

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Adsorption Analysis. II. The Adsorption of Higher Fatty Acids¹

BY HAROLD G. CASSIDY

R. J. Anderson and his co-workers in their studies of the lipids of various bacteria² occasionally obtained fractions which in some respects appeared to be mixtures and yet which resisted the usual methods of separation. Under these circumstances it seemed desirable to attempt to separate these mixtures by adsorption analysis.^{3,4}

The substances involved are colorless, and their other characteristics make it additionally difficult to locate any zones which might be formed on adsorption columns. For this reason it appeared desirable first to investigate this method systematically, using known substances similar to those in the mixtures referred to above. Lauric, myristic, palmitic and stearic acids were chosen as easily available model substances.

Materials.—All solvents were distilled before use. *Petroleum ether* (b. p. 30–60° or 30–70°) and *ligroin* (b. p. 90–105°) were in addition dried over sodium wire.

The other substances were used as received, their sources and characteristics being as follows: *Activated Clay*, Filtrol Corporation⁵; *Alumina I*, an old sample of aluminum oxide—it lost 10.6% of its weight on ignition; *Alumina III*, "Aluminum oxydat.anhydric.(standardisiert) zur chromatographischen Adsorptionsanalyse nach Brockmann," Merck; *Carbon I*, decolorizing, activated, Merck; *Carbons II to VIII*,⁶ industrial carbons used commercially for a variety of purposes, the numbers referring to the order in which they were tested, the comparisons being made on the weight basis; *Magnesium Oxide I*, Micron brand, California Chemical Company; *Silica Gel I*, Howe & French, Inc.; *Lauric Acid* (m. p. 43–44°), *Myristic Acid* (m. p. 53.5–54°), *Palmitic Acid* (m. p. 62–64°) and *Stearic Acid* (m. p. 68–70°), all Eastman Kodak Company.

Methods.—The substance to be adsorbed was weighed into a flask and dissolved in 100 cc. of the solvent in question. This solution was mixed and the adsorbent rapidly weighed in to the nearest two or three milligrams. The well-stoppered flask was then swirled at intervals for an hour or so, and then left at room temperature overnight to ensure equilibrium.⁶ For analysis the liquid in equi-

librium with the adsorbent was decanted through a filter-paper into a graduated cylinder and allowed to drain, then the adsorbent with adsorbed material was drained into the filter paper. An estimate was made of the amount of liquid mechanically held back by the adsorbent (this was usually less than 1%). The volume of liquid drained from the adsorbent was recorded and (in almost all cases) all this liquid was evaporated to obtain the weight of unadsorbed substance. From this weight and the volume recorded above the concentration of the equilibrium solution was calculated. The weight of substance adsorbed was calculated after correcting for the estimated small amount of liquid held back by the adsorbent. The results obtained were probably quite reasonably accurate in view of the volatile nature of the solvent generally used (petroleum ether). All adsorptions, unless specifically stated otherwise, were made at room temperature.

Results.—As a first step, the adsorptions of several fatty acids from petroleum ether solutions were determined on the "polar" and "basic" adsorbents Alumina I and Magnesium Oxide I (Fig. 1 and 2), and on "non-polar" Carbon I. (No separate curves are given for this experiment with Carbon I because the data agree with those shown in Fig. 3, and this latter was a more extensive experiment, see below.) Here it may be seen that the alumina did not appear to differentiate between the different fatty acids, since at a given equilibrium concentration substantially equal numbers of molecules of the different acids were adsorbed by one gram of adsorbent. This was not the case with the magnesium oxide and carbon. Here at a given equilibrium concentration more molecules of the higher molecular weight acid were adsorbed than of the lower molecular weight acid.⁷

The behavior of the Alumina I, on which equal numbers of molecules of different molecular weights were adsorbed at a given equilibrium concentration, led to the examination of Alumina III. This was found to behave in exactly the same manner and therefore no separate curves are given for it. The differences in adsorbability of the fatty acids found in the preliminary experiment with Carbon I were confirmed by a more extensive

that equilibrium was attained rapidly, being virtually complete within five minutes.

(7) Results with Magnesium Oxide I were not satisfactory. The results were not reproducible. The adsorbent varied greatly in particle size and tended to form thixotropic gels at the higher concentrations of fatty acid.

