R., D.B. Jenkins and C.B. Ungermann, *J. Am. Oil Chem. Soc. 66*:334 (1989).
4. Snyder, L.R., *Principles of Adsorption Chromatography: The Separation of Nonionic Organic Compounds*, Marcel Dekker, Inc., New York, 1968.
5. Radke, C.J., and J.M. Prausnitz, *AIChE J. 18*:761 (1972).
6. Pfannkoch, E.A., and P.J. Gill, Poster Presentation, 81st Annual Meeting of the American Oil Chemists' Society, Baltimore, April 23–25, 1990.
7. Sips, R., *J. Chem. Phys. 18*:1024 (1954).
8. Katritzky, A.R., and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds*, Vol. 4, Pt. 3, Pergamon Press, Oxford, 1984.
9. Arnett, E., *Prog. Phys. Org. Chem*:1 (1963).
10. Snyder, L.R., *Principles of Adsorption Chromatography: The Separation of Nonionic Organic Compounds*, Marcel Dekker, Inc., New York, 1968, p. 194.

[Received December 6, 1991; accepted August 9, 1992]