(1) Parts of the data are taken from the dissertation submitted by H. G. Cassidy to the faculty of the Graduate School, Yale University, 1939, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

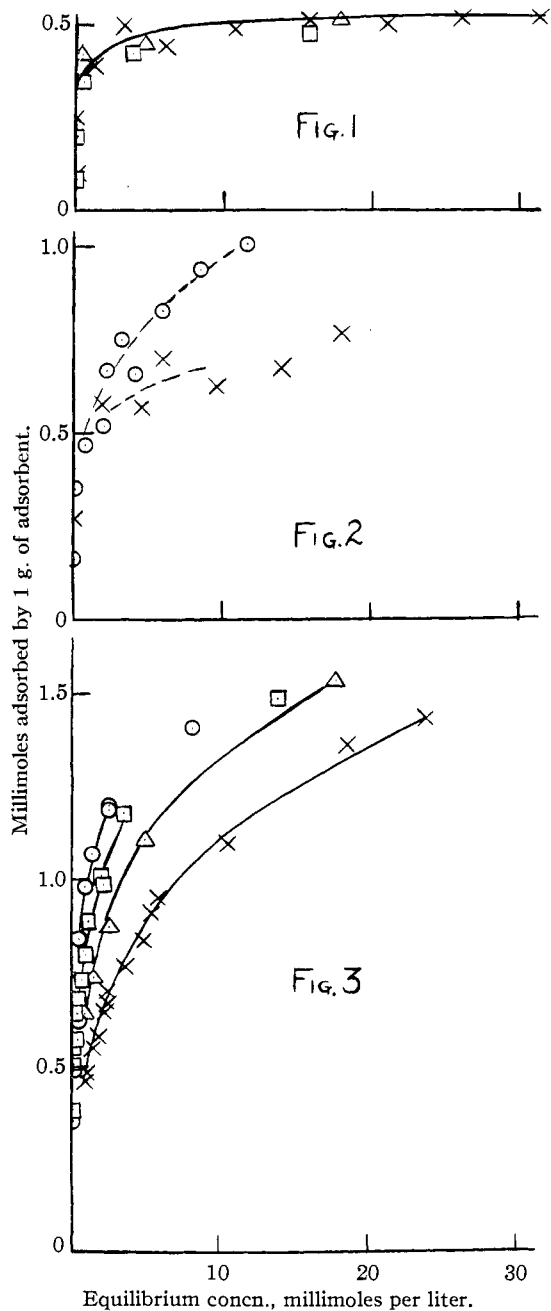
(2) Anderson, "Fortschritte der Chemie organischer Naturstoffe," III, p. 145, Verlag Julius Springer, Vienna, 1939.

(3) Zechmeister and Cholnoky, "Die chromatographische Adsorptionsmethode," Verlag Julius Springer, Vienna, 1938.

(4) Cassidy, *J. Chem. Ed.*, **16**, 88 (1939).

(5) Thanks are due to the Cliffs Dow Chemical Company, Darco Corporation, and Industrial Chemical Sales for generous samples of different grades and types of activated carbons, and to the Filtrol Corporation for the activated clay.

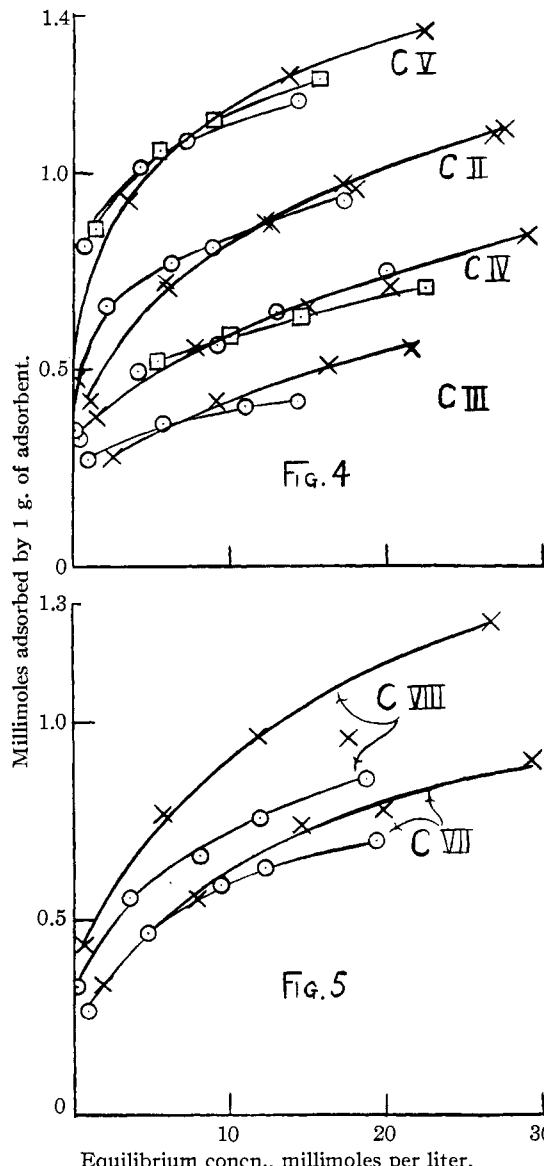
(6) Preliminary experiments with Carbon I and lauric acid showed



Equilibrium concn., millimoles per liter.
 × Lauric, Δ myristic, □ palmitic, O stearic acids.
 Fig. 1.—Adsorption on Alumina I from petroleum ether.
 Fig. 2.—Adsorption on Magnesium oxide I from petroleum ether.
 Fig. 3.—Adsorption on Carbon I from petroleum ether.

experiment (Fig. 3) in which more than half of the points for each curve were obtained by a desorption process in which the adsorbents plus adsorbed substances were returned, after draining, to the adsorption flasks and fresh solvent added. New equilibrium concentrations were thus reached,

and the process could be repeated with the adsorbates from these determinations. The fit of the points on the curves indicates that true reversible adsorption was being dealt with.



Equilibrium concn., millimoles per liter.
 × Lauric, □ palmitic, O stearic acids.
 Fig. 4.—Adsorptions on Carbons⁸ II, III, IV and V from petroleum ether.
 Fig. 5.—Adsorptions on Carbons VII and VIII from petroleum ether.

A study of seven more carbons was made⁸ (Figs. 4 and 5) with the aim of finding the adsorbent which gave the greatest differences in adsorption

(8) Curves are given for carbons C II, C III, C IV, C V, C VII and C VIII. The curves for Carbon VI were so nearly identical with those of Carbon I that no separate curves are given for this carbon. Most of these carbons appear to contain water.

curves between the separate fatty acids. It can be seen from these curves that there are wide qualitative and quantitative differences in behavior between the various carbons. This is to be expected since they are prepared commercially to be specially fitted for certain of a wide variety of purposes.

Carbon VIII (Fig. 5) was of special interest because it markedly reversed the adsorbabilities of the fatty acids by adsorbing the lower molecular weight acid (lauric) more strongly than the higher (stearic). This will be referred to again in connection with its interest for adsorption analysis.

Adsorptions of lauric, palmitic and stearic acids on Carbon I from ligroin (Fig. 6B) were carried out for comparison with the adsorptions from petroleum ether (Fig. 3). The acids are less soluble in petroleum ether than in ligroin. For example, at 23.5° a saturated solution of stearic acid in petroleum ether contained 59.7 millimoles per kilo and in ligroin 77.7 millimoles per kilo. Curves also were obtained for adsorptions from petroleum ether at 11–13° (Fig. 6A).

"Polar" and "acidic" Silica Gel I (Fig. 7A) and an activated clay (Fig. 7B) were investigated in order to extend the types of adsorbents studied.

Discussion of Results

It is not desirable at this time and with these limited data to enter into a very extensive discussion of the factors responsible for the variations in adsorption behavior found among these different adsorbents. A few conclusions may, however, be drawn.

No general statement may be made about the relative adsorbabilities of two given fatty acids on all carbons from petroleum ether. On one carbon the higher molecular weight acid may be better adsorbed and on another there may be no appreciable difference in adsorbabilities, while on a third carbon the acid with lower molecular weight may be better adsorbed.

For this reason also the relative solubilities of the fatty acids in petroleum ether cannot be said to have a very important effect on their adsorbabilities, for though stearic acid is less soluble than lauric, that acid is not necessarily better adsorbed than lauric (compare Figs. 3 and 5).

That the solubilities of these acids may have some relation to their adsorption behaviors is, however, concluded from the markedly decreased adsorption on Carbon I from ligroin (Fig. 6B) as

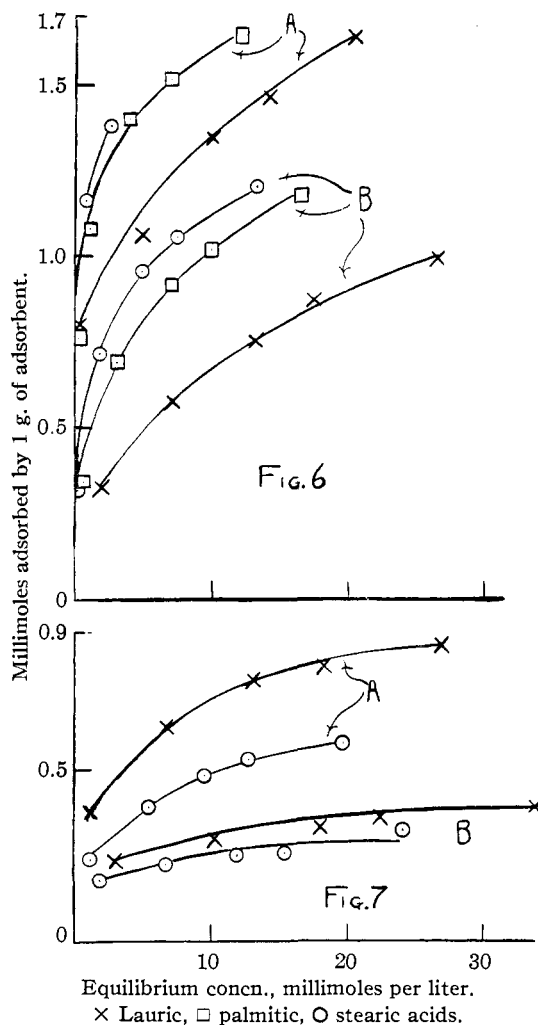


Fig. 6A.—Adsorption on Carbon I from petroleum ether at 11–13°

Fig. 6B.—Adsorption on Carbon I from ligroin at room temperature.

Fig. 7A.—Adsorption on Silica gel I from petroleum ether.

Fig. 7B.—Adsorption on active clay from petroleum ether.

compared with petroleum ether (Fig. 3). Ligroin is a hydrocarbon mixture of higher boiling fractions than those found in petroleum ether and the acids are more soluble in it. It may be noted from these curves that the positions of the acids relative to each other are not changed, only the degrees of adsorption. Not enough data are available to decide definitely whether there is a greater spread between any two of the curves with ligroin than with petroleum ether.

It is seen from Figs. 3 and 6A that adsorption is increased with lowering in temperature. This is as would be expected of true adsorption. The positions of the curves for the acids relative to

each other have not been changed, but there is insufficient evidence to decide whether there is a greater or lesser spread between any two curves at the higher or lower temperatures.

In applying the data reported here to adsorption analysis it may be reasoned that, assuming no influence of the acids upon the adsorbabilities of each other in a mixture, the acid with a greater adsorbability as indicated by its adsorption isotherm will form a zone above that with a lesser adsorbability in the adsorption column.^{3,4} This follows, too, from the theory of Wilson, as he has pointed out.⁹ This assumption is, however, one which should be made with caution.

It is particularly interesting that adsorbents of the same type (*i. e.*, carbons) have been obtained on which the relative adsorbabilities of lauric and stearic acids are reversed, for this gives a means of comparing the positions of adsorption on the columns of these two acids, as well as their separa-

(9) Wilson, *THIS JOURNAL*, **62**, 1583 (1940).

bilities, with their adsorption isotherms on these adsorbents. These points will be considered in a later communication.

The decrease which is found in adsorption from ligroin indicates that this solvent might have useful properties as an eluent or desorbing liquid for fractional removal of adsorbed acids from portions of adsorption columns.

I am indebted to Professor R. J. Anderson, who provided some of the materials used in this work.

Summary

As a first step in the systematic study of adsorption analysis as a means of separating higher fatty acids it has been shown by comparisons of the adsorption isotherms that lauric, myristic, palmitic and stearic acids differ markedly in their adsorption behaviors toward carbons, aluminas, magnesium oxide, active clay and silica gel.

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Adsorption Analysis. III. Relation between Adsorption Isotherm and Position on the Adsorption Column¹

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In a previous paper² the adsorption behaviors of lauric, myristic, palmitic and stearic acids in petroleum ether solutions were compared toward a number of different types of adsorbents. This was a first step in a systematic attempt to find the most suitable adsorbent for the separation of these fatty acids from their mixtures. In the course of that investigation adsorbents were found some of which (a) adsorbed the higher molecular weight acids better than the lower, others of which (b) adsorbed the lower molecular weight acids better than those of higher molecular weight, and still others of which (c) did not differentiate appreciably between the different acids.

Availability of adsorbents with these different behaviors made it possible to examine the following problem. If the simple assumption may be made that there is little influence of each of the acids in a mixture upon the adsorbabilities of the

(1) Part of the data is taken from the dissertation submitted by H. G. Cassidy to the Faculty of the Graduate School, Yale University, 1939, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Cassidy, *THIS JOURNAL*, **62**, 3073 (1940).

others, then it would be expected that the acid with the greater adsorbability, as indicated by its adsorption isotherm, would form a zone above that of the acid with the lesser adsorbability when a mixture of the two is chromatographed, and the differences in adsorbabilities as judged from a comparison of the respective isotherms would give an indication of the ease of separability of the two acids. If this assumption were valid, or approximately so, the search for suitable adsorbents for making separations such as this one would be greatly simplified, for isotherms of this type are comparatively easily obtained.

The following data show that adsorption isotherms obtained for these higher fatty acids from their pure solutions are of uncertain value as criteria of separability of the acids by the method of chromatographic adsorption analysis.

Materials and Solvents.—These were the same as those described previously.²

Methods.—The Tswett adsorption method was used. The column of adsorbent was placed in a glass tube. It was supported on a small pad of cotton which in turn